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(54) **ELECTROMAGNETIC WINDSHIELD WIPER SYSTEM**

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(60) Provisional application No. 62/638,516, filed on Mar. 5, 2018.

(51) **Int. Cl.**

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B60S 1/44	(2006.01)
B60R 16/023	(2006.01)
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(58) **Field of Classification Search**
CPC B60S 1/0807; B60S 1/0818; B60S 1/16; H02K 11/33
See application file for complete search history.

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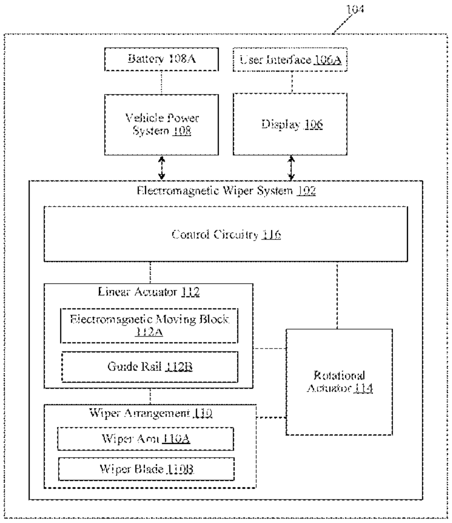
(57) **ABSTRACT**

An electromagnetic wiper system for a windshield of a vehicle includes a linear actuator, a wiper-arrangement, and control circuitry. The linear actuator includes at least one guide rail having permanent magnets and an electromagnetic moving block. The electromagnetic moving block includes at least one perforation that surrounds the at least one guide rail and at least one electromagnetic coil that surrounds the at least one perforation. The wiper-arrangement includes a wiper arm and a wiper blade, wherein at least the wiper arm is coupled to the electromagnetic moving block. The control circuitry controls a linear motion of the electromagnetic moving block along the at least one guide rail to steer the wiper arm that is coupled to the electromagnetic moving block back and forth across a length of the windshield to the windshield, wherein the electromagnetic moving block induces minimal friction during the linear motion.

19 Claims, 4 Drawing Sheets



(51) **Int. Cl.**

B60S 1/34	(2006.01)
B60S 1/06	(2006.01)

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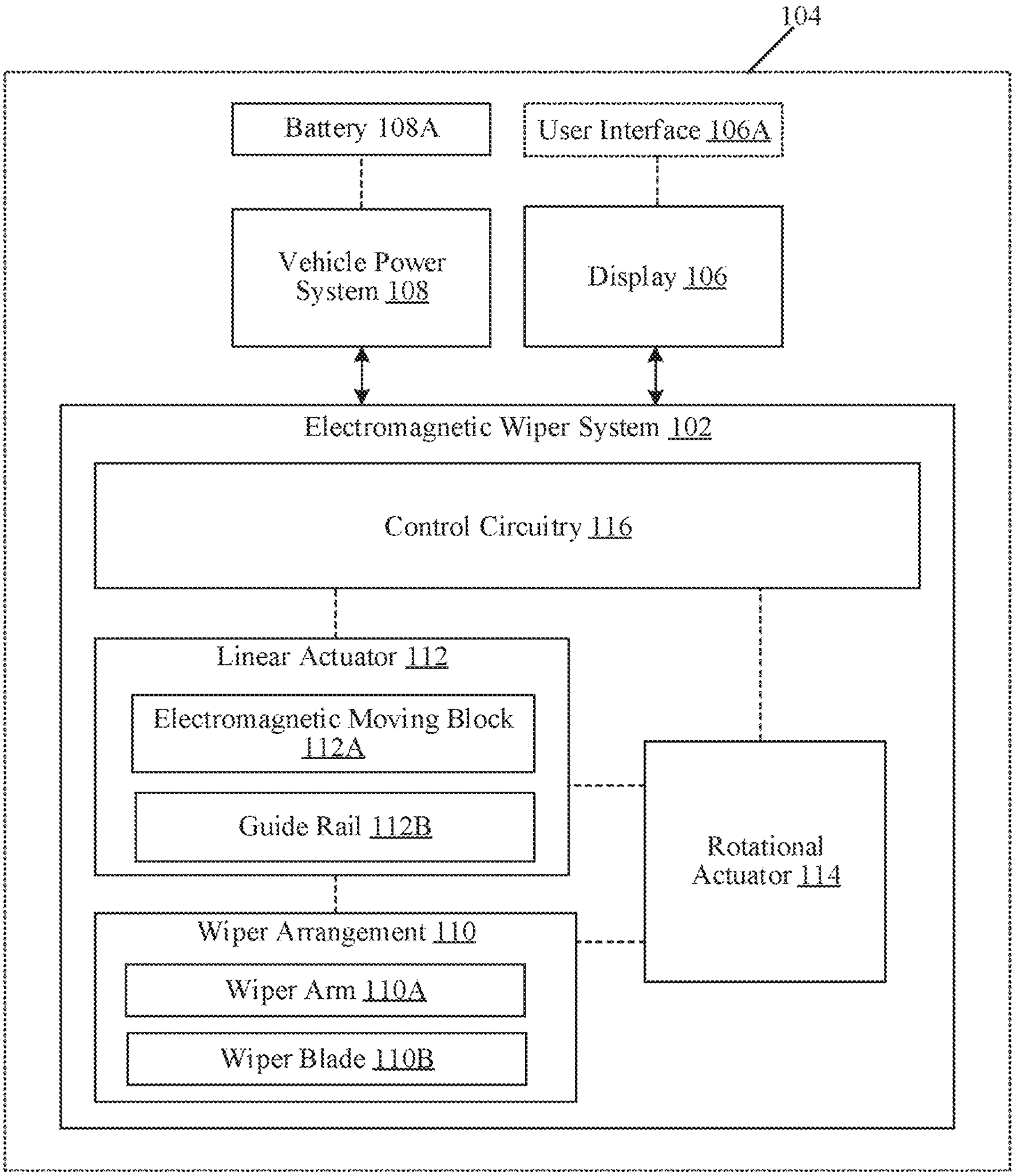
104
Battery 108A
User Interface 106A
Vehicle Power System 108
Display 106
Electromagnetic Wiper System 102
Control Circuitry 116
Linear Actuator 112
Electromagnetic Moving Block 112A
Guide Rail 112B
Rotational Actuator 114
Wiper Arrangement 110
Wiper Arm 110A
Wiper Blade 110B

FIG. 1A

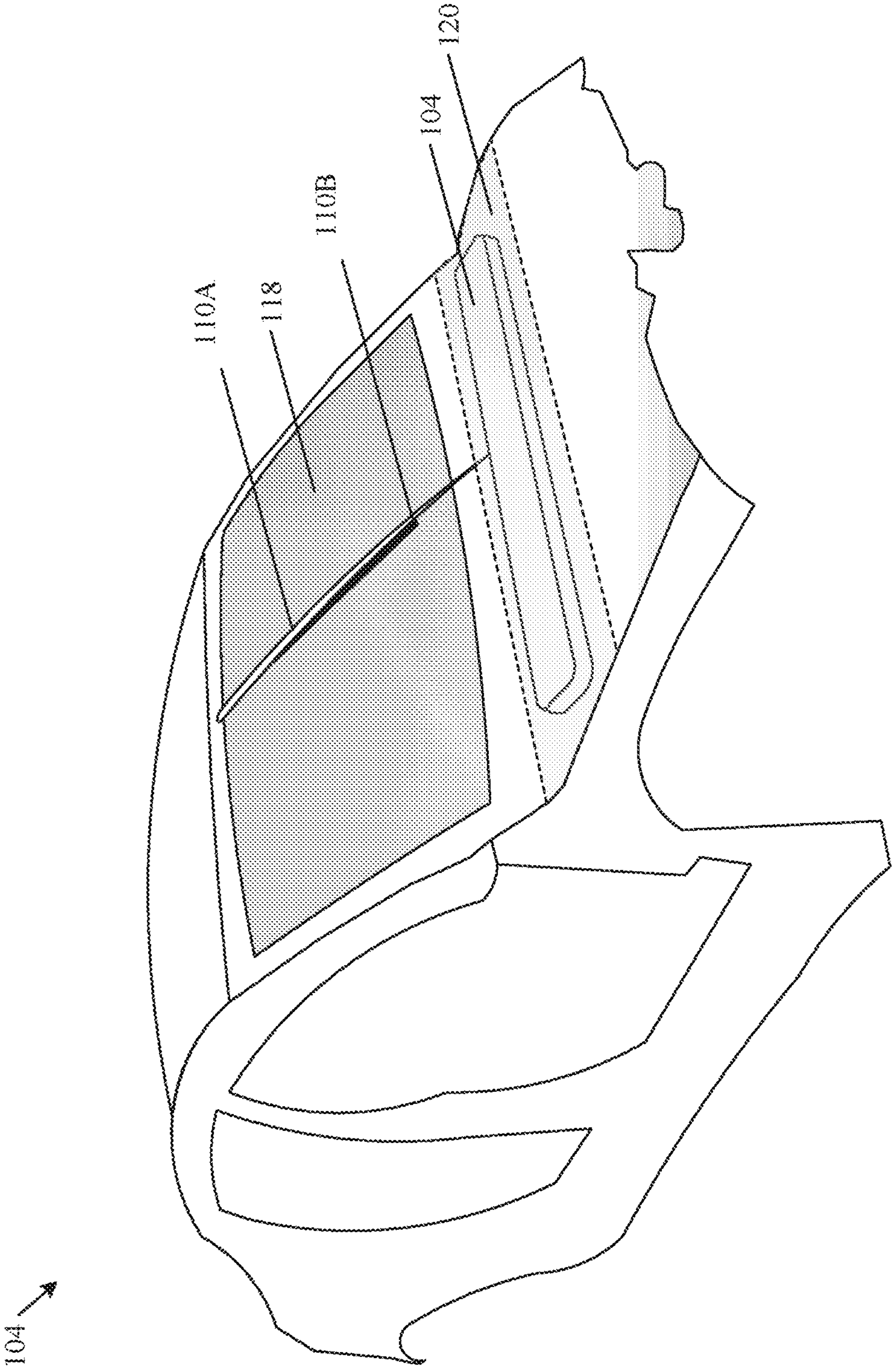

FIG. 1B

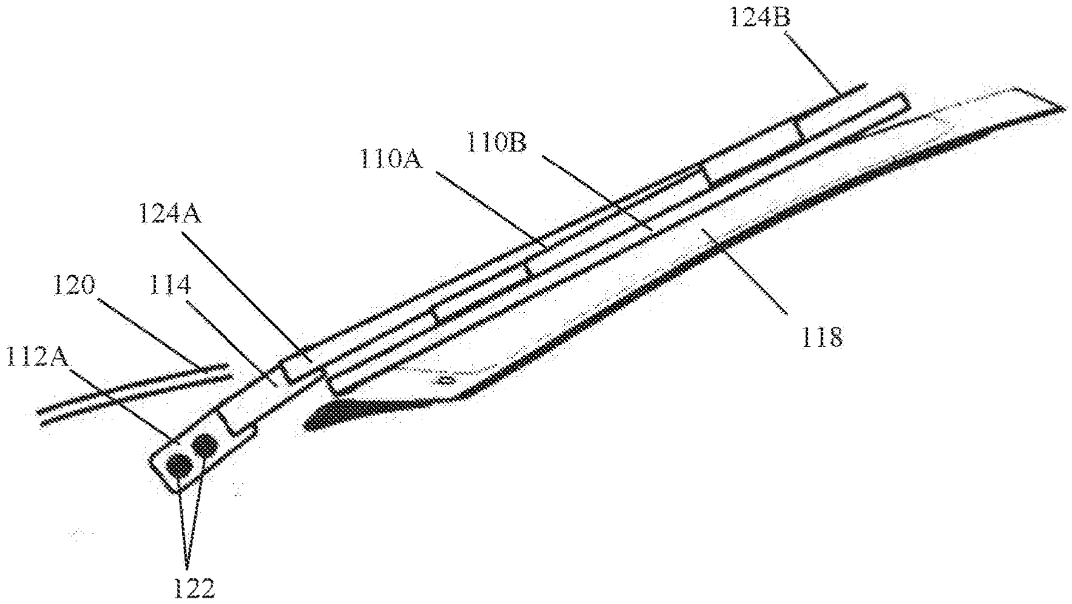
124B
110B
110A
124A
120
114
112A
118
122

FIG. 1C

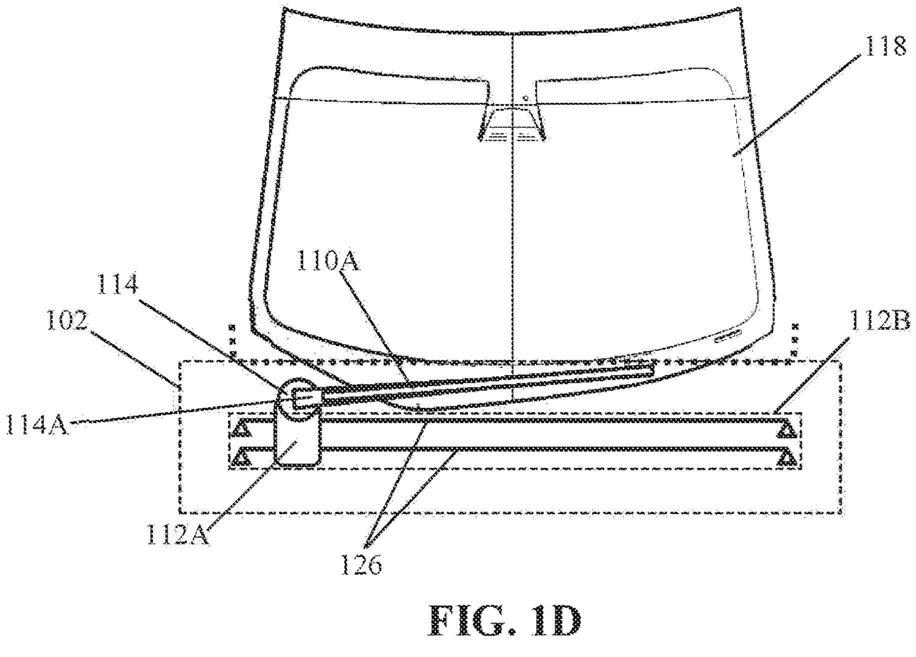
118
110A
114
102
112B
114A
112A
126

FIG. 1D

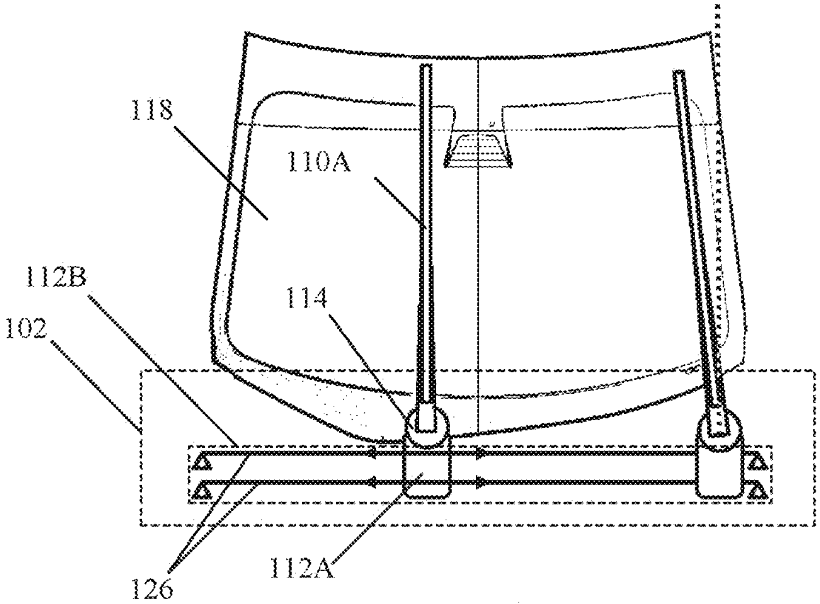

FIG. 1E

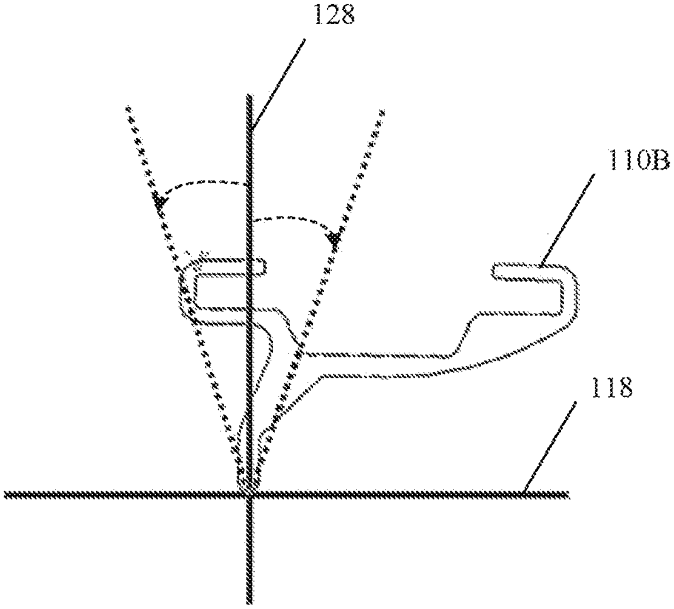

FIG. 1F

ELECTROMAGNETIC WINDSHIELD WIPER SYSTEM

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 16/291,186, entitled "ELECTROMAGNETIC WINDSHIELD WIPER SYSTEM", filed Mar. 4, 2019, which claims priority to U.S. Provisional Application No. 62/638,516, entitled "ELECTROMAGNETIC WINDSHIELD WIPER SYSTEM", filed Mar. 5, 2018, each of which is hereby incorporated herein by reference in its entirety and made part of the present U.S. Utility patent application for all purposes.

FIELD

Various embodiments of the disclosure relate to a windshield wiper system. More specifically, various embodiments of the disclosure relate to an electromagnetic windshield wiper system that exhibits power efficiency and produces minimal friction during operation.

BACKGROUND

Advancements in the field of windshield cleaning systems and ergonomic vehicle design have led to an increase in the demand for windshield wiper systems that are not only visually appealing but are also effective in cleaning the windshields of a vehicle. In certain scenarios, a driver or in-vehicle cameras (e.g., in case of assisted and autonomous driving) require an unobstructed field-of-view of the path ahead from inside of a vehicle. Conventional windshield wiper systems that use multiple wiper blades usually have a cluttered design and do not sufficiently clear the windshield, which may hamper the unobstructed field-of-view of the path ahead.

In some conventional wiper systems, electrical motors are used to move one or more wiper blades to clean a windshield of a vehicle. The electrical motors include many mechanical components, such as gears and bearings, to slide the wiper blades. However, such sliding motion of the mechanical components creates significant friction resulting in the need for additional power to be supplied by the in-vehicle battery, which decreases vehicle range. Further, the gears and bearings of the conventional systems are susceptible to rust and wear, which may lead to poor and in-efficient cleaning of windshields. Such corrosion and system deterioration is especially true in geographical areas subject to harsh weather conditions, like significant rainfall or snowfall. When these systems corrode accident risk increases, and may result in driver-assist or autonomous-driving functionality being rendered inoperable.

In addition, as the curvature of windshields becomes more complex, conventional wiper systems have difficulty adapting to varying surface profiles and thus affecting their ability to effectively clean windshield contaminants. For example, conventional systems are not capable of effectively cleaning a windshield that curves around a driver, that is the windshield provides a view directly in front of the driver but also to the left and to the right. Further, conventional wiper systems have varying influence from aerodynamic effects as they traverse from the bottom of the windshield to the top and vice-versa, due to airflow vector changes.

Further limitations and disadvantages of conventional and traditional approaches will become apparent to one skilled in the art by comparing the described systems with some aspects of the present disclosure, as set forth in the remainder of the present application and with reference to the drawings. Hence, there is need for a new windshield wiper system that overcomes the aforementioned drawbacks.

SUMMARY

An electromagnetic windshield wiper system for a vehicle is substantially shown in, and/or described in connection with, at least one of the FIGURES, as set forth more completely in the claims.

This and other features and their advantages of the present disclosure may be appreciated from a review of the following detailed description of the present disclosure, along with the accompanying FIGURES in which like reference numerals refer to like parts throughout.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1**A is a block diagram that illustrates an exemplary electromagnetic wiper system, in accordance with an embodiment of the present disclosure.

FIG. **1**B illustrates the electromagnetic wiper system of FIG. **1**A installed in a vehicle as a modular component of the vehicle, in accordance with an embodiment of the present disclosure.

FIGS. **1**C to **1**E collectively illustrate different operative states of the exemplary electromagnetic wiper system of FIG. **1**A, in accordance with an embodiment of the present disclosure.

FIG. **1**F illustrates an extent of the angle of attack of a wiper arm of the exemplary electromagnetic wiper system of FIG. **1**A with respect to a reference axis, in accordance with an embodiment of the present disclosure.

DETAILED DESCRIPTION

The following described implementations may be found in the disclosed electromagnetic wiper system for a vehicle. The disclosed electromagnetic wiper system may have a modular architecture that can be readily installed in a vehicle. The electromagnetic wiper system includes a wiper-arrangement that may include a wiper arm and a wiper blade. The wiper arm and the wiper blade may be attached to each other, and thus, form a linear mono wiper in an uncluttered design.

The disclosed electromagnetic wiper system may further include a linear actuator that may include a guide rail and an electromagnetic moving block. The guide rail may include a plurality of permanent magnet bars that may be disposed horizontally along a curvature of the windshield of the vehicle. The electromagnetic moving block may act as an electromagnetic train, and may include a plurality of perforations and at least an electromagnetic coil that surrounds the plurality of perforations in the electromagnetic moving block. The disclosed electromagnetic wiper system may further include control circuitry that controls the linear motion of the electromagnetic moving block through the plurality of permanent magnet bars. The linear motion of the electromagnetic moving block through the plurality of permanent magnet bars may be controlled to steer the wiper arm that may be coupled to the electromagnetic moving block, back and forth across the entire length of the windshield to wipe a defined region, for example, the entire transparent area (i.e., near cent percent area) of the windshield. The plurality of permanent magnet bars may pass through the plurality of perforations surrounded by the electromagnetic coil in the electromagnetic moving block. This may result in minimal friction during the linear motion of the electromagnetic moving block. Alternatively stated, the disclosed electromagnetic wiper system may utilize the current carrying electromagnetic coil in the electromagnetic moving block to generate a magnetic induction-based electrodynamic force to steer the wiper arm, and is thereby able to efficiently and effectively minimize friction that otherwise may exist between the moving elements of a conventional wiper system.

In accordance with an embodiment, when not in operation, the control circuitry causes the linear mono wiper to be stowed beneath the hood of the vehicle. This improves the aerodynamic performance of the vehicle during operation, especially at high speeds, and reduces exposure to environmental damage, like direct sun exposure. In contrast to conventional wiper systems that do not apply a constant force on the windshield, the control circuitry according to the present disclosure adjust the inclination angle and/or angle of attack of the wiper arm with respect to a reference axis during the linear motion of the electromagnetic moving block. Such adjustment of the extent of inclination of the wiper arm may enable effective cleaning of the windshield and improve washer spray performance. As a result of the uncluttered design and almost frictionless movement of the electromagnetic moving block, the disclosed electromagnetic wiper system improved the field-of-view of the path for drivers, driver-assist functions, and autonomous-driving functions.

FIG. **1**A is a block diagram that illustrates an exemplary electromagnetic wiper system, in accordance with an embodiment of the present disclosure. As shown in FIG. **1**A an electromagnetic wiper system **102** is part of a vehicle **104**. Vehicle **104** also includes a display **106**, a user interface **106**A for the display **106**, a vehicle power system **108**, and a battery **108**A (or a battery-pack) for the vehicle power system **108** in the vehicle **104**. As shown in FIG. **1**A, the electromagnetic wiper system **102** includes a wiper arrangement **110**, a linear actuator **112**, a rotational actuator **114**, and control circuitry **116** that is communicatively coupled to the linear actuator **112** and the rotational actuator **114**. The wiper arrangement **110** includes a wiper arm **110**A and a wiper blade **110**B. The linear actuator **112** may further include an electromagnetic moving block **112**A and a guide rail **112**B.

In described embodiments, the electromagnetic wiper system **102** is a magnetic induction based windshield wiper system. The electromagnetic wiper system **102** may have a modular architecture. The electromagnetic wiper system **102** may be pre-formed as a sub-assembled module and subsequently installed into vehicle **104**, thereby reducing the installation time during general assembly of components into vehicle **104**. An exemplary embodiment of the electromagnetic wiper system **102** is shown in FIG. **1**B. The control circuitry **116** of the electromagnetic wiper system **102** may control the linear actuator **112** and the rotational actuator **114** to steer the wiper arrangement **110** across the entire length of a windshield of the vehicle **104**.

Vehicle **104** may be an electric vehicle, a hybrid vehicle, a vehicle with driver-assist capabilities, and/or a vehicle with autonomous-drive capabilities. In embodiments, the vehicle **104** may be an air-borne vehicle, a water-borne vehicle, or a hybrid of an air-borne, or a land-borne vehicle.

The display **106** may include suitable logic, circuitry, interfaces, and/or code that renders various types of information and controls via the user interface (UI) **106**A.

UI **106**A may be a customized graphical user interface (GUI) that displays the various types of information, controls, or settings to operate the electromagnetic wiper system **102**. The electromagnetic wiper system **102** may also be controlled or operated by a hardware control button or a wiper switch provided in the vehicle **104**. The display **106** may be a touch screen that receives an input from the one or more occupants of the vehicle **104**. Examples of the display **106** include, but are not limited to a display of the infotainment head unit, a projection-based display, a see-through display, and/or an electro-chromic display.

The vehicle power system **108** may regulate the charging and the power output of the battery **108**A to various electric circuits and the loads of the vehicle **104**, such as the electromagnetic wiper system **102** and the display **106**. In accordance with an embodiment, the vehicle power system **108** may include power electronics. The vehicle power system **108** may be communicatively connected to the control circuitry **116** to receive control signals from the control circuitry **116** (or an electronic control unit (ECU)) to modulate the current and power distribution for different operational components of the electromagnetic wiper system **102**. The control circuitry **116** control a plurality of operational parameters of the electromagnetic wiper system **102** based on the adaptive modulation of the power and current to the different operational components of the electromagnetic wiper system **102**. Exemplary parameters include, but are not limited to, the velocity of the electromagnetic moving block **112**A, the angle of inclination of a wiper arm of the wiper arrangement **110** (or a change in the angle of inclination), the movement frequency of the wiper arm **110**A, and the frequency that any washer fluid is released from a spray washer unit (not shown) and the duration of any such release.

The battery **108**A may be a rechargeable source of electric power for one or more electric circuits or loads (not shown), such as the electromagnetic wiper system **102** and the display **106** of the vehicle **104**. In some embodiments, instead of a single battery, a battery pack has a plurality of batteries arranged in a planar or non-planar array to power the vehicle **104**.

Although not shown, the vehicle **104** may include an in-vehicle network, which provides communication channels and ports for communication between various control units, components, and/or systems of the vehicle **104**, such as communication ports for exchanging data among the display **106**, the control circuitry **116** of the electromagnetic wiper system **102**, and other associated circuitry in the vehicle **104**. The in-vehicle network may facilitate access control and/or communication between the control circuitry **116** and other ECUs, such as a telematics control unit (TCU) of the vehicle **104**. Various devices or components in the vehicle **104** may connect to the in-vehicle network, in accordance with various wired and wireless communication protocols. Examples of the wired and wireless communication protocols for the in-vehicle network may include, but are not limited to, a vehicle area network (VAN), a CAN bus, Domestic Digital Bus (D2B), Time-Triggered Protocol (TTP), FlexRay, IEEE 1394, Carrier Sense Multiple Access With Collision Detection (CSMA/CD) based data communication protocol, Inter-Integrated Circuit (I.sup.2C), Inter Equipment Bus (IEBus), Society of Automotive Engineers (SAE) J1708, SAE J1939, International Organization for Standardization (ISO) 11992, ISO 11783, Media Oriented Systems Transport (MOST), MOST25, MOST50, MOST150, Plastic optical fiber (POF), Power-line communication (PLC), Serial Peripheral Interface (SPI) bus, and/or Local Interconnect Network (LIN).

The wiper arrangement **110** includes the wiper arm **110**A and the wiper blade **110**B. The wiper arm **110**A may be attached with the wiper blade **110**B along a length of the wiper blade **110**B to form a linear mono wiper providing an uncluttered design to the electromagnetic wiper system **102**. At least one end of the wiper arm **110**A may be coupled to the electromagnetic moving block **112**A, and the other end may be a free end (i.e., not coupled to any structure), as shown, for example, in FIG. **1**B. An example of the wiper arrangement **110** is shown and described in FIG. **1**C.

As shown in FIG. **1**C, the linear actuator **112** includes moving components that exhibit translational motion, for example the electromagnetic moving block **112**A, and stationary (or affixed) components, for example, the guide rail **112**B. The assembly of the electromagnetic moving block **112**A and the guide rail **112**B collectively move the wiper arm **110**A of the wiper arrangement **110** in a linear motion along the length of a windshield of the vehicle **104**. In embodiments, the linear actuator **112** is a linear motor, such as a linear inductor motion. In embodiments, the linear actuator **112** has mechanical components that convert the rotation of a motor shaft into a linear motion of the electromagnetic moving block **112**A.

The rotational actuator **114** may have a fixed portion (e.g., a coupler) to connect to the electromagnetic moving block **112**A. The rotational actuator **114** may include a shaft that attach to one end of the wiper arm **110**A. Based on control signals from the control circuitry **116**, the wiper arrangement **110** may be stowed and/or and the specific wiping angle may be set. For example, the shaft of the rotational actuator **114** may rotate to stow the wiper arrangement **110** and/or set or change the wiping angle. Rotational actuator **114** may be a stepper motor, servo motor, digital-servo motor, or another motor. An example of the rotational actuator **114** is shown and described in FIGS. **1**C and **1**D.

As shown in FIGS. **1**D and **1**E, the control circuitry **116** controls the linear motion of the electromagnetic moving block **112**A along the guide rail **112**B to allow steering of the wiper arm **110**A coupled to the electromagnetic moving block **112**A. The control circuitry **116** may also control other components of the electromagnetic wiper system **102**, such as the linear actuator **112**, a washer spray, and the rotational actuator **114**. The control circuitry **116** may include, but is not limited to including, a microcontroller, an Application-Specific Integrated Circuit (ASIC) processor, a microcontroller, a state machine, and/or other processors or control circuits.

During operation, a trigger signal (or instruction) may be received at the control circuitry **116** of the electromagnetic wiper system **102** to initiate operation of the electromagnetic wiper system **102**. Based on the received trigger signal, the control circuitry **116** may generate and transmit control signals (or control instructions) to the vehicle power system **108**, to provide power specific to the linear actuator **112**, the rotational actuator **114**, or a spray washer attached with the wiper arrangement **110**. The trigger signal may be received at the control circuitry **116** based on a user input. For example, a driver of the vehicle **104** may switch "ON" the wiper switch or select a UI control on the UI **106**A via the display **106**, to start the operation of the electromagnetic wiper system **102**. In embodiments, the trigger signal is generated without human interaction with the vehicle **104**, based on the one or more in-vehicle sensors, such as an in-vehicle camera, an in-vehicle radar, an in-vehicle moisture sensor, and/or in-vehicle camera or sensors coupled to a neural network that determines the presence of rain or another condition requiring clearing of the windshield. In embodiments, vehicle sensors (such as a camera or radar) capture a field-of-view through a defined region of the windshield. The sensors may detect a weather condition. Examples of the different weather conditions include, but are not limited to, snow fall, rain, wind, humid, smoke, fog, or arid weather condition. In some implementations, a degree of a weather condition may be further detected, for example, heavy rain fall, light snowfall, strong dirt carrying winds, and the like, which may impact visibility. The sensors may generate real time or near-real time trigger signals for auto-activation and controlled operations of the electromagnetic wiper system **102**.

FIG. **1**B illustrates the electromagnetic wiper system of FIG. **1**A installed in a vehicle as a modular component of the vehicle, in accordance with an embodiment of the present disclosure. As show in FIG. **1**B, vehicle **104** is fitted with the electromagnetic wiper system **102** as a modular component. FIG. **1**B also shows a windshield **118** and a hood **120** that may be raised to provide a compartment that stows the wiper arrangement **110** when not in operation. The wiper arm **110**A may be attached with the wiper blade **110**B to form a mono wiper blade of the wiper arrangement **110**. In embodiments, the control circuitry **116** is embedded within the chassis of the electromagnetic wiper system **102**. In embodiments, the control circuitry **116** or one or more features of the control circuitry **116** is implemented in an ECU of vehicle **104**.

FIGS. **1**C to **1**E collectively illustrate different operative states of the exemplary electromagnetic wiper system of FIG. **1**A, in accordance with an embodiment of the present disclosure. As shown in FIG. **1**C, wiper blade **110**B is attached to the wiper arm **110**A along a length of the wiper arm **110**A. The wiper blade **110**B may be in contact with the windshield **118** to physically wipe a defined region of the windshield **118**. FIG. **1**C also shows the positioning of the electromagnetic moving block **112**A of the linear actuator **112** and the rotational actuator **114** below the hood **120** of the vehicle **104**.

In accordance with an embodiment, the electromagnetic moving block **112**A includes a plurality of perforations **122**. The electromagnetic moving block **112**A may be also referred to an electromagnetic train. The electromagnetic moving block **112**A may be mounted on the guide rail **112**B such that the guide rail **112**B passes through the plurality of perforations **122**. The guide rail **112**B may be one or a plurality of permanent magnet bars. The number of perforations in the electromagnetic moving block **112**A may be equal to the number of permanent magnet bars. At least one electromagnetic coil may be provided within the electromagnetic moving block **112**A to surround the plurality of perforations **122** in the electromagnetic moving block **112**A.

In accordance with an embodiment, one end, such as a first end **124**A, of the wiper arm **110**A is coupled to the electromagnetic moving block **112**A and the other end, such as a second end **124**B, may be a free end, as shown. In some embodiments, the first end **124**A of the wiper arm **110**A is coupled to the rotational actuator **114**, which in turn is coupled to the electromagnetic moving block **112**A.

FIG. **1**D illustrates the electromagnetic wiper system **102** with the wiper arm **110**A in a stowed mode. Also shown is the guide rail **112**B that includes a plurality of permanent magnet bars **126** disposed horizontally along a curvature of the windshield **118** of the vehicle **104**. In an embodiment, the guide rail **112**B is affixed to a chassis of the electromagnetic wiper system **102**. The chassis may be further affixed to the body of the vehicle **104**. The electromagnetic moving block **112**A may be mounted on the guide rail **112**B such that the plurality of permanent magnet bars **126** of the guide rail **112**B pass through the plurality of perforations **122** present in the electromagnetic moving block **112**A. The control circuitry **116** may direct rotational actuator **114** to stow components of the wiper arrangement **110**, such as the wiper arm **110**A under the hood **120** of the vehicle **104**.

In accordance with an embodiment, the rotational actuator **114** includes a shaft **114**A. The shaft **114**A may be attached to the first end **124**A of the wiper arm **110**A and the control circuitry **116** may control the rotation of the shaft **114**A. Using the rotational actuator **114** the control circuitry **116** may send signals to stow the wiper arrangement **110** and set specific attack angles for wiping the windshield **118**. The attack angle is the angle of the wiper arm **110**A with respect to the windshield **118**. In other embodiments, the wiper arm **110**A is rotated without the use of the rotational actuator **114**. For example, the wiper arm **110**A is rotated by applying differential forces on the electromagnetic moving block **112**A by the plurality of permanent magnet bars **126**.

As shown in FIG. **1**E, the control circuitry **116** may control a linear motion of the electromagnetic moving block **112**A through the plurality of permanent magnet bars **126** to steer the wiper arm **110**A coupled to the electromagnetic moving block **112**A, back and forth across a length of the windshield **118** to wipe a defined region of the windshield **118**.

In embodiments, the guide rail **112**B includes straight permanent magnet bars disposed along the entire length of the windshield **118**. In such embodiments, the wiper arrangement **110**, including the wiper arm **110**A, moves in a straight line along the length of the windshield **118** of the vehicle **104**. In embodiments, the guide rail **112**B includes a plurality of curved permanent magnet bars (not shown) parallel to the curvature of the windshield **118**. In such embodiments, the wiper arrangement **110**, including the wiper arm **110**A, moves along the curvature of the windshield **118**. In other embodiments, the curved permanent magnet bars have a different curvature compared to the curvature of the windshield **118**. In embodiments, the control circuitry **116** controls the attack angle of the wiper arm **110**A to ensure that the wiper arm stays in contact with the windshield **118**. In other embodiments, a mechanical part, such as a spring, maintains the wiper arm **110**A in contact with windshield **118**.

In accordance with an embodiment, in response to the received trigger signal, the control circuitry **116** of the electromagnetic wiper system **102** positions the wiper arm **110**A, including the wiper blade **110**B attached to the wiper arm **110**A, at a specific inclination angle, for example, an inclination angle of approximately "90.degree." (i.e., an upright position) with respect to a longitudinal axis of the windshield **118**. The wiper arm **110**A may be positioned at the specific inclination angle from a previous position of the wiper arm **110**A, for example, an inclination angle near "0.degree." (e.g., in the stowed mode). The positioning of the wiper arm **110**A at the specific inclination angle with respect to the longitudinal axis may be done by use of the rotational actuator **114**. Based on the received trigger signal, the rotational actuator **114** may rotate the shaft **114**A. Then, the control circuitry **116** may cause an electrodynamic force to be induced to move the electromagnetic moving block **112**A through the plurality of permanent magnet bars **126** in a linear motion. Using this electrodynamic force produces minimal friction compared to conventional systems. To reduce friction, an air gap between the electromagnetic moving block **112**A and the permanent magnet bars **126** may be created. Alternatively, oil or grease may be placed in the plurality of perforations **122** to reduce friction.

In embodiments, the control circuitry **116** may be further control a spray fluid that may be used to clean the windshield **118**. To improve cleaning, a consistent blade force of the wiper blade **110**B on the windshield **118** may be maintained throughout the back and forth movement of the wiper arm **110**A.

FIG. **1**F illustrates an extent of the angle of attack of a wiper arm of the exemplary electromagnetic wiper system of FIG. **1**A with respect to a reference axis, in accordance with an embodiment of the present disclosure. With reference to FIG. **1**F, there is shown a reference axis **128**, which is perpendicular to the linear motion of the electromagnetic moving block **112**A and may be considered to be parallel to at least a portion of the windshield **118**. The control circuitry **116** may adjust the angle of attack and/or the inclination angle of the wiper arm **110**A with respect to the reference axis **128** during the linear motion of the electromagnetic moving block **112**A.

The angle of attack for the wiper arm **110**A (or wiper blade **110**B) may be adjusted within a range (for example, "−6.degree. to +6.degree." with respect to the reference axis **128**). The inclination angle and angle of attack may be adjusted based on a defined criteria, such as a weather condition, a type of deposit (for example, soil, water, or snow) accumulated on the windshield **118**, a priority setting to first wipe a driver-sensitive region of the windshield **118**, or other defined conditions that may facilitate the wiper arm **110**A to clear the desired area of the windshield **118**, such as a maximum area, the area in front of the certain sensors, or another area of the windshield **118**. The inclination angle may also be adjusted to define the coverage area for wiping.

The rotational actuator **114** may be an operational component of the electromagnetic wiper system **102** that performs the angular displacement of the wiper arm **110**A. At a given time, the wiper arm **110**A may be inclined at a specific inclination angle with respect to the reference axis **128**. For example, in a non-operational state, the wiper arm **110**A may be inclined at "0 degree" or near "0" degree inclination angle beneath the hood **120** of the vehicle **104**. In operational state, the wiper arm **110**A may be inclined at a specific inclination angle, such as "90 degrees" (+/−6 degrees) with respect to the reference axis **128**. After the specific inclination angle is set as per the defined criteria for the wiper arm **110**A, the linear actuator **112** may be activated to move the wiper arm **110**A along the length of the windshield **118**. The control circuitry **116** may control the supply of current/power to the electromagnetic coil within the electromagnetic moving block **112**A, to induce a time-varying/moving magnetic field within the electromagnetic moving block **112**A. As a result of the design, and almost frictionless movement of the electromagnetic moving block, the disclosed electromagnetic wiper system **102** is more power efficient that traditional systems, while also providing an unobstructed field-of-view for sensors and/or drivers of the vehicle **104**. This may facilitate drivers, driver-assist functionality, and/or autonomous-driving functionality to make precise and quick decisions. Both the inclination angle and the angle of attack may be adjusted over time based upon operational conditions and/or linear position of the electromagnetic moving block **112**A.

While the present disclosure has been described with reference to certain embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the scope of the present disclosure. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the present disclosure without departing from its scope. Therefore, it is intended that the present disclosure not be limited to the particular embodiment disclosed, but that the present disclosure will include all embodiments that fall within the scope of the appended claims. Equivalent elements, materials, processes or steps may be substituted for those representatively illustrated and described herein. Moreover, certain features of the disclosure may be utilized independently of the use of other features, all as would be apparent to one skilled in the art after having the benefit of this description of the disclosure.

As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any contextual variants thereof, are intended to cover a non-exclusive inclusion. For example, a process, product, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements, but may include other elements not expressly listed or inherent to such process, product, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition "A or B" is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B is true (or present).

Although the steps, operations, or computations may be presented in a specific order, this order may be changed in different embodiments. In some embodiments, to the extent multiple steps are shown as sequential in this specification, some combination of such steps in alternative embodiments may be performed at the same time. The sequence of operations described herein can be interrupted, suspended, reversed, or otherwise controlled by another process. It will also be appreciated that one or more of the elements depicted in the drawings/FIGURES can also be implemented in a more separated or integrated manner, or even removed or rendered as inoperable in certain cases, as is useful in accordance with a particular application.

What is claimed is:

1. A method comprising:

receiving real time sensor data from a plurality of devices associated with a vehicle, wherein the plurality of devices comprises at least an imaging device and a second device;

analyzing, by a neural network, the real time sensor data;

determining a presence of a precipitation-based weather condition based at least in part on said analyzing the real time sensor data;

determining a presence of at least one of a non-precipitation condition based at least in part on said analyzing the real time sensor data;

characterizing at least one of a degree of the determined precipitation weather condition or a degree of the determined non-precipitation condition; and

modifying an operation of the vehicle based at least in part on said characterizing at least one of a degree of the determined precipitation weather condition or a degree of the determined non-precipitation condition.

2. The method of claim **1**, wherein the imaging device is configured to capture a plurality of images of a field-of-view through a predefined region of a windshield of the vehicle, wherein the real time sensor data comprises the plurality of images.

3. The method of claim **1**, wherein the second device comprises a device other than an imaging device.

4. The method of claim **1**, wherein the second device comprises a moisture sensor.

5. The method of claim **1**, wherein the second device comprises a radar device.

6. The method of claim **1**, wherein the precipitation-based weather condition or the non-precipitation condition negatively affects visibility through a window of the vehicle.

7. The method of claim **6**, wherein the precipitation-based weather condition corresponds to a presence of a weather element other than rain.

8. The method of claim **7** wherein the non-precipitation condition corresponds to a presence of smoke proximate to the vehicle.

9. The method of claim **1**, wherein the non-precipitation condition corresponds to a presence of wind having a wind speed that satisfies a threshold wind speed.

10. The method of claim **1**, wherein said modifying the operation of the vehicle comprises at least one of activating a window management system or deactivating the window management system.

11. The method of claim **10**, wherein the window management system is a windshield wiper system.

12. The method of claim **1**, wherein said modifying the operation of the vehicle comprises activating an electromagnetic wiper system of the vehicle, wherein said activating the electromagnetic wiper system of the vehicle comprises controlling a linear actuator to cause linear motion of an electromagnetic moving block through a plurality of permanent magnet bars disposed horizontally along a curvature of a windshield of the vehicle to steer a wiper arm that is coupled to the electromagnetic moving block.

13. A method comprising:

receiving real time sensor data from a plurality of devices associated with a vehicle;

analyzing, by a neural network, the real time sensor data;

determining a presence of a first weather condition based at least in part on said analyzing the real time sensor data;

determining a presence of a second condition based at least in part on analyzing the real time sensor data, wherein the second condition is different from the first weather condition;

characterizing at least one of a degree of the determined first weather condition or a degree of the determined second condition; and

modifying an operation of the vehicle based at least in part on the characterizing at least one of the degree of the determined first weather condition or the degree of the determined second condition.

14. The method of claim **13**, wherein the plurality of devices comprises an imaging device is configured to capture a plurality of images of a field-of-view through a predefined region of a windshield of the vehicle, wherein the real time sensor data comprises the plurality of images.

15. The method of claim **13**, wherein the plurality of devices comprises at least one of a radar device or a moisture sensor.

16. The method of claim **13**, wherein the first weather condition corresponds a presence of at least one of snowfall, fog, rain, smoke, or wind, and wherein the second weather condition corresponds a presence of a different one of the at least one of the snowfall, the fog, the rain, the smoke, or the wind.

17. A method comprising:

receiving first real time sensor data from an imaging device associated with a vehicle,

receiving second real time sensor data from a non-imaging device associated with the vehicle;
analyzing, using machine learning, the first real time sensor data and the second real time sensor data;
determining a presence of a precipitation weather condition based at least in part on said analyzing;
determining a presence of a non-precipitation weather condition based at least in part on said analyzing; and
modifying an operation of the vehicle based at least in part on characterizing at least one of a degree of the determined precipitation weather condition or a degree of the determined non-precipitation condition.

18. The method of claim **17**, wherein the imaging device comprises at in-vehicle camera, and wherein the non-imaging device comprises at least one of an in-vehicle radar device or an in-vehicle moisture sensor.

19. The method of claim **17**, wherein the non-precipitation condition corresponds a presence of at least one of snowfall, fog, smoke, or wind.

* * * * *

US011545666B2

(12) **United States Patent**
Wang et al.

(10) **Patent No.: US 11,545,666 B2**
(45) **Date of Patent: Jan. 3, 2023**

(54) **COMPOSITIONS AND METHODS FOR DRY ELECTRODE FILMS INCLUDING MICROPARTICULATE NON-FIBRILLIZABLE BINDERS**

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(73) Assignee: **Tesla, Inc.**, Austin, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 433 days.

(21) Appl. No.: **16/366,220**

(22) Filed: **Mar. 27, 2019**

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Related U.S. Application Data

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(51) **Int. Cl.**

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H01M 10/0525	(2010.01)
H01M 4/04	(2006.01)
H01M 4/1393	(2010.01)
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C08L 1/28	(2006.01)
C08L 27/16	(2006.01)
C08L 27/18	(2006.01)

(52) **U.S. Cl.**
CPC ***H01M 4/623*** (2013.01); ***H01M 4/0404*** (2013.01); ***H01M 4/0435*** (2013.01); ***H01M 4/1393*** (2013.01); ***H01M 4/583*** (2013.01); ***H01M 4/622*** (2013.01); ***H01M 10/0525*** (2013.01); *C08L 1/286* (2013.01); *C08L 27/16* (2013.01); *C08L 27/18* (2013.01); *C08L 2203/20* (2013.01); *Y02E 60/10* (2013.01)

(58) **Field of Classification Search**
CPC C08L 1/286; C08L 2203/20; C08L 27/16; C08L 27/18; H01M 10/0525; H01M 4/0404; H01M 4/0435; H01M 4/1393; H01M 4/583; H01M 4/622; H01M 4/623; Y02E 60/10
See application file for complete search history.

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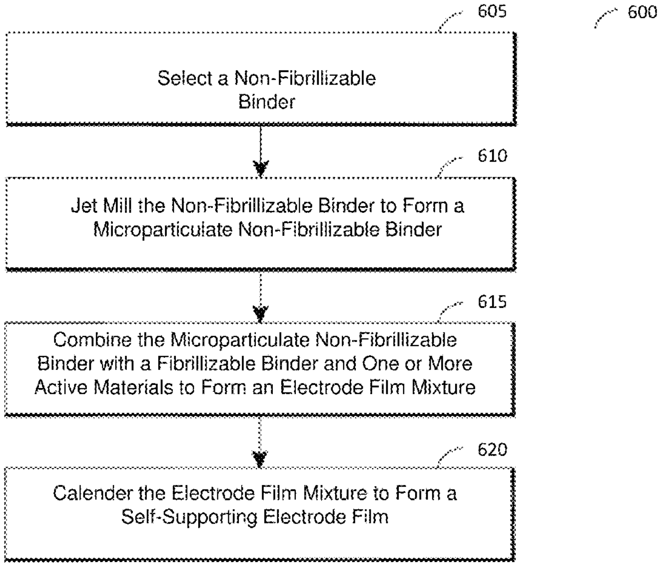
(74) *Attorney, Agent, or Firm* — Knobbe, Martens, Olson & Bear, LLP

(57) **ABSTRACT**

Provided herein are dry process electrode films, and energy storage devices incorporating the same, including a microparticulate non-fibrillizable binder having certain particle sizes. The electrode films exhibit improved mechanical and processing characteristics. Also provided are methods for processing such microparticulate non-fibrillizable electrode film binders, and for incorporating the microparticulate non-fibrillizable binders in electrode films.

18 Claims, 7 Drawing Sheets
(5 of 7 Drawing Sheet(s) Filed in Color)



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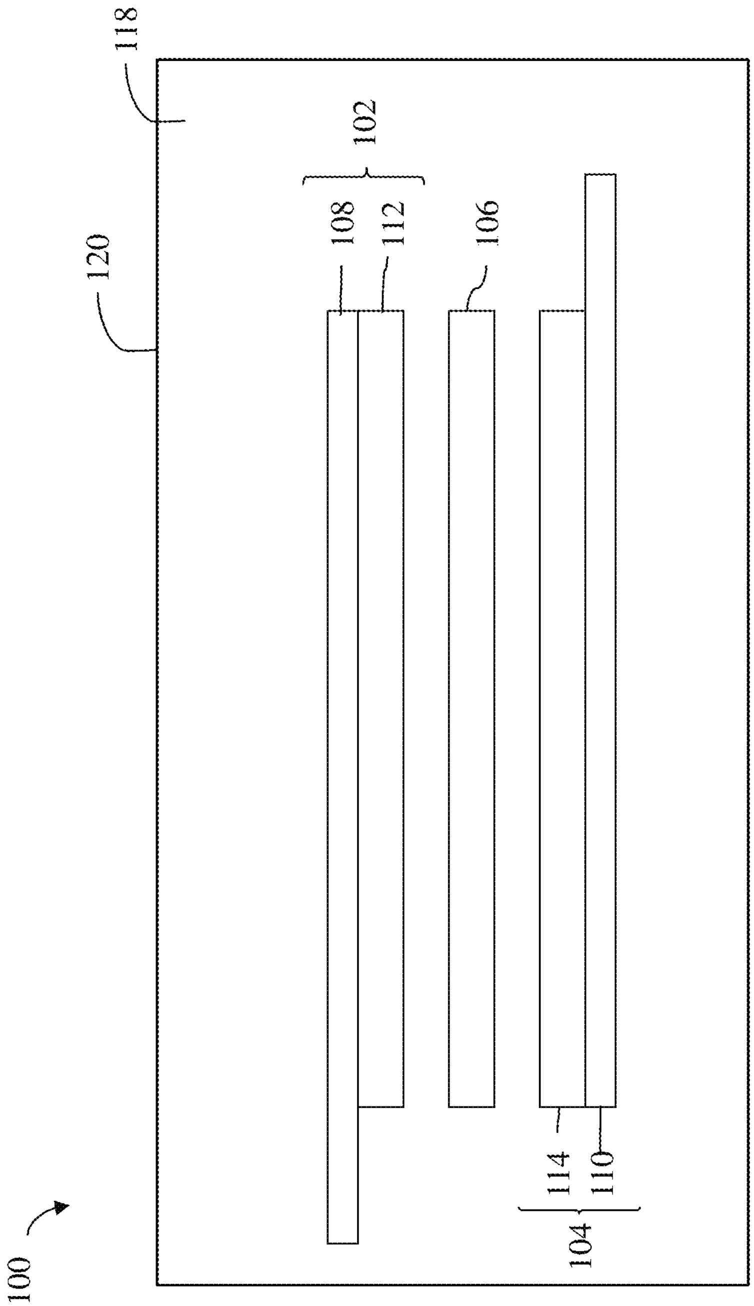

FIG. 1

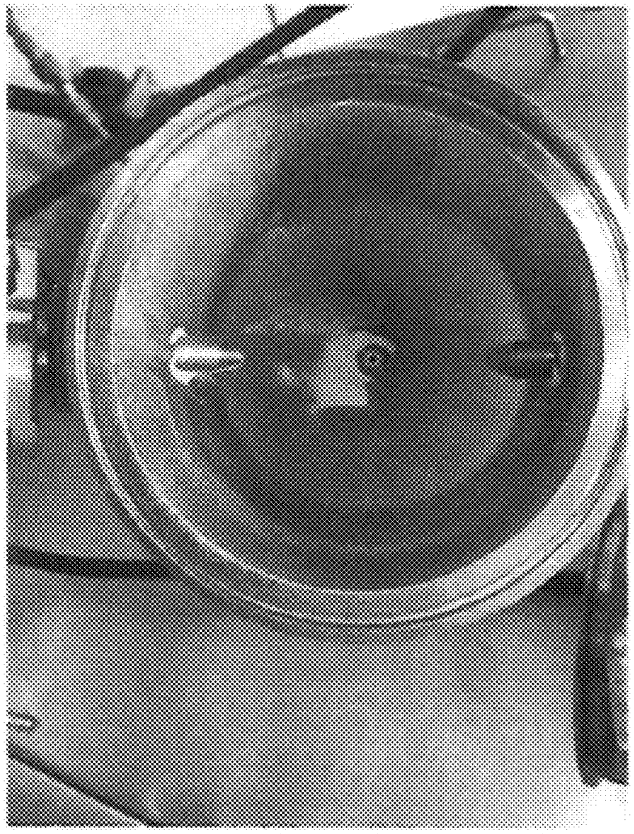

FIG. 2A

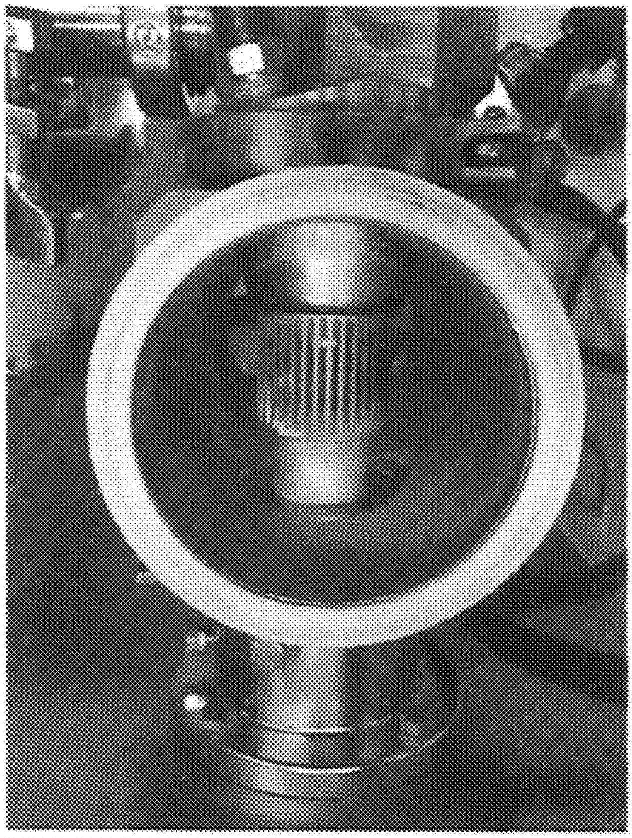

FIG. 2B

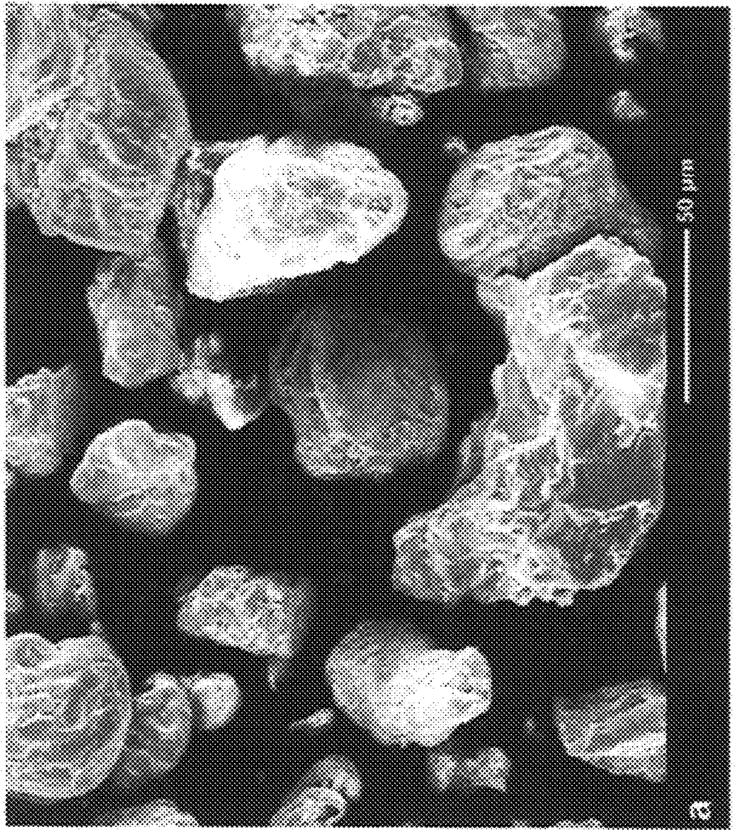

FIG. 3A

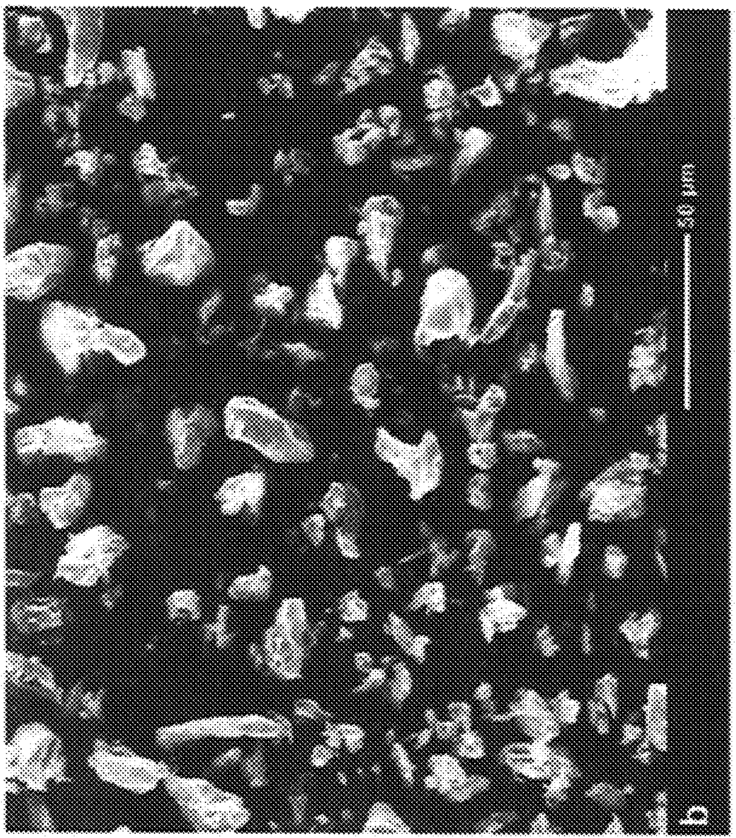

FIG. 3B

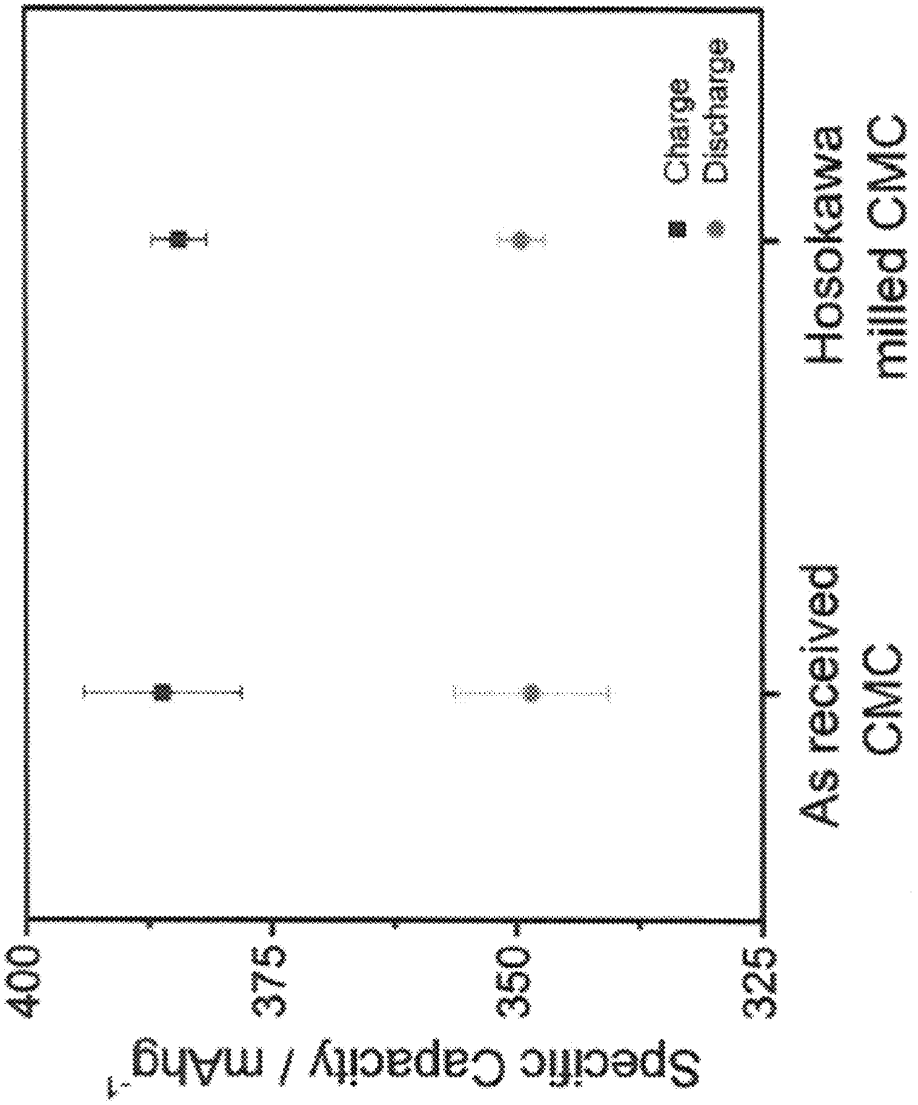
Specific Capacity / mAhg⁻¹
400
375
350
325
As received CMC
Hosokawa milled CMC
■ Charge
● Discharge

FIG. 4

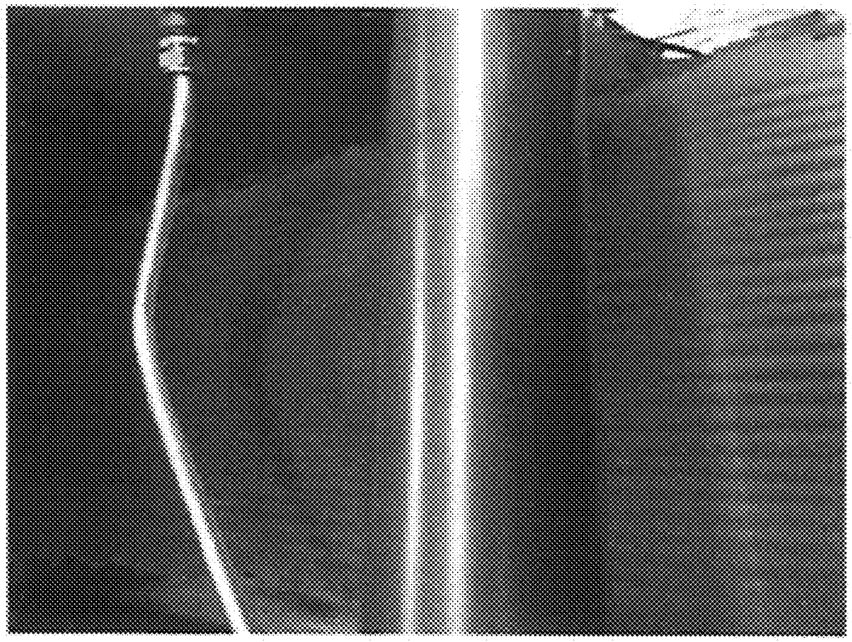

FIG. 5B

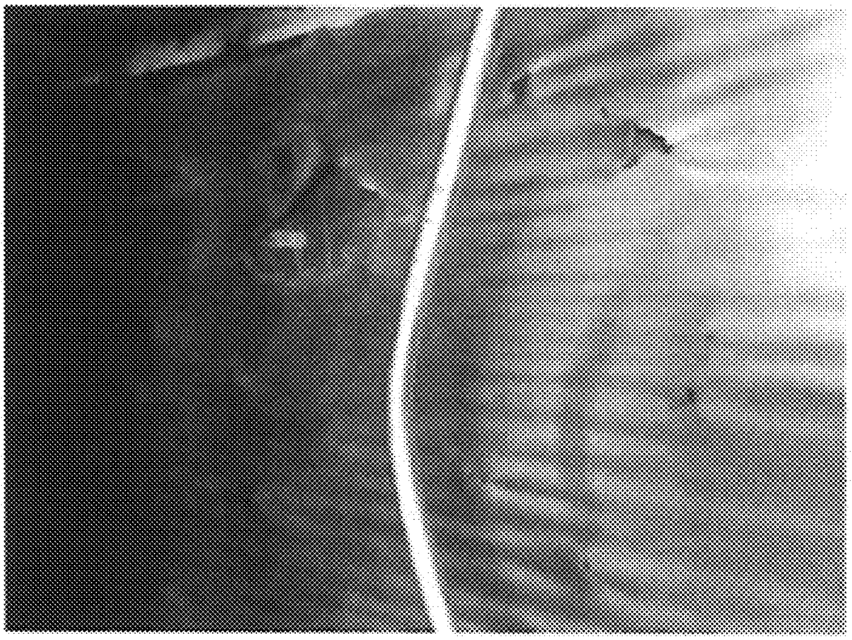

FIG. 5A

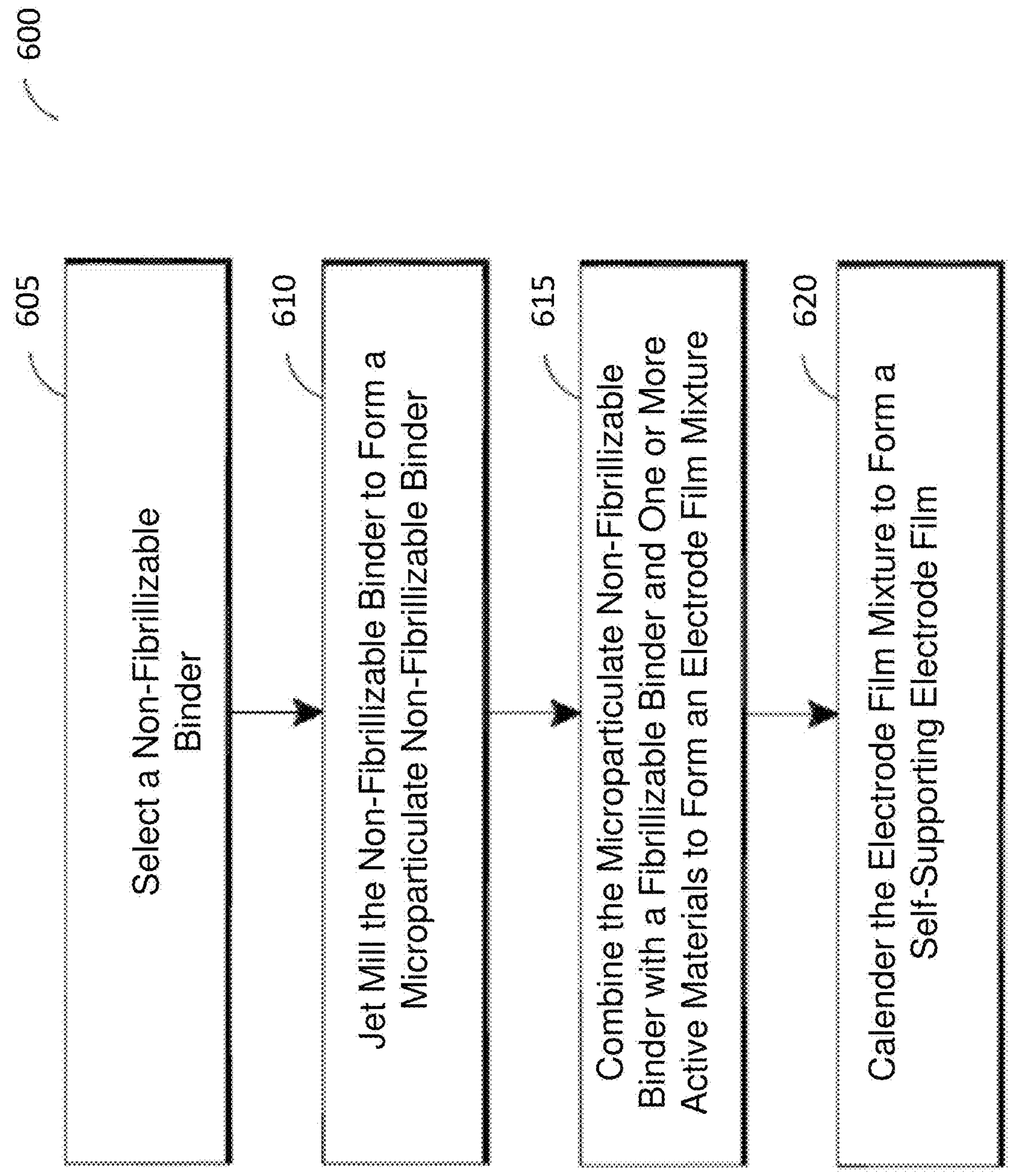
600
605
Select a Non-Fibrillizable Binder
610
Jet Mill the Non-Fibrillizable Binder to Form a Microparticulate Non-Fibrillizable Binder
615
Combine the Microparticulate Non-Fibrillizable Binder with a Fibrillizable Binder and One or More Active Materials to Form an Electrode Film Mixture
620
Calender the Electrode Film Mixture to Form a Self-Supporting Electrode Film

FIG. 6

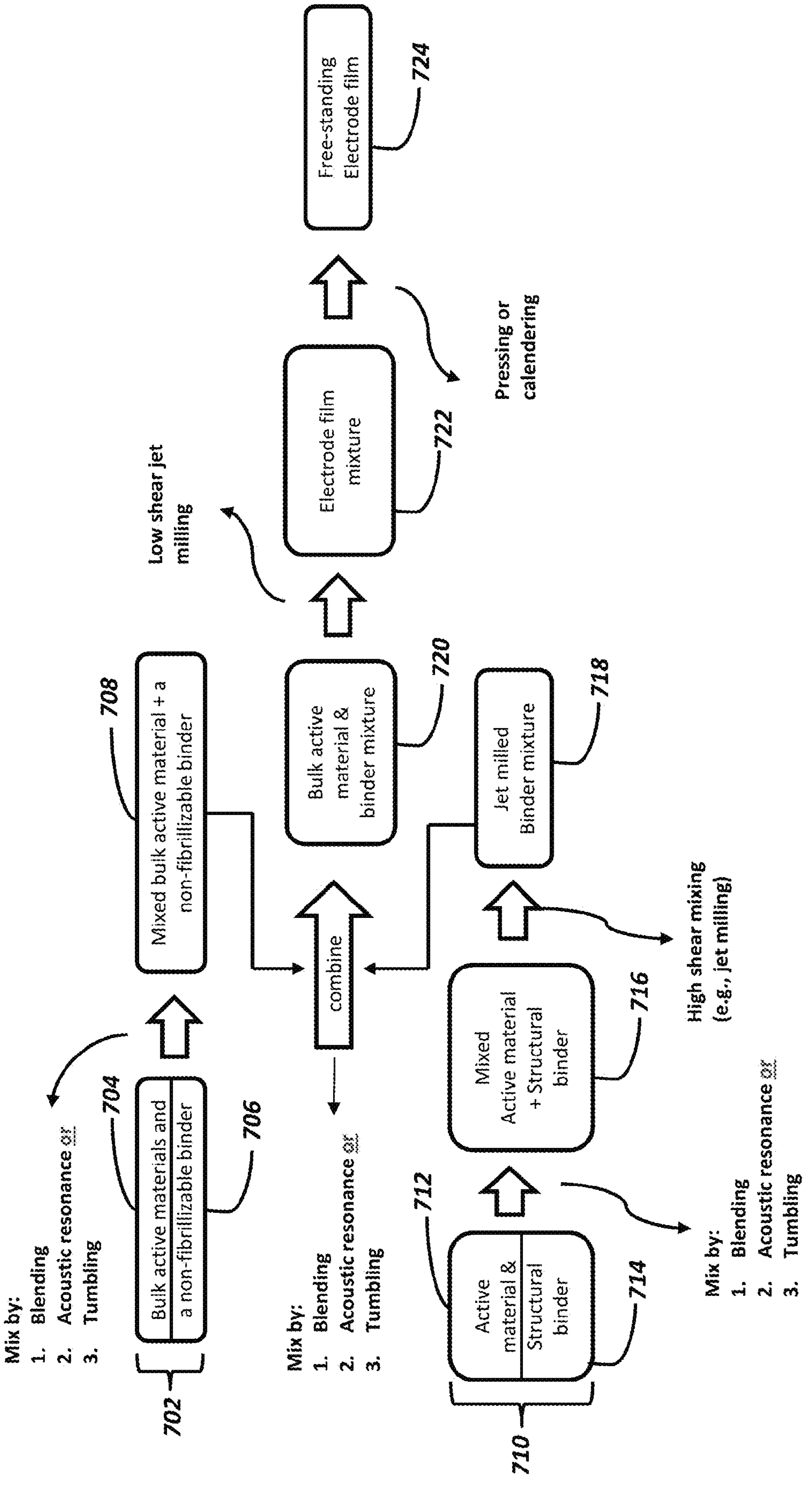
702
Bulk active materials and
a non-fibrillizable binder
704
706
Mix by:
1. Blending
2. Acoustic resonance or
3. Tumbling
Mixed bulk active material + a non-fibrillizable binder
708
710
Active material &
Structural binder
712
714
Mix by:
1. Blending
2. Acoustic resonance or
3. Tumbling
Mixed Active material + Structural binder
716
High shear mixing (e.g., jet milling)
Jet milled Binder mixture
718
combine
Mix by:
1. Blending
2. Acoustic resonance or
3. Tumbling
Bulk active material & binder mixture
720
Low shear jet milling
Electrode film mixture
722
Pressing or calendering
Free-standing Electrode film
724

FIG. 7

COMPOSITIONS AND METHODS FOR DRY ELECTRODE FILMS INCLUDING MICROPARTICULATE NON-FIBRILLIZABLE BINDERS

INCORPORATION BY REFERENCE TO ANY PRIORITY APPLICATIONS

Any and all applications for which a foreign or domestic priority claim is identified in the Application Data Sheet as filed with the present application are hereby incorporated by reference in their entirety under 37 CFR 1.57. This application claims the benefit of U.S. Provisional Patent Application No. 62/650,903, filed Mar. 30, 2018, entitled "COMPOSITIONS AND METHODS FOR DRY ELECTRODE FILMS INCLUDING MICROPARTICULATE NON-FIBRILLIZABLE BINDERS" the entirety of which is hereby incorporated by reference.

BACKGROUND

Field of the Invention

The present invention relates generally to energy storage devices, and specifically to materials and methods for dry electrode films including microparticulate non-fibrillizable binders.

Description of the Related Art

Electrical energy storage cells are widely used to provide power to electronic, electromechanical, electrochemical, and other useful devices. Such cells include batteries such as primary chemical cells and secondary (rechargeable) cells, fuel cells, and various species of capacitors, including ultracapacitors. Increasing the operating power and energy of energy storage devices, including capacitors and batteries, would be desirable for enhancing energy storage, increasing power capability, and broadening real-world use cases.

Energy storage devices including electrode films combining complimentary attributes may increase energy storage device performance in real-world applications. Furthermore, existing dry and solvent-free methods of fabrication may impose a practical limit to the composition of an electrode. Thus, new electrode film formulations, and methods for their fabrication, may result in expanded possibilities for electrode film formulation, and consequently in improved performance.

SUMMARY

For purposes of summarizing the invention and the advantages achieved over the prior art, certain objects and advantages of the invention are described herein. Not all such objects or advantages may be achieved in any particular embodiment of the invention. Thus, for example, those skilled in the art will recognize that the invention may be embodied or carried out in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other objects or advantages as may be taught or suggested herein.

In a first aspect, a self-supporting dry electrode film including a microparticulate, non-fibrillizable binder having particle sizes of about 0.5 μm to about 40 μm is provided.

In a second aspect, a dry electrode film of an energy storage device is provided. The dry electrode film includes a dry active material and a dry binder comprising a fibrillizable binder and a microparticulate non-fibrillizable binder having a D_{50} particle size of about 0.5-40 μm, and wherein the dry electrode film is free-standing.

In some embodiments, the microparticulate non-fibrillizable binder has a D_{50} particle size of about 1-25 μm. In some embodiments, the dry binder comprises up to 50 wt. % of the microparticulate non-fibrillizable binder.

In some embodiments, the microparticulate non-fibrillizable binder is selected from at least one of cellulose and a cellulose derivative. In some embodiments, the microparticulate non-fibrillizable binder is selected from at least one of cellulose, a cellulose ester, a cellulose ether, cellulose nitrate, a carboxyalkylcellulose, a cellulose salt and a cellulose salt derivative. In some embodiments, the microparticulate non-fibrillizable binder is selected from at least one of cellulose, cellulose acetate, methylcellulose, ethylcellulose, hydroxylpropylcellulose (HPC), hydroxyethylcellulose (HEC), cellulose nitrate, carboxymethylcellulose (CMC), carboxyethylcellulose, carboxypropylcellulose, carboxyisopropylcellulose, sodium cellulose, sodium cellulose nitrate and sodium carboxyalkylcellulose. In some embodiments, the microparticulate non-fibrillizable binder is selected from at least one of carboxymethylcellulose (CMC) and polyvinylidene fluoride (PVDF). In some embodiments, the cellulose or the cellulose derivative has a number average molecular weight of about 10,000 to about 500,000. In some embodiments, the cellulose derivative has a degree of substitution of about 0.7 to about 1.5.

In some embodiments, the fibrillizable binder comprises polytetrafluoroethylene (PTFE). In some embodiments, the dry electrode film is substantially free of holes, cracks and surface pits. In some embodiments, the dry electrode film has a tensile strength of at least about 1 N. In some embodiments, the dry active material comprises graphite.

In a third aspect, an electrode comprising the dry electrode film in contact with a current collector is provided. In a fourth aspect, a lithium ion battery comprising the electrode is provided.

In a fifth aspect, a method of fabricating a dry electrode film of an energy storage device is provided. The method includes processing a dry non-fibrillizable binder at high shear to form a dry microparticulate non-fibrillizable binder, combining a dry fibrillizable binder with the dry microparticulate non-fibrillizable binder to form a dry electrode film mixture, and calendering the dry electrode film mixture to form a free-standing dry electrode film.

In a sixth aspect, a method of fabricating a dry electrode film of an energy storage device is provided. The method includes providing a dry microparticulate non-fibrillizable binder, mixing the dry microparticulate non-fibrillizable binder with a dry first active material by a first nondestructive mixing process to form a dry bulk active material mixture, mixing a dry fibrillizable binder with a second dry active material by a high shear mixing process to form a dry structural binder mixture, mixing the dry bulk active material mixture and the dry structural binder mixture by a second nondestructive mixing process to form a dry electrode film mixture, and producing a free standing dry electrode film from the dry electrode film mixture.

In some embodiments, the method further comprises processing a dry non-fibrillizable binder at high shear to form the dry microparticulate non-fibrillizable binder.

All of these embodiments are intended to be within the scope of the invention herein disclosed. These and other embodiments of the present invention will become readily apparent to those skilled in the art from the following detailed description of the preferred embodiments having reference to the attached figures, the invention not being limited to any particular preferred embodiment(s) disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawing(s) will be provided by the Office upon request and payment of the necessary fee.

FIG. **1** depicts an embodiment of an energy storage device.

FIG. **2**A is a photograph of the inside of a grind chamber of a jet mill with three jets pointing at the same point. FIG. **2**B is an image of a classifier with a spinning wheel that selects an output size of particles.

FIG. **3**A depicts an SEM image of commercially available CMC particles. FIG. **3**B depicts jet-milled CMC particles that have been treated according to Example 1.

FIG. **4** provides a chart providing charge and discharge specific capacities for dry graphite anodes fabricated according to Example 1, and compare anodes fabricated with commercially available CMC and milled CMC.

FIG. **5**A depicts an image of an anode film prepared with commercially available CMC particles. FIG. **5**B depicts an image of an anode film prepared with jet milled CMC particles according to the treatment of Example 1.

FIG. **6** provides a flow chart depicting a method for fabricating a free-standing electrode film by combining non-fibrillizable binder with fibrillizable binder.

FIG. **7** provides a flow chart depicting a method for parallel processing of electrode film binders.

DETAILED DESCRIPTION

Provided herein are various embodiments of electrode films for use in energy storage devices. In particular, in certain embodiments, energy storage devices disclosed herein include electrode films including a microparticulate non-fibrillizable binder having certain particle sizes. The electrode films were discovered to exhibit improved mechanical and processing characteristics. Also provided are methods for processing such microparticulate non-fibrillizable electrode film binders, and for incorporating the microparticulate non-fibrillizable binders into electrode films. The present disclosure reveals that increased uniformity of distribution of materials in electrode films can be realized when the particle sizes of certain components are within the ranges provided herein.

Lithium ion batteries have been relied on as a power source in numerous commercial and industrial uses, for example, in consumer devices, productivity devices, and in battery-powered vehicles. However, demands placed on energy storage devices are continuously—and rapidly—growing. For example, the automotive industry is developing vehicles that rely on compact and efficient energy storage, such as plug-in hybrid vehicles and pure electric vehicles.

Some components that affect the storage potential of an energy storage device include the electrodes, and more specifically, the electrode films comprising each electrode in the device. The electrochemical capabilities of electrodes, for example, the capacity and efficiency of battery electrodes, is governed by various factors. For example, distribution of active material, binder and additive(s); the physical properties of materials therein, such as particle size and surface area of active material; the surface properties of the active materials; and the physical characteristics of the electrode film, such as cohesiveness, and adhesiveness to a conductive element. Dry processing methods traditionally used a high shear and/or high-pressure processing step to break up and commingle electrode film materials, which may contribute to structural advantages over electrode films produced using a wet process.

In principle, electrode films having a more uniform distribution of active materials, binders, and other components will exhibit higher performance. Generally, it is thought that electrode films may suffer reduced performance due to the mechanical properties of the film components, and interactions therebetween. For example, it is thought that mechanical limitations may result from poor adhesion between an active layer and a current collector, and poor cohesion in the electrode film, for example, between active materials and binders. Such processes may lead to losses in performance in both power delivery and energy storage capacity. It is thought that losses in performance may be due to deactivation of active materials, for example, due to losses in ionic conductivity, in electrical conductivity, or a combination thereof. For example, as adhesion between active layers and current collectors decreases, cell resistance may increase. Decreases in cohesion between active materials may also lead to increases in cell resistance, and in some cases electrical contact may be lost, removing some active material from the ionic and electrical transfer cycles in the cell. Without wishing to be limited by theory, it is thought that volumetric changes in the active materials may contribute to such processes. For example, additional degradation may be observed in electrodes incorporating certain active materials, such as silicon-based materials, that undergo significant volumetric changes during cell cycling. Lithium intercalation-deintercalation processes may correspond to such volumetric changes in some systems. Generally, these mechanical degradation processes may be observed in any electrode, for example a cathode, an anode, a positive electrode, a negative electrode, a battery electrode, a capacitor electrode, a hybrid electrode, or other energy storage device electrode. It is anticipated that increasing uniformity of electrode film materials will mitigate at least some of these problems.

More specifically, uniform distribution of binders in an electrode film may provide a film with improved mechanical characteristics. Such an improvement may provide a number of practical benefits. For example, an electrode film having a uniform distribution of binder components may exhibit reduced incidence of defects and/or reduced severity of defects, compared to an electrode film having poorer distribution of binder materials. For further example, an electrode film having a uniform distribution of binder components may exhibit higher tensile strength and/or ductility, which may facilitate the manufacture of an energy storage device. Specifically, electrode films having higher tensile strength and/or ductility may be easier to apply to a current collector or other substrate. These factors can be especially relevant when dry electrode processing techniques are used, as the electrode film may be handled as a free-standing film, defined further herein as a "self-supporting film."

Smaller particle sizes may in principle allow for more uniform distribution of electrode film materials including active materials, binders, and other components. However, in practice, some components may aggregate when reduced below a certain size threshold. Thus, the particle sizes of various components of the electrode film may be advantageously incorporated within ranges. In the present disclosure, it was discovered that microparticulate non-fibrillizable binders may be incorporated in electrode films at certain particle sizes. Smaller particle sizes and more intimate contact of active materials, binders, and additives may be realized, leading to a better device. Smaller particle sizes may permit the more consistent manufacture of electrode films. These electrode films may be made with a reduced variation in properties between electrode films manufactured using substantially identical processes, and/or under substantially identical conditions.

When an electrode film is produced by a dry, solvent-free process, water dispersion is not available, and uniform dispersion of the cellulose may be more difficult to achieve. Commercially available CMC in powder form is generally limited to D_{50} particle size of approximately 40-70 μm. More specific sizes within this range are limited to certain degrees of substitution. It is thought that the larger particle size fraction presents various problems such as dispersion inhomogeneity of CMC, localized pressure during calender rolling, adhesion of CMC particles to heated calender rollers, which may lead to problems described herein such as electrode film defects. It is thought that reduction of cellulose particle size to be commensurate with active material particles may ameliorate the problems described herein. As the CMC is better dispersed and on the order of the particle size of active material particles, calendar pressure is thought to be more uniformly distributed throughout the electrode film, which may lead to more consistency and less damage to the active material particles, such as graphite particles. Additionally, the improvement in consistency on film formation may enable the production of a uniform continuous roll film.

Some embodiments include electrode films made by a dry process for use in batteries, where the electrode films include a microparticulate non-fibrillizable binder having a particle size in the range of 0.5 to 40 μm, and at least one fibrillizable binder. Embodiments include dry electrodes and fabrication processes that provide microparticulate non-fibrillizable binder particles having the sizes in the range of about 0.5 to about 40 μm, and electrode film incorporating such microparticulate non-fibrillizable binder particles. Such electrode films may have a more uniform distribution of active materials, binders, and other components. Electrode films incorporating such microparticulate non-fibrillizable binder particles may exhibit improved tensile strength and/or processability. In certain embodiments, the microparticulate non-fibrillizable binder is a cellulose, for example, carboxymethylcellulose (CMC). The electrode film may be suitable for use as an anode of a lithium ion battery. In certain embodiments, the electrode film includes graphite.

A dry or self-supporting electrode film incorporating such microparticulate non-fibrillizable binder particles may provide improved characteristics relative to a typical electrode film. For example, a dry or self-supporting electrode film may provide one or more of improved film strength, improved cohesiveness, improved adhesiveness, improved electrical performance, or reduced incidence of defects. The defects may include holes, cracks, surface pits in the electrode film. The adhesiveness may be adhesiveness to a current collector. The electrical performance may be specific capacity. The film strength may be tensile strength.

An electrode film described herein, or an energy storage device incorporating an electrode film described herein, may advantageously be characterized by improved specific capacity (which may be measured in mAh/g). Further improvements that may be realized in various embodiments include reduced capacity fade over the life of the device.

Some embodiments relate to dry electrode processing techniques. Dry electrode fabrication processes may be as disclosed in one or more of U.S. Publication No. 2006/0114643, U.S. Publication No. 2006/0133013, U.S. Pat. No. 9,525,168, or U.S. Pat. No. 7,935,155, each of which is incorporated by reference herein in the entirety.

Further provided herein are methods for reducing the particles sizes of microparticulate non-fibrillizable binders. A pressurized jet milling process was found to reduce the particle size of the microparticulate non-fibrillizable binder. For example, a non-fibrillizable binder can be placed into a jet mill and "jet milled" to reduce the particle size to be on the order of the median (D_{50}) particle size of the active material(s) to be included in the electrode film. In some embodiments, the active material may be graphite having a median particle size of about 15 μm. In further embodiments, the microparticulate non-fibrillizable binder can be a cellulose, for example, CMC. Suitable pressurized jet milling conditions include a grind gas pressure of 100-500 psi. The jet milling may include separation of milled particles by particle size. For example, particles of the microparticulate non-fibrillizable binder having a given size can be separated by a classifier.

One embodiment is a method of fabricating a free-standing electrode film. With reference to FIG. **6**, the method **600** may include selecting a non-fibrillizable binder (**605**); jet-milling the non-fibrillizable binder to form a microparticulate non-fibrillizable binder having a median particle size (**610**). Step **610** may comprise milling the non-fibrillizable binder to result in particles on the order of the active material particle size, which may be, for example, about 0.5 to about 40 μm; combining the microparticulate non-fibrillizable binder particles with a fibrillizable binder and one or more active materials to form an electrode film mixture (**615**); and calendering the electrode film mixture to form a self-supporting and/or free-standing electrode film (**620**). In some embodiments, each step is dry and solvent-free. In some embodiments, the microparticulate non-fibrillizable binder is polyvinylidene fluoride (PVDF) and/or CMC. In further embodiments, the microparticulate non-fibrillizable binder is CMC. In still further embodiments, the fibrillizable binder is PTFE. In yet further embodiments, the active material comprises graphite. A method of fabricating a free-standing electrode film may comprise one or more parallel processing steps as provided in FIG. **7**.

With reference to FIG. **7**, the parallel processing method begins with an upper (as shown) parallel processing path **702** and a lower (as shown) parallel processing path **710**. In the upper (as shown) parallel processing path **702**, a bulk active material mixture **708** is formed by nondestructively mixing a bulk active material **704** with a non-fibrillizable binder **706**. The non-fibrillizable binder **706** may be a microparticulate non-fibrillizable binder, as described previously herein. The non-fibrillizable binder **704** may be, for example, PVDF and/or CMC. The bulk active material **706** may be graphite. In the lower (as shown) parallel processing path **710**, a second active material **712** and a structural binder **714** are combined under nondestructive mixing. The structural binder **714** may be PTFE, and the second active material **712** may be graphite. The mixed structural binder and second active material form an initial binder mixture **716** that is then jet-milled in a high shear, high intensity process to form a structural binder mixture **718**. The bulk active material mixture **708** is then combined with the structural binder mixture **718** in a nondestructive mixing process to form a bulk active material and binder mixture **720**, which is then processed by a low shear jet milling to form an electrode film mixture **722**. The low shear jet milling may be performed at a high feed rate, for example, relative to the initial jet milling used to form the structural binder mixture **718**. The electrode film mixture **722** may then be pressed or calendered into a self-supporting and free-standing electrode film **724**. Generally, no solvents are required in any stage of the process.

In various embodiments, a dry powder, for example, a mixture including binder particles and active material particles, can be mixed by a mild process using, for example a convection, pneumatic or diffusion mixer as follows: a tumbler with and without mixing media (for example, glass bead, ceramic ball), a paddle mixer, a blade blender or an acoustic mixer. The mild mixing process may be nondestructive with respect to any active materials in the mixture. Without limitation, graphite particles may be preserved of size following the mild mixing process. In further embodiments, the powder mixing sequence and conditions can be varied to improve uniform distribution of active material, binder, and optional additive(s).

The materials and methods provided herein can be implemented in various energy storage devices. As provided herein, an energy storage device can be a capacitor, a lithium ion capacitor (LIC), an ultracapacitor, a battery, a lithium ion battery, or a hybrid energy storage device combining aspects of two or more of the foregoing. In preferable embodiments, the device is a lithium ion battery.

An energy storage device can be of any suitable configuration, for example planar, spirally wound, button shaped, or pouch. An energy storage device can be a component of a system, for example, a power generation system, an uninterruptible power source systems (UPS), a photo voltaic power generation system, an energy recovery system for use in, for example, industrial machinery and/or transportation. An energy storage device may be used to power various electronic device and/or motor vehicles, including hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and/or electric vehicles (EV).

FIG. **1** shows a side cross-sectional schematic view of an example of an energy storage device **100** having an electrode film including a microparticulate non-fibrillizable binder as provided herein. The energy storage device **100** may be classified as, for example, a capacitor, a battery, a capacitor-battery hybrid, or a fuel cell. In one embodiment, device **100** is a lithium ion battery.

The device has a first electrode **102**, a second electrode **104**, and a separator **106** positioned between the first electrode **102** and second electrode **104**. The first electrode **102** and the second electrode **104** are adjacent to respective opposing surfaces of the separator **106**. The energy storage device **100** includes an electrolyte **118** to facilitate ionic communication between the electrodes **102**, **104** of the energy storage device **100**. For example, the electrolyte **118** may be in contact with the first electrode **102**, the second electrode **104** and the separator **106**. The electrolyte **118**, the first electrode **102**, the second electrode **104**, and the separator **106** are housed within an energy storage device housing **120**. One or both of the first electrode **102** and the second electrode **104** may comprise a microparticulate non-fibrillizable binder as described herein.

One or more of the first electrode **102**, the second electrode **104**, and the separator **106**, or constituent thereof, may comprise porous material. The pores within the porous material can provide containment for and/or increased surface area for contact with an electrolyte **118** within the housing **120**. The energy storage device housing **120** may be sealed around the first electrode **102**, the second electrode **104** and the separator **106**, and may be physically sealed from the surrounding environment.

In some embodiments, the first electrode **102** can be an anode (a “negative electrode”) and the second electrode **104** can be a cathode (a “positive electrode”). The separator **106** can be configured to electrically insulate two electrodes adjacent to opposing sides of the separator **106**, such as the first electrode **102** and the second electrode **104**, while permitting ionic communication between the two adjacent electrodes. The separator **106** can comprise a suitable porous, electrically insulating material. In some embodiments, the separator **106** can comprise a polymeric material. For example, the separator **106** can comprise a cellulosic material (e.g., paper), a polyethylene (PE) material, a polypropylene (PP) material, and/or a polyethylene and polypropylene material.

Generally, the first electrode **102** and second electrode **104** each comprise a current collector and an electrode film. Electrodes **102** and **104** comprise electrode films **112** and **114**, respectively. Electrode films **112** and **114** can have any suitable shape, size and thickness. For example, the electrode films can have a thickness of about 30 microns (μm) to about 250 microns, for example, about 50 microns, about 100 microns, about 150 microns, about 200 microns, about 250 microns, about 300 microns, about 400 microns, about 500 microns, about 750 microns, about 1000 microns, about 2000 microns, or values therebetween. The electrode films generally comprise one or more active materials, for example, anode active materials or cathode active materials as provided herein. The electrode films **112** and/or **114** may be dry and/or self-supporting electrode films as provided herein, and having advantageous properties, such as tensile strength, or capacity, as provided herein. The first electrode film **112** and/or the second electrode film **114** may also include a microparticulate non-fibrillizable binder as described herein, and may also include one or more additional binders. The electrode films **112** and/or **114** may be prepared by a process as described herein. The electrode films **112** and/or **114** may be wet or self-supporting dry electrodes as described herein.

As shown in FIG. **1**, the first electrode **102** and the second electrode **104** include a first current collector **108** in contact with first electrode film **112**, and a second current collector **110** in contact with the second electrode film **114**, respectively. The first current collector **108** and the second current collector **110** facilitate electrical coupling between each corresponding electrode film and an external electrical circuit (not shown). The first current collector **108** and/or the second current collector **110** comprise one or more electrically conductive materials, and have can have any suitable shape and size selected to facilitate transfer of electrical charge between the corresponding electrode and an external circuit. For example, a current collector can include a metallic material, such as a material comprising aluminum, nickel, copper, rhenium, niobium, tantalum, and noble metals such as silver, gold, platinum, palladium, rhodium, osmium, iridium and alloys and combinations of the foregoing. For example, the first current collector **108** and/or the second current collector **110** can comprise, for example, an aluminum foil or a copper foil. The first current collector **108** and/or the second current collector **110** can have a rectangular or substantially rectangular shape sized to provide transfer of electrical charge between the corresponding electrode and an external circuit.

In some embodiments, the at least one active material includes a treated carbon material, where the treated carbon material includes a reduction in a number of hydrogen-containing functional groups, nitrogen-containing functional groups and/or oxygen-containing functional groups, as described in U.S. Patent Publication No. 2014/0098464. For example, the treated carbon particles can include a reduction in a number of one or more functional groups on one or more surfaces of the treated carbon, for example about 10% to about 60% reduction in one or more functional groups compared to an untreated carbon surface, including about 20% to about 50%. The treated carbon can include a reduced number of hydrogen-containing functional groups, nitrogen-containing functional groups, and/or oxygen-containing functional groups. In some embodiments, the treated carbon material comprises functional groups less than about 1% of which contain hydrogen, including less than about 0.5%. In some embodiments, the treated carbon material comprises functional groups less than about 0.5% of which contains nitrogen, including less than about 0.1%. In some embodiments, the treated carbon material comprises functional groups less than about 5% of which contains oxygen, including less than about 3%. In further embodiments, the treated carbon material comprises about 30% fewer hydrogen-containing functional groups than an untreated carbon material.

In some embodiments, energy storage device **100** can be a lithium ion battery. In some embodiments, the electrode film of a lithium ion battery electrode can comprise a microparticulate non-fibrillizable binder as described herein, one or more active materials, and a fibrillized binder matrix.

In further embodiments, the energy storage device **100** is charged with a suitable lithium-containing electrolyte. For example, device **100** can include a lithium salt, and a solvent, such as a non-aqueous or organic solvent. Generally, the lithium salt includes an anion that is redox stable. In some embodiments, the anion can be monovalent. In some embodiments, a lithium salt can be selected from hexafluorophosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), lithium perchlorate ($LiClO_4$), lithium bis(trifluoromethansulfonyl)imide ($LiN(SO_2CF_3)_2$), lithium trifluoromethansulfonate ($LiSO_3CF_3$), and combinations thereof. In some embodiments, the electrolyte can include a quaternary ammonium cation and an anion selected from the group consisting of hexafluorophosphate, tetrafluoroborate and iodide. In some embodiments, the salt concentration can be about 0.1 mol/L (M) to about 5 M, about 0.2 M to about 3 M, or about 0.3 M to about 2 M. In further embodiments, the salt concentration of the electrolyte can be about 0.7 M to about 1 M. In certain embodiments, the salt concentration of the electrolyte can be about 0.2 M, about 0.3 M, about 0.4 M, about 0.5 M, about 0.6 M, about 0.7 M, about 0.8 M. about 0.9 M, about 1 M, about 1.1 M, about 1.2 M, or values therebetween.

In some embodiments the energy storage device electrolyte can include a liquid solvent. The solvent need not dissolve every component, and need not completely dissolve any component, of the electrolyte. In further embodiments, the solvent can be an organic solvent. In some embodiments, a solvent can include one or more functional groups selected from carbonates, ethers and/or esters. In some embodiments, the solvent can comprise a carbonate. In further embodiments, the carbonate can be selected from cyclic carbonates such as, for example, ethylene carbonate (EC), propylene carbonate (PC), vinyl ethylene carbonate (VEC), vinylene carbonate (VC), fluoroethylene carbonate (FEC), and combinations thereof, or acyclic carbonates such as, for example, dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), and combinations thereof. In certain embodiments, the electrolyte can comprise $LiPF_6$, and one or more carbonates.

In some embodiments, the lithium ion battery is configured to operate at about 2.5 to 4.5 V, or 3.0 to 4.2 V. In further embodiments, the lithium ion battery is configured to have a minimum operating voltage of about 2.5 V to about 3 V, respectively. In still further embodiments, the lithium ion battery is configured to have a maximum operating voltage of about 4.1 V to about 4.4 V, respectively.

Definitions

As used herein, the terms “battery” and “capacitor” are to be given their ordinary and customary meanings to a person of ordinary skill in the art. The terms “battery” and “capacitor” are nonexclusive of each other. A capacitor or battery can refer to a single electrochemical cell that may be operated alone, or operated as a component of a multi-cell system.

As used herein, the voltage of an energy storage device is the operating voltage for a single battery or capacitor cell. Voltage may exceed the rated voltage or be below the rated voltage under load, or according to manufacturing tolerances.

As provided herein, a “self-supporting” electrode film is an electrode film that incorporates binder matrix structures sufficient to support the film or layer and maintain its shape such that the electrode film or layer can be free-standing. When incorporated in an energy storage device, a self-supporting electrode film or active layer is one that incorporates such binder matrix structures. Generally, and depending on the methods employed, such electrode films are strong enough to be employed in energy storage device fabrication processes without any outside supporting elements, such as a current collector or other film. For example, a “self-supporting” electrode film can have sufficient strength to be rolled, handled, and unrolled within an electrode fabrication process without other supporting elements. A dry electrode film described herein, such as a cathode electrode film or an anode electrode film, may be self-supporting.

As provided herein, a “solvent-free” electrode film is an electrode film that contains no detectable processing solvents, processing solvent residues, or processing solvent impurities. A dry electrode film described herein, such as a cathode electrode film or an anode electrode film, may be solvent-free.

A “wet” electrode, “wet process” electrode, or slurry electrode as provided herein, is an electrode prepared by at least one step involving a slurry of active material(s), binder(s), and optionally additive(s). A wet electrode generally will include a detectable amount of processing solvent residues, and/or processing solvent impurities, even after the electrode is dried, due to the solvents used during processing.

As used herein, a “nondestructive” process is a process in which an electrode active material, including the surface of the electrode active material, is not substantially modified during the process. Thus, the analytical characteristics and/or performance in an application, such as incorporation in an energy storage device, of the active material, are identical or nearly identical to those which have not undergone the process. For example, a coating on the active material may be undisturbed or substantially undisturbed during the process. A non-limiting example of a nondestructive process is “nondestructively mixing or blending,” or jet milling at a reduced pressure, increased feed rate, decreased velocity (e.g., blender speed), and/or change in other process parameter(s) such that the shear imparted upon an active material remains below a threshold at which the analytical characteristics and/or performance of the active material would be adversely affected, when implemented into an energy storage device. A "nondestructive" process can be distinguished from a high shear process which substantially modifies an electrode active material, such as the surface of an electrode active material, and substantially affects the analytical characteristics and/or the performance of the active material. For example, high shear blending or jet milling can have detrimental effects on the surface of an electrode active material. A high shear process may be implemented, at the detriment to the active material surface characteristics, to provide other benefits, such as fibrillization of binder material, or otherwise forming a binder/active material matrix to assist in forming a self-supporting electrode film. Embodiments herein provide similar benefits, while avoiding the detrimental effects of excessive use of high shear processes. In general, the nondestructive processes herein are performed at one or more of a higher feed rate, lower velocity, and/or lower pressure, resulting in a lower shear process than the more destructive processes that will otherwise substantially modify an electrode active material, and thus affect performance.

In some embodiments, an electrode film as provided herein includes at least one active material and at least one binder. The at least one active material can be any active material known in the art. The at least one active material may be a material suitable for use in the anode or cathode of a battery. Anode active materials can be comprised of, for example, an insertion material (such as carbon, graphite, and/or graphene), an alloying/dealloying material (such as silicon, silicon oxide, tin, and/or tin oxide), a metal alloy or compound (such as Si—Al, and/or Si—Sn), and/or a conversion material (such as manganese oxide, molybdenum oxide, nickel oxide, and/or copper oxide). The anode active materials can be used alone or mixed together to form multi-phase materials (such as Si—C, Sn—C, SiOx-C, SnOx-C, Si—Sn, Si-SiOx, Sn-SnOx, Si-SiOx-C, Sn-SnOx-C, Si—Sn—C, SiOx-SnOx-C, Si-SiOx-Sn, or Sn-SiOx-SnOx). The cathode active material can be, for example, a metal oxide, metal sulfide, or a lithium metal oxide. The lithium metal oxide can be, for example, a lithium nickel manganese cobalt oxide (NMC), a lithium manganese oxide (LMO), a lithium iron phosphate (LFP), a lithium cobalt oxide (LCO), a lithium titanate (LTO), and/or a lithium nickel cobalt aluminum oxide (NCA). In some embodiments, cathode active materials can be comprised of, for example, a layered transition metal oxide (such as $LiCoO_2$ (LCO), $Li(NiMnCo)O_2$ (NMC) and/or $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$(NCA)), a spinel manganese oxide (such as $LiMn_2O_4$ (LMO) and/or $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO)) or an olivine (such as $LiFePO_4$).

The at least one active material may include one or more carbon materials. The carbon materials may be selected from, for example, graphitic material, graphite, graphene-containing materials, hard carbon, soft carbon, carbon nanotubes, porous carbon, conductive carbon, or a combination thereof. A graphite can be synthetic or naturally derived. Activated carbon can be derived from a steam process or an acid/etching process. In some embodiments, the graphitic material can be a surface treated material. In some embodiments, the porous carbon can comprise activated carbon. In some embodiments, the porous carbon can comprise hierarchically structured carbon. In some embodiments, the porous carbon can include structured carbon nanotubes, structured carbon nanowires and/or structured carbon nanosheets. In some embodiments, the porous carbon can include graphene sheets. In some embodiments, the porous carbon can be a surface treated carbon.

In some embodiments, a cathode electrode film of a lithium ion battery or hybrid energy storage device can include about 70 weight % to about 98 weight % of the at least one active material, including about 70 weight % to about 92 weight %, or about 70 weight % to about 96 weight %. In some embodiments, the cathode electrode film can comprise up to about 10 weight % of the porous carbon material, including up to about 5 weight %, or about 1 weight % to about 5 weight %. In some embodiments, the cathode electrode film comprises up to about 5 weight %, including about 1 weight % to about 3 weight %, of the conductive additive. In some embodiments, the cathode electrode film comprises up to about 20 weight % of binder, for example, about 1.5 weight % to 10 weight %, about 1.5 weight % to 5 weight %, or about 1.5 weight % to 3 weight %. In some embodiments, the cathode electrode film comprises about 1.5 weight % to about 3 weight % binder.

In some embodiments, an anode electrode film may comprise at least one active material, a binder, and optionally a conductive additive. In some embodiments, the conductive additive may comprise a conductive carbon additive, such as carbon black. In some embodiments, the at least one active material of the anode may comprise synthetic graphite, natural graphite, hard carbon, soft carbon, graphene, mesoporous carbon, silicon, silicon oxides, tin, tin oxides, germanium, lithium titanate, mixtures, or composites of the aforementioned materials. In some embodiments, an anode electrode film can include about 80 weight % to about 98 weight % of the at least one active material, including about 80 weight % to about 98 weight %, or about 94 weight % to about 97 weight %. In some embodiments, the anode electrode film comprises up to about 5 weight %, including about 1 weight % to about 3 weight %, of the conductive additive. In some embodiments, the anode electrode film comprises up to about 20 weight % of the binder, including about 1.5 weight % to 10 weight %, about 1.5 weight % to 5 weight %, or about 3 weight % to 5 weight %. In some embodiments, the anode electrode film comprises about 4 weight % binder. In some embodiments, the anode film may not include a conductive additive.

Some embodiments include an electrode film, such as of an anode and/or a cathode, having one or more binders. The one or more binders include a microparticulate non-fibrillizable binder having a particle size in the range of 0.5 μm to 40 μm as described herein, and in some embodiments, along with a fibrillizable binder. The microparticulate non-fibrillizable binder may be cellulose or a derivative of cellulose. A derivative of cellulose can include, for example, cellulose esters such as cellulose acetate; cellulose ethers such as methylcellulose, ethylcellulose, hydroxylpropylcellulose (HPC), or hydroxyethylcellulose (HEC); cellulose nitrate; or a carboxyalkylcellulose, for example, carboxymethylcellulose (CMC), carboxyethylcellulose, carboxypropylcellulose, or carboxyisopropylcellulose. In further embodiments, the cellulose or cellulose derivative may comprise a cellulose salt. In still further embodiments, a cellulose salt cation may be selected from sodium, ammonium, or lithium. For example, the cellulose or cellulose derivative may comprise a sodium cellulose or a sodium cellulose derivative selected from a sodium cellulose ester, sodium cellulose ether, a sodium cellulose nitrate, or a sodium carboxyalkylcellulose. In preferable embodiments, the microparticulate non-fibrillizable binder is CMC. The CMC may comprise sodium carboxymethylcellulose.

A cellulose derivative may be characterized by its degree of substitution. For example, the degree of substitution may be about 0.7 to about 1.5, or about 1.2. Certain degrees of substitution may be desirable, when the material is implemented within an electrode film, in order to provide desirable characteristics. However, commercially available CMC in powder form was found to be limited to certain particle sizes and degrees of substitution. For example, commercially available CMC powders having a degree of substitution of 1.2 were found to be available only in larger particles sizes. Smaller particle sizes down to about 40 μm were found to be limited to a degree of substitution of 0.7, which was observed to be an unfavorable degree of substitution. As mentioned above, smaller CMC powder has not been available, as there has been no recognized need for such material, and certainly not at a desirable degree of substitution.

In some embodiments, the cellulose or cellulose derivative may include crosslinks. Further, a cellulose or cellulose derivative may be characterized by its molecular weight, which generally is number average molecular weight. In some embodiments, the cellulose or cellulose derivative has a number average molecular weight of about 10,000 to about 500,000, or about 50,000 to about 400,000.

The one or more binders can include polytetrafluoroethylene (PTFE), a polyolefin, polyalkylenes, polyethers, styrene-butadiene, co-polymers of polysiloxanes and polysiloxane, branched polyethers, polyvinylethers, co-polymers thereof, and/or admixtures thereof. The binder can include a cellulose. The cellulose can be a carboxyalkylcellulose, for example, carboxymethylcellulose (CMC). In some embodiments, the polyolefin can include polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), co-polymers thereof, and/or mixtures thereof. For example, the binder can include polyvinylene chloride, poly(phenylene oxide) (PPO), polyethylene-block-poly(ethylene glycol), poly(ethylene oxide) (PEO), poly(phenylene oxide) (PPO), polyethylene-block-poly(ethylene glycol), polydimethylsiloxane (PDMS), polydimethylsiloxane-coalkylmethylsiloxane, co-polymers thereof, and/or admixtures thereof. In certain embodiments, the fibrillizable binder is PTFE. A dry self-supporting electrode film may comprise interpenetrating networks of the aforementioned binders. In some embodiments, the one or more binders comprise CMC, PVDF, and PTFE.

The binder may include various suitable ratios of the polymeric components. The microparticulate non-fibrillizable binder can be up to 50 weight % of the binder. For example, the microparticulate non-fibrillizable binder can be about 0.1 weight % to about 50 weight %, about 0.5 weight % to about 10 weight %, about 0.5 weight % to about 5 weight %, about 0.5 to about 2 weight %, or about 0.5 to about 1 weight %. PTFE can be up to about 98 weight % of the binder, for example, from about 20 weight % to about 95 weight %, about 20 weight % to about 90 weight %, including about 20 weight % to about 80 weight %, about 30 weight % to about 70 weight %, about 30 weight % to about 50 weight %, or about 50 weight % to about 90 weight %. In some embodiments, the one or more binders comprises about 0.1 to about 2 weight % CMC, about 0.1 to about 2 weight % PVDF, and about 1 to about 4 weight % PTFE. In certain embodiments, the one or more binders comprises about 1 weight % CMC, about 1 weight % PVDF, and about 2 weight % PTFE.

In some embodiments, the microparticulate non-fibrillizable binder particles may have a median particle size of about 0.5 μm to about 40 μm, for example, about 1 μm to about 25 μm, about 2 μm to about 20 μm, about 5 μm to about 15 μm, or about 10 μm to about 15 μm. The electrode film mixture may additionally include binder particles other than the microparticulate non-fibrillizable binder particles, for example, PTFE binder particles, having selected sizes. In some embodiments, the binder particles may be about 50 nm, about 100 nm, about 150 nm, about 200 nm, about 250 nm, about 300 nm, about 350 nm, about 400 nm, about 450 nm, about 500 nm, about 1 μm, about 2 μm, about 3 μm, about 4 μm, about 5 μm, about 10 μm, about 50 μm, about 100 μm, or values therebetween.

A dry fabrication process can refer to a process in which no or substantially no solvents are used in the formation of an electrode film. For example, components of the electrode film, including active materials and binders, may comprise dry particles. The dry particles for forming the electrode film may be combined to provide a dry particle electrode film mixture. In some embodiments, the electrode film may be formed from the dry particle electrode film mixture such that weight percentages of the components of the electrode film and weight percentages of the components of the dry particles electrode film mixture are substantially the same. In some embodiments, the electrode film formed from the dry particle electrode film mixture using the dry fabrication process may be free from, or substantially free from, any processing additives such as solvents and solvent residues resulting therefrom. In some embodiments, the resulting electrode films are self-supporting films formed using the dry process from the dry particle mixture. In some embodiments, the resulting electrode films are free-standing films formed using the dry process from the dry particle electrode film mixture. A process for forming an active layer or electrode film can include fibrillizing the fibrillizable binder component(s) such that the film comprises a fibrillized binder matrix. In further embodiments, a free-standing electrode film may be formed in the absence of a current collector. In still further embodiments, an electrode film may comprise a fibrillized polymer matrix such that the film is self-supporting. It is thought that a matrix, lattice, or web of fibrils can be formed to provide mechanical structure to the electrode film.

In some embodiments, an energy storage device electrode film, wherein the electrode film is dry and/or self-supporting film including a microparticulate non-fibrillizable binder described herein, may provide a specific capacity on charge or discharge of about 300 mAh/g, about 325 mAh/g, about 350 mAh/g, about 375 mAh/g, about 400 mAh/g, about 425 mAh/g, about 450 mAh/g, about 500 mAh/g, or a range of values therebetween. In further embodiments, an energy storage device electrode film, wherein the electrode film is dry and/or self-supporting film including a microparticulate non-fibrillizable binder described herein, may provide a first cycle efficiency of about 90%, about 91%, about 92%, about 93%, or a range of values therebetween.

An electrode film may have a selected thickness suitable for certain applications. The thickness of an electrode film as provided herein may be greater than that of an electrode film prepared by conventional processes. In some embodiments, the electrode film can have a thickness of about 250 microns, about 300 microns, about 350 microns, about 400 microns, about 450 microns, about 500 microns, about 750 microns, about 1 mm, or about 2 mm, or a range of values therebetween.

In some embodiments, a free-standing and/or self-supporting electrode film including a microparticulate non-fibrillizable binder described herein may have a tensile strength of at least about 1 N. In further embodiments, the tensile strength may be about 1 N, about 1.1 N, about 1.2 N, about 1.3 N, about 1.4 N, about 1.5 N, about 1.6 N, about 1.7 N, about 1.8 N, about 1.9 N, about 2 N, greater than about 2 N, or a range of values therebetween.

In some embodiments, a set (of, e.g., at least 3 electrode films) of free-standing and/or self-supporting electrode films including a microparticulate non-fibrillizable binder described herein fabricated under substantially identical conditions may have variation in specific capacity of less than about 3% standard deviation (sd), for example, about 2.5% sd, about 2% sd, about 1.5% sd, about 1% sd, about 0.5% sd, or a range of values therebetween.

In some embodiments, a free-standing and/or self-supporting electrode film including a microparticulate non-fibrillizable binder described herein may be characterized by a specific energy density 20-30% higher than a wet battery electrode of comparable constitution, e.g., of active materials.

In specific examples below, electrode films including a microparticulate non-fibrillizable binder were fabricated.

EXAMPLE 1

Dry battery anode electrode films were fabricated, which included 96% by weight graphite and 4% by weight binder, wherein the binder included 2% PTFE, 1% CMC and 1% PVDF. Other electrode film compositions can be envisioned and prepared, and the disclosure herein is not limited to the specific compositions disclosed.

Using a Hosokawa 100 AFG pressurized jet mill with a classifier attachment, as received CMC powders were milled with a size output selection. Sigma Aldrich® sodium carboxymethylcellulose with a degree of substitution of 1.2 was used as the feed material. A classifier rotation speed of 8000 rpm was used in order to size select for a D_{50} of 10 μm. Grind gas pressure was 120 psi with an initial chamber mass of 100 g. This resulted in a production rate of approximately 0.1 kg/hr. Pictures of the 100 AFG machine can be seen in FIGS. **2**A and **2**B. As received CMC powder from Sigma Aldrich® had a D_{50} particle size of approximately 70 μm while the Hosokawa milled CMC had a D_{50} of approximately 10 μm. This difference can be seen in SEM images in FIGS. **3**A and **3**B. When Hosokawa milled CMC was used in a dry anode electrode parallel process, an increase in first cycle efficiency and cell to cell consistency was observed compared to as received CMC. Electrochemical data for this comparison is shown in FIG. **4**. Using as received CMC, a charge and discharge specific capacity of 386 mAh/g and 348 mAh/g respectively (90.2% efficiency) were achieved. Using milled CMC, a charge and discharge specific capacity of 384 mAh/g and 349 mAh/g respectively (90.9% efficiency) were achieved.

In addition to electrochemical performance enhancement, the smaller D_{50} particle size of CMC mitigated electrode defects, such as holes, cracks or surface pits. Dry powder formulations using CMC powder as received from the manufacturer with D_{50} particle size of 70 μm produced electrode free-standing films with defects as observed in FIG. **5**. These defects were circumvented using milled CMC with D_{50} particle size of about 10 μm as illustrated in FIG. **6**. The rationale for these empirical results lies in the larger surface area offered by the smaller D_{50} CMC particle size. At a fixed binder weight ratio in an electrode formulation, the higher surface may offer a stronger binding strength to the active material powder matrix and a weaker affinity for the heated rollers used to produce films or used to calender down film thicknesses. In contrast, the larger D_{50} CMC particle size may offer a weaker binding strength to the active materials powder matrix and a stronger affinity to heated rollers used to produce films or used to calender down film thicknesses. This stronger affinity to the heated calender rollers can be attributed to a larger single spot size of the larger D_{50} particle size of CMC binder particles found in unmilled powder, which came into direct contact to the heated calender rollers during dry processing. As such, the larger CMC particles could be incidentally removed from the electrode powder sample during powder-to-film formation or extracted from the film during film-to-film thickness reduction process, leaving behind defects in the electrode. Tensile strength measurements of free-standing electrode films also support the idea that a stronger binding cohesion strength of the finely milled CMC polymer binder. The tensile strength results indicate that electrode films at similar thicknesses produced using CMC binder with a smaller D_{50} particle size (10 μm vs. about 70 μm) were stronger than those produced with larger particle size. Empirical results are presented in Table 1.

TABLE 1

CMC Type	Median Particle Size	Graphite Film Thickness	Graphite Film Tensile Strength
As received	73.4 ± 1.6 μm	300-301 μm	0.936 N
Resodyne processed	66.0 ± 2.3 μm	299-301 μm	1.01 N
Jet milled ("Hosokawa")	10.1 ± 0.8 μm	298-300 μm	1.74 N

While certain embodiments of the inventions have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the disclosure. Indeed, the novel methods and systems described herein may be embodied in a variety of other forms. Furthermore, various omissions, substitutions and changes in the systems and methods described herein may be made without departing from the spirit of the disclosure. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the disclosure. Accordingly, the scope of the present inventions is defined only by reference to the appended claims.

Features, materials, characteristics, or groups described in conjunction with a particular aspect, embodiment, or example are to be understood to be applicable to any other aspect, embodiment or example described in this section or elsewhere in this specification unless incompatible therewith. All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. The protection is not restricted to the details of any foregoing embodiments. The protection extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

Furthermore, certain features that are described in this disclosure in the context of separate implementations can also be implemented in combination in a single implementation. Conversely, various features that are described in the context of a single implementation can also be implemented in multiple implementations separately or in any suitable subcombination. Moreover, although features may be described above as acting in certain combinations, one or more features from a claimed combination can, in some cases, be excised from the combination, and the combination may be claimed as a subcombination or variation of a subcombination.

Moreover, while operations may be depicted in the drawings or described in the specification in a particular order, such operations need not be performed in the particular order shown or in sequential order, or that all operations be performed, to achieve desirable results. Other operations that are not depicted or described can be incorporated in the example methods and processes. For example, one or more additional operations can be performed before, after, simultaneously, or between any of the described operations. Further, the operations may be rearranged or reordered in other implementations. Those skilled in the art will appreciate that in some embodiments, the actual steps taken in the processes illustrated and/or disclosed may differ from those shown in the figures. Depending on the embodiment, certain of the steps described above may be removed, others may be added. Furthermore, the features and attributes of the specific embodiments disclosed above may be combined in different ways to form additional embodiments, all of which fall within the scope of the present disclosure. Also, the separation of various system components in the implementations described above should not be understood as requiring such separation in all implementations, and it should be understood that the described components and systems can generally be integrated together in a single product or packaged into multiple products. For example, any of the components for an energy storage system described herein can be provided separately, or integrated together (e.g., packaged together, or attached together) to form an energy storage system.

For purposes of this disclosure, certain aspects, advantages, and novel features are described herein. Not necessarily all such advantages may be achieved in accordance with any particular embodiment. Thus, for example, those skilled in the art will recognize that the disclosure may be embodied or carried out in a manner that achieves one advantage or a group of advantages as taught herein without necessarily achieving other advantages as may be taught or suggested herein.

Conditional language, such as "can," "could," "might," or "may," unless specifically stated otherwise, or otherwise understood within the context as used, is generally intended to convey that certain embodiments include, while other embodiments do not include, certain features, elements, and/or steps. Thus, such conditional language is not generally intended to imply that features, elements, and/or steps are in any way required for one or more embodiments or that one or more embodiments necessarily include logic for deciding, with or without user input or prompting, whether these features, elements, and/or steps are included or are to be performed in any particular embodiment.

Conjunctive language such as the phrase "at least one of X, Y, and Z," unless specifically stated otherwise, is otherwise understood with the context as used in general to convey that an item, term, etc. may be either X, Y, or Z. Thus, such conjunctive language is not generally intended to imply that certain embodiments require the presence of at least one of X, at least one of Y, and at least one of Z.

Language of degree used herein, such as the terms "approximately," "about," "generally," and "substantially" as used herein represent a value, amount, or characteristic close to the stated value, amount, or characteristic that still performs a desired function or achieves a desired result.

The scope of the present disclosure is not intended to be limited by the specific disclosures of preferred embodiments in this section or elsewhere in this specification, and may be defined by claims as presented in this section or elsewhere in this specification or as presented in the future. The language of the claims is to be interpreted broadly based on the language employed in the claims and not limited to the examples described in the present specification or during the prosecution of the application, which examples are to be construed as non-exclusive.

What is claimed is:

1. A dry electrode film of an energy storage device, comprising:

a dry active material; and

a dry binder comprising a fibrillizable binder and a microparticulate non-fibrillizable binder having a D_{50} particle size of about 1-25 μm;

wherein the microparticulate non-fibrillizable binder is selected from at least one of cellulose and a cellulose derivative;

wherein the dry electrode film is free-standing; and

wherein the dry electrode film has a tensile strength of at least about 1 N.

2. The dry electrode film of claim **1**, wherein the microparticulate non-fibrillizable binder has a D_{50} particle size of about 5-15 μm.

3. The dry electrode film of claim **1**, wherein the dry binder comprises up to 50 wt. % of the microparticulate non-fibrillizable binder.

4. The dry electrode film of claim **1**, wherein the microparticulate non-fibrillizable binder is selected from at least one of cellulose, a cellulose ester, a cellulose ether, cellulose nitrate, a carboxyalkylcellulose, a cellulose salt and a cellulose salt derivative.

5. The dry electrode film of claim **1**, wherein the microparticulate non-fibrillizable binder is selected from at least one of cellulose, cellulose acetate, methylcellulose, ethylcellulose, hydroxylpropylcellulose (HPC), hydroxyethylcellulose (HEC), cellulose nitrate, carboxymethylcellulose (CMC), carboxyethylcellulose, carboxypropylcellulose, carboxyisopropylcellulose, sodium cellulose, sodium cellulose nitrate and sodium carboxyalkylcellulose.

6. The dry electrode film of claim **1**, wherein the dry electrode film comprises a thickness of at least about 250 μm.

7. The dry electrode film of claim **1**, wherein the cellulose or the cellulose derivative has a number average molecular weight of about 10,000 to about 500,000.

8. The dry electrode film of claim **1**, wherein the cellulose derivative has a degree of substitution of about 0.7 to about 1.5.

9. The dry electrode film of claim **1**, wherein the fibrillizable binder comprises polytetrafluoroethylene (PTFE).

10. The dry electrode film of claim **1**, wherein the dry electrode film is substantially free of holes, cracks and surface pits.

11. The dry electrode film of claim **1**, wherein the dry electrode film has a tensile strength of at least about 1.5 N.

12. The dry electrode film of claim **1**, wherein the dry active material comprises graphite.

13. An electrode comprising the dry electrode film of claim **1** in contact with a current collector.

14. A lithium ion battery comprising the electrode of claim **13**.

15. The dry electrode film of claim **6**, wherein the additional non-fibrillizable binder comprises polyvinylidene fluoride (PVDF).

16. The dry electrode film of claim **1**, wherein the dry binder further comprises an additional non-fibrillizable binder.

17. The dry electrode film of claim **1**, wherein the dry electrode film comprises at least about 92 wt. % of the dry active material.

18. The lithium ion battery of claim **14**, wherein the lithium ion battery has a first cycle efficiency of at least about 90%.

* * * * *

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(12) **United States Patent**
Saidi

(10) **Patent No.: US 11,545,667 B2**
(45) **Date of Patent: Jan. 3, 2023**

(54) **COMPOSITIONS AND METHODS FOR PASSIVATION OF ELECTRODE BINDERS**

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(72) Inventor: **Mohammed-Yazid Saidi**, La Mesa, CA (US)

(73) Assignee: **Tesla, Inc.**, Austin, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 253 days.

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PCT Pub. Date: **Sep. 27, 2018**

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H01M 10/0525 (2010.01)
(Continued)

(52) **U.S. Cl.**
CPC .... ***H01M 4/623*** (2013.01); ***H01M 4/133*** (2013.01); ***H01M 4/139*** (2013.01); (Continued)

(58) **Field of Classification Search**
None
See application file for complete search history.

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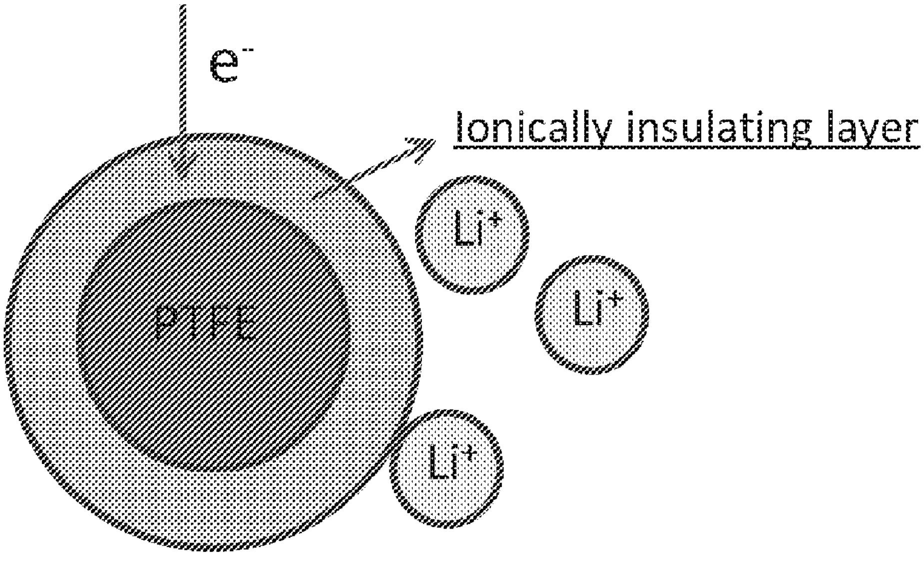
Primary Examiner — Robert S Carrico
(74) *Attorney, Agent, or Firm* — Knobbe, Martens, Olson & Bear, LLP

(57) **ABSTRACT**

Passivation methods and compositions for electrode binders are disclosed. A coated binder particle for use in an electrode film of an energy storage device is provided. The coated binder particle can comprise a coating over the surface of a binder particle, wherein the coating provides ionic insulation to the binder particle. In some embodiments, the coating covers the entire surface of the binder particle. In still further embodiments, a coated binder particle in an energy storage device blocks ionic contact between the binder and an electrolyte.

22 Claims, 8 Drawing Sheets



(51) **Int. Cl.**

H01M 4/133	(2010.01)
H01M 4/139	(2010.01)
H01M 4/1393	(2010.01)
H01G 11/06	(2013.01)
C08L 27/18	(2006.01)

(52) **U.S. Cl.**

CPC ***H01M 4/1393*** (2013.01); ***H01M 4/625*** (2013.01); ***H01M 10/0525*** (2013.01); *C08L 27/18* (2013.01); *C08L 2203/16* (2013.01); *H01G 11/06* (2013.01)

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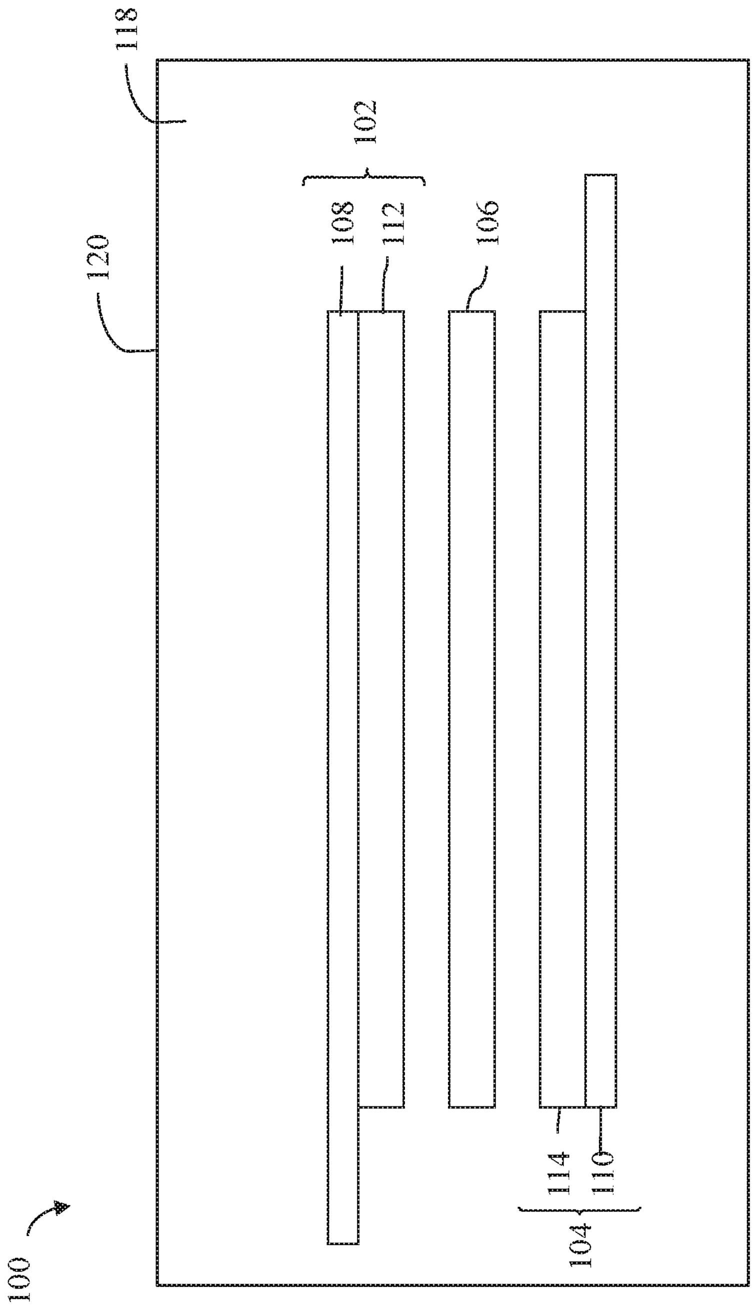

FIG. 1

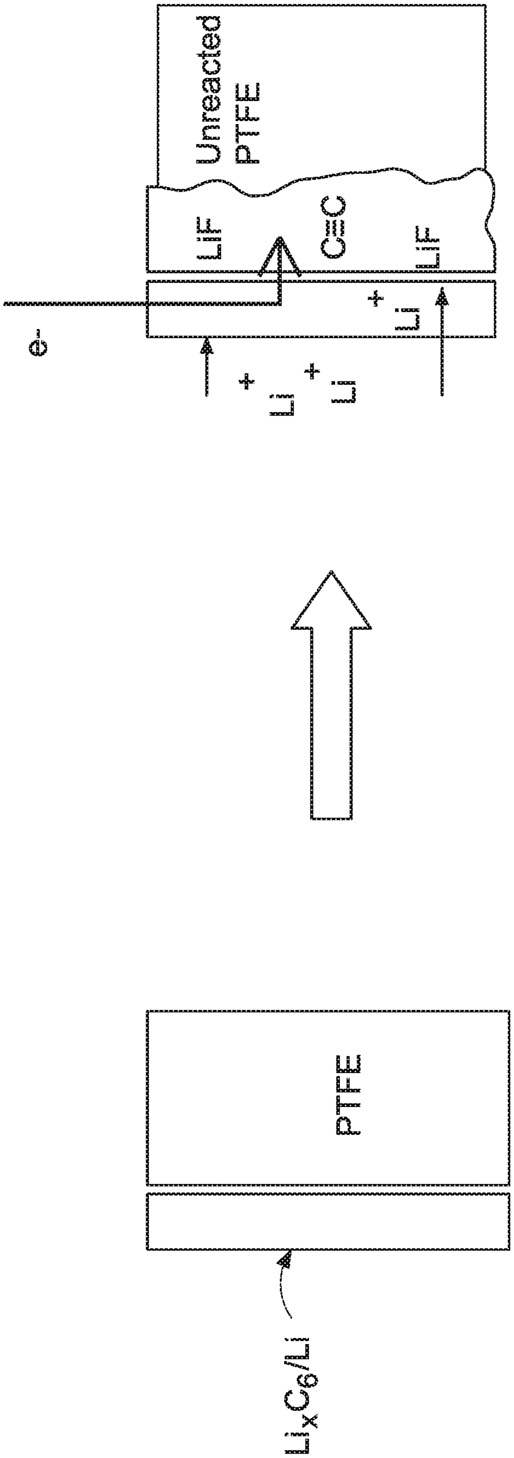

FIG. 2

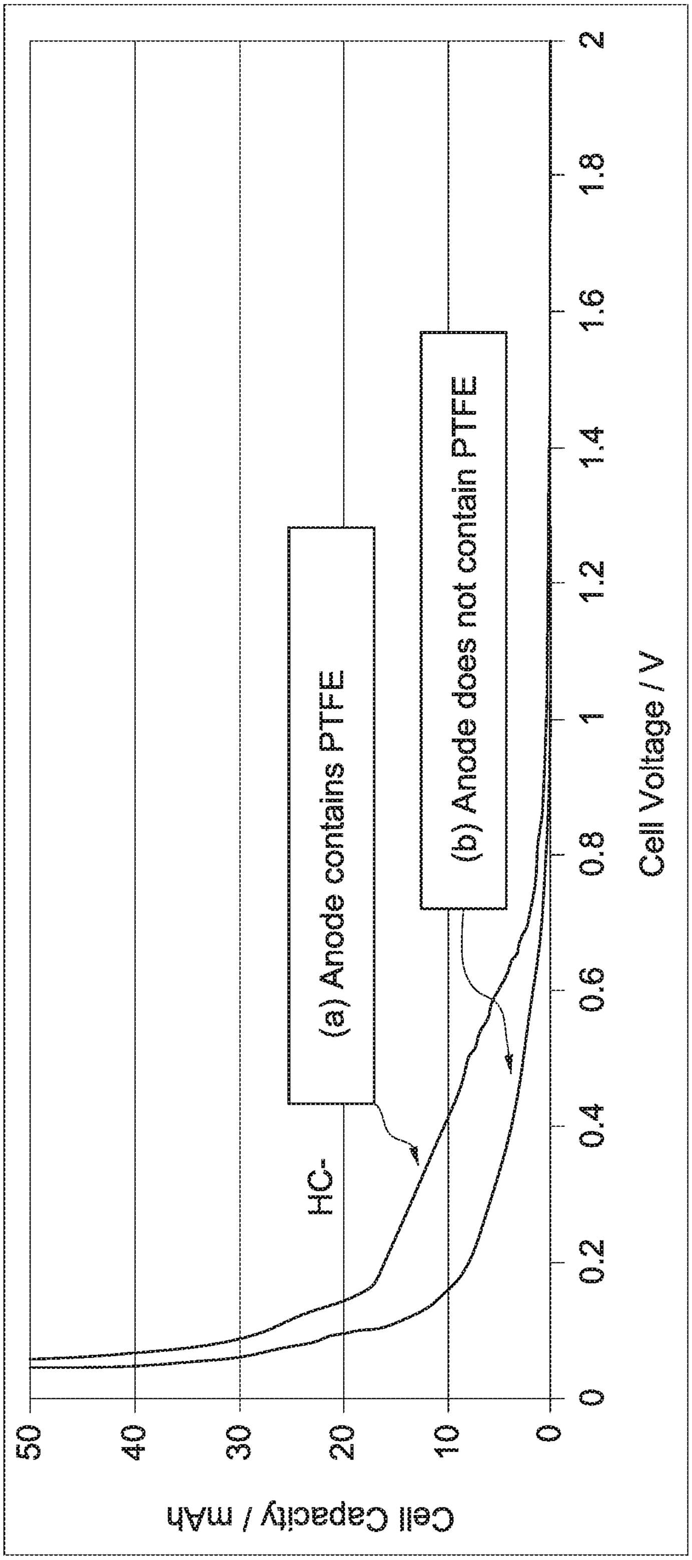
Cell Capacity / mAh
50
40
30
20
10
0
Cell Voltage / V
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
HC-
(a) Anode contains PTFE
(b) Anode does not contain PTFE

FIG. 3

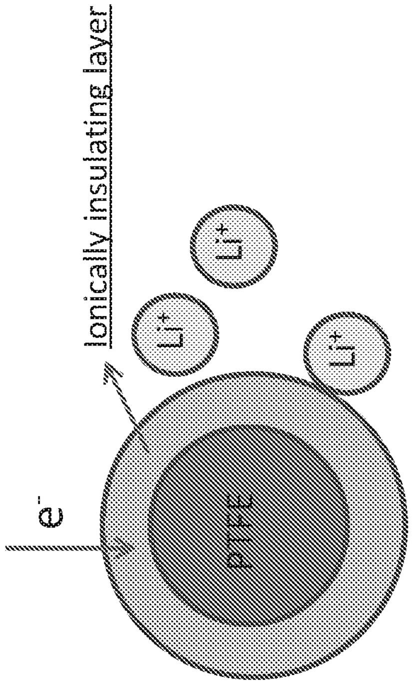

FIG. 4

FIG. 5

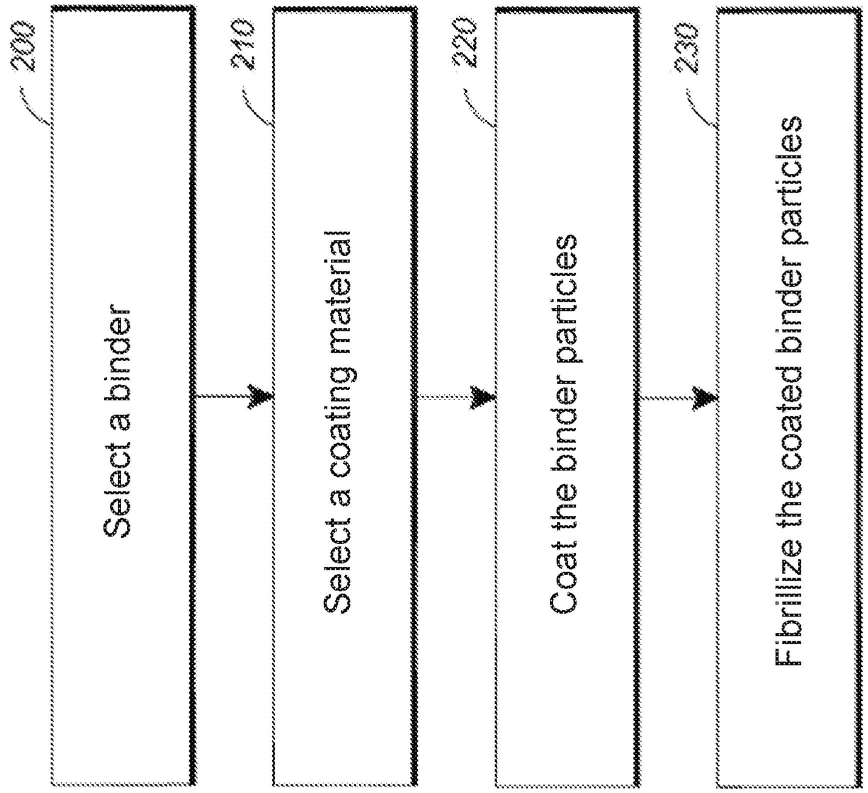
200
Select a binder
210
Select a coating material
220
Coat the binder particles
230
Fibrillize the coated binder particles

FIG. 6

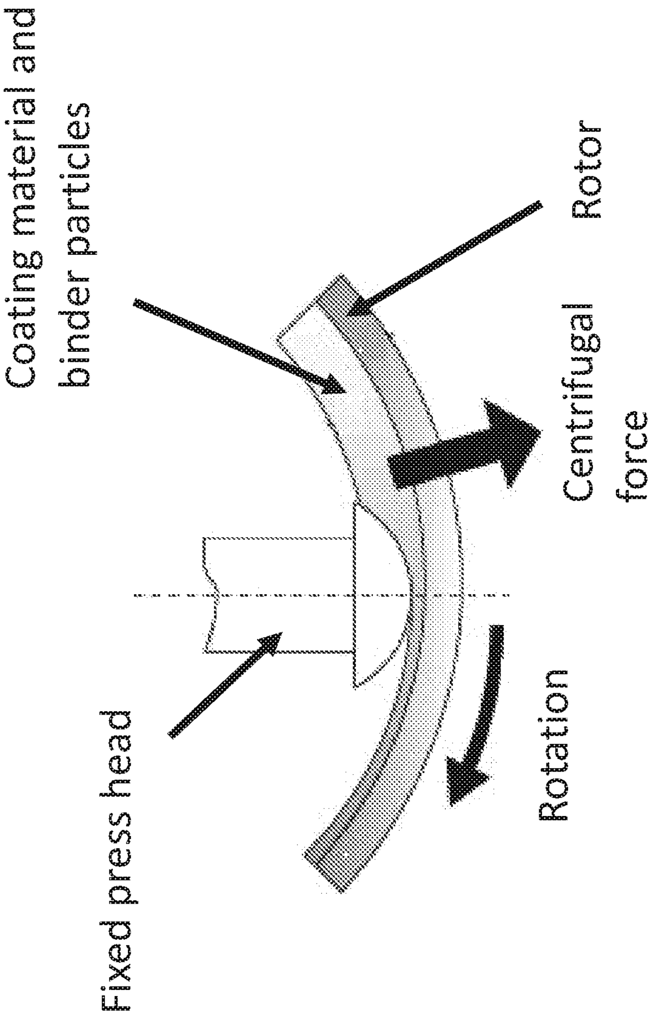
Coating material and binder particles
Rotor
Centrifugal force
Fixed press head
Rotation

FIG. 7

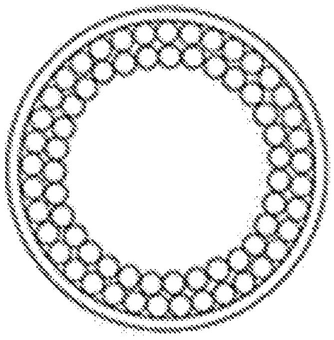

FIG. 8C

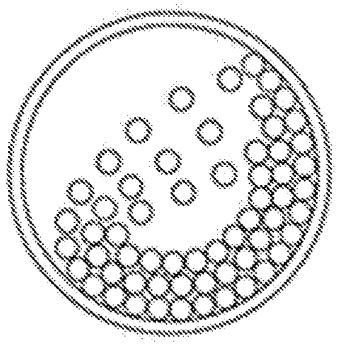

FIG. 8B

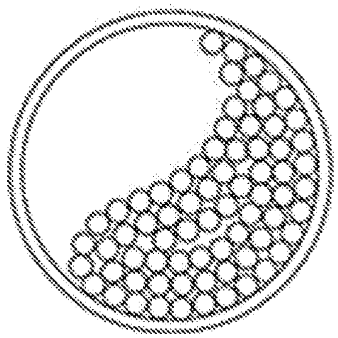

FIG. 8A

COMPOSITIONS AND METHODS FOR PASSIVATION OF ELECTRODE BINDERS

INCORPORATION BY REFERENCE TO ANY PRIORITY APPLICATIONS

The present application claims the benefit of priority to U.S. Provisional Patent Application No. 62/474,231, filed Mar. 21, 2017. The entire disclosure of the aforementioned application is expressly incorporated by reference in its entirety.

BACKGROUND

Field of the Invention

The present invention relates generally to energy storage devices, and specifically to passivation methods and compositions for electrode binders for use in energy storage devices.

Description of the Related Art

Electrical energy storage cells are widely used to provide power to electronic, electromechanical, electrochemical, and other useful devices. Such cells include batteries such as primary chemical cells and secondary (rechargeable) cells, fuel cells, and various species of capacitors, including ultracapacitors. Increasing the operating voltage and temperature of energy storage devices, including capacitors and batteries, would be desirable for enhancing energy storage, increasing power capability, and broadening real-world use cases.

However, at higher operating voltages, the electrode binders within the electrode films of energy storage devices may undergo degradation processes that result in a reduction in performance, or in outright cell failure. Over the life of an energy storage device, deterioration of device performance may manifest as reduced storage capacity, capacitance fade, increased equivalent series resistance (ESR) of the device, self-discharge, pseudocapacity, and/or gas formation. Thus, there is a need for electrode binders having improved stability under elevated voltage and temperature conditions of operation.

SUMMARY

For purposes of summarizing the invention and the advantages achieved over the prior art, certain objects and advantages of the invention are described herein. Not all such objects or advantages may be achieved in any particular embodiment of the invention. Thus, for example, those skilled in the art will recognize that the invention may be embodied or carried out in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other objects or advantages as may be taught or suggested herein.

In some embodiments, a coated binder particle for use in an electrode film of an energy storage device is provided. The coated binder particle can comprise a coating over the surface of a binder particle, wherein the coating provides ionic insulation to the binder particle. In some embodiments, the coating covers some, most, or substantially all of the entire surface of the binder particle. In still further embodiments, a coated binder particle, when implemented within an energy storage device, does not make ionic contact with an electrolyte, or has reduced contact with an electrolyte, relative to a binder particle which is not coated.

In some embodiments, an energy storage device comprising the coated binder particle is provided, wherein the energy storage device comprises an electrode film including the coated binder particle.

In some embodiments, a method for coating a binder particle for use in an electrode film of an energy storage device is provided. In some embodiments, the method can comprise selecting a binder, selecting a coating material, and coating the binder particles. The method can include fibrillizing the coated binder particles. Generally, the coating material is an ionic insulator. In some embodiments, the coating material is an electrical conductor.

In a first aspect, a method for fabricating an energy storage device is provided, comprising combining polymeric binder particles with an ionically insulating coating material, mixing the binder particles and the coating material to form coated binder particles such that the binder particles are not fibrillized during mixing, combining the coated binder particles with active material particles to form a first mixture, milling at least some of the first mixture to form an electrode film mixture; and calendering the electrode film mixture to form a free-standing electrode film.

In an embodiment of the first aspect, the polymeric binder particles comprise polytetrafluoroethylene (PTFE).

In an embodiment of the first aspect, the active material particles comprise graphite.

In an embodiment of the first aspect, the coated binder particles comprise composite particles of binder and coating material.

In an embodiment of the first aspect, the coating material comprises conductive carbon.

In an embodiment of the first aspect, the coating material comprises an electrically conductive material.

In an embodiment of the first aspect, mixing comprises milling.

In an embodiment of the first aspect, the milling is conducted in a mill comprising media.

In an embodiment of the first aspect, milling at least some of the first mixture is a high shear process at a shear velocity sufficient to fibrillize the binder particles.

In an embodiment of the first aspect, the high shear process comprises jet-milling.

In an embodiment of the first aspect, surface color of the binder particles is not visible to the naked eye following the mixing step.

In an embodiment of the first aspect, the coated binder particles do not aggregate.

In a second aspect, an electrode film is provided, comprising active material particles and fibrillized polymeric binder particles coated with a coating material, wherein the coating material is ionically insulating and electrically conductive, and wherein the fibrillized polymeric binder particles form a matrix within the electrode film such that the electrode film is self-supporting.

In an embodiment of the second aspect, the binder particles comprise polytetrafluoroethylene (PTFE).

In an embodiment of the second aspect, the active material comprises graphite.

In an embodiment of the second aspect, the binder particles form composite particles with the coating material.

In an embodiment of the second aspect, the coating material comprises conductive carbon.

In an embodiment of the second aspect, the binder particles comprise composite particles of PTFE and conductive carbon.

In an embodiment of the second aspect, an energy storage device is provided, wherein the energy storage device includes the electrode film.

In an embodiment of the second aspect, the energy storage device includes an electrolyte comprising lithium ions in contact with the electrode film.

In an embodiment of the second aspect, the binder particles are insulated from contact with the lithium ions.

In an embodiment of the second aspect, the energy storage device is a battery.

In a third aspect, a milling apparatus for coating a fibrillizable binder suitable for binding electrode active materials is provided, comprising a container forming an inner volume, and a media, fibrillizable binder particles and an ionically insulating coating material within the inner volume, wherein the media and container are configured to move relative to each other so as to coat the binder particles with the coating material to form coated binder particles.

All of these embodiments are intended to be within the scope of the invention herein disclosed. These and other embodiments of the present invention will become readily apparent to those skilled in the art from the following detailed description of the preferred embodiments having reference to the attached figures, the invention not being limited to any particular preferred embodiment(s) disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** depicts an embodiment of an energy storage device.

FIG. **2** depicts an energy storage device in which decomposition of polytetrafluoroethylene (PTFE) in the presence of lithium ions is taking place.

FIG. **3** depicts a lithium half cell showing the presence of a reduction plateau for (a) an electrode including graphite and PTFE and (b) an electrode including graphite and polyvinylidene difluoride, (PVdF), a non-PTFE binder. The plateau in the PTFE electrode (graph (a)) indicates an additional consumption of charge.

FIG. **4** is a schematic diagram depicting a polytetrafluoroethylene polymer particle coated with an ionically insulating layer according to the Example.

FIG. **5** is a photograph depicting coated binder particles according to the Example.

FIG. **6** depicts a flowchart for a method for coating binder particles in an embodiment.

FIG. **7** depicts a mixing apparatus that may be used in an embodiment of the coating process.

FIGS. **8**A-**8**C depict cross sections of a roller mill including ball shaped media at various rotational speeds that may be used in coating binder particles in an embodiment.

DETAILED DESCRIPTION

Various embodiments of methods and compositions for reducing electrode binder decomposition in energy storage devices are disclosed. An energy storage device as provided herein may include a binder as provided herein. Further, an energy storage device as provided herein may be constructed by a method as provided herein.

Fluorinated binders, and in particular polytetrafluoroethylene (PTFE) are binders commonly used in electrodes. Such binders enable the manufacturing of self-standing films without the aid of a solvent. It has been found that, under some modes of operation of energy storage devices, such as at elevated voltages, electrochemical reactions of the electrode binder(s) may occur, which can lead to decomposition of the binder(s). It is believed that electrochemical decomposition of fluorinated polymers may occur in the presence of lithium ions. Lithium being an electropositive metal, it may act as a reductant, and may act as a reductant of PTFE. For example, under elevated voltages a fluorinated electrode binder may decompose to form fluoride salts, for example, lithium fluoride. This fluorinated binder degradation can cause chemical and physical changes in the binder. These changes can affect the structural integrity of the electrode, such as the electrode film, due to, for example, the reduced binding abilities of the binder. This degradation can also cause the active materials in the electrode to lose or reduce electrical and/or ionic contact. Additionally, the decomposition reaction can lead to loss of lithium ions from the electrode, reducing the energy or capacity of the energy storage device. Thus, the overall performance of the device may be reduced. Certain embodiments of energy storage devices provided herein can incorporate features to reduce decomposition of electrode binder materials during operation.

Without wishing to be bound by theory, it is thought that a PTFE binder in a graphite anode can undergo an electrochemical reaction at about 0.5 V vs. a reference Li/Li^+ electrode. It is thought that the decomposition mechanism includes reduction of $—CF_2—CF_2—$ units in the polymer to acetylenic units. The reaction is thought to proceed as follows:

$$—(CF_2—CF_2)_n\text{-}+4nLi^+ +4ne^- \rightarrow \text{-}(C{\equiv}C)_n\text{-}+4nLiF$$

The hypothesized mechanism of decomposition is depicted in FIG. **2**.

Testing of cells including PTFE-containing reference electrodes demonstrate characteristics consistent with consumption of charge by PTFE binder reduction. As one example, a formation profile of a reference PTFE/graphite half cell was found to include a hump that is believed to correspond to reduction of PTFE. FIG. **4** depicts a graph of reference cell capacity versus cell voltage for lithium half cells (a) an electrode including graphite and PTFE, and (b) an electrode including graphite and polyvinylidene difluoride, (PVdF), a non-PTFE binder. The plateau in the PTFE electrode (graph (a)) indicates an additional consumption of charge relative to the electrode that does not include PTFE. Thus, it is believed that coating PTFE binder particles with a substance that is not conductive of lithium ions, as described herein, may reduce or prevent degradation of the PTFE.

An energy storage device described herein may advantageously be characterized by reduced equivalent series resistance over the life of the device, which may provide a device with increased power density. In some embodiments, energy storage devices described herein may be characterized by reduced loss of capacity over the life of the device. Further improvements that may be realized in various embodiments include improved cycling performance, including improved storage stability during cycling, and reduced capacitance fade.

Coated Binders

Provided herein are compositions and methods for electrode binders. Further provided herein are coated binder particles for use in an energy storage device, wherein the binder particles are coated with a coating material. In some embodiments, a coated electrode binder is provided.

The binder material can comprise a fluorinated binder, for example, polytetrafluoroethylene (PTFE), ultra-high molecular weight polyethylene (UHMWPE), polyvinylidene fluoride/polyvinylidene difluoride (PVDF), a

PVDF co-polymer, poly(ethylene oxide) (PEO), or combinations thereof. In some embodiments, the binder is a fibrillizable polymer. In a preferred embodiment, the binder comprises PTFE.

Generally, the coating material is an ionically insulating material, wherein the coating material blocks ions in the electrolyte from making ionic contact with the binder material. Without wishing to be limited by theory, it is thought that lithium ions in an electrolyte of an energy storage device can mediate degradation of polymeric binder materials. Thus, the coating material may be one which blocks electrolyte ions from reaching the binder, thereby limiting (for example, slowing) reaction, for example, reduction of the binder. Preferably the coating material forms an ionically insulating layer on the surface of the binder particles. In some embodiments, the binder particles are insulated from contact with lithium ions. Preferably, the coating covers all or substantially all of the surface of the binder particles, such that contact between the binder particles and the electrolyte is reduced or substantially eliminated. In some embodiments, substantially all of the surface of a binder particle is coated. Coated, or substantially coated, may refer to a coating wherein degradation of PTFE is not an observed failure mode of the energy storage device. However, even coating some of the surface of the binder particles may provide benefit.

The coated binder may comprise coated binder particles. In some embodiments, the coated binder particles may comprise composite particles. The coated binder particles may comprise composite binder particles of conductive carbon and PTFE. Thus, in some embodiments an electrode film mixture may comprise coated binder particles. In further embodiments, an electrode film mixture may comprise composite binder particles.

Without wishing to be limited by theory, several roles for the coating are herein proposed to account for its influence on the electrode performance. It is thought that the coating can act as an electron conductor to enhance electron transport between active particles in the electrode. It is additionally thought that the coating may act as a surface chemistry modifier to improve long term stability and/or binder performance. It is additionally thought that the coating may act as a physical protective layer that may suppress or mitigate failures of one or more components in the cell such as electrolyte breakdown or degradation. It is additionally thought that the coating materials take part in the primary electrode functions of electron transfer and lithium transport.

In further embodiments, an electrode comprising a coated binder particle provided herein is resistant to degradation at a voltage exceeding 0.5 V vs. an Li/Li$^+$ reference potential. In particular embodiments, no degradation of a coated PTFE binder is observed in an electrode film at a voltage exceeding 0.5 V vs. an Li/Li$^+$ reference potential following at least one charge/discharge cycle. In further embodiments, no degradation of a coated PTFE binder is observed in an electrode film at a voltage exceeding 0.5 V vs. an Li/Li$^+$ reference potential following 10, 100, or 500 charge/discharge cycles.

Generally, the coating material is an ionically insulating material. In some embodiments, the coating material is an electrical conductor. In further embodiments, the coating material can comprise a carbon material, for example, carbon black, conductive carbon, graphene-containing carbon, graphite, and combinations thereof. The coating material may be a particulate material, for example, a powdered carbon material. In further embodiments, the coating material can comprise a plurality of carbon materials. In still further embodiments, the coating material can comprise a ductile metal. The ductile metal can be, for example, Cu, Sn or Sb. Preferably, the binder particle comprises PTFE and the coating material comprises conductive carbon. In further embodiments, the conductive carbon comprises graphite, carbon black, graphene, or combinations thereof. In still further embodiments, an electrode of an energy storage device comprises the coated binder particles. In yet further embodiments, the electrode is an anode.

In some embodiments, the coating material does not include any anode active materials. In further embodiments, the coating material does not include graphite.

Generally, the coating will form a physical, adhesive bond to the binder particles. Chemical and/or electrostatic adhesion is thought to be the basis for the bond between the coating and the binder particles. Thus, the adhesion may be due to interface interactions such as swapping and/or sharing of electronic charge(s) and in some cases atoms. Furthermore, it is thought that the charge impacted from one element through mechanical means may create a force that bonds the coating and binder. The strength of the bond may be affected by a number of factors including: surface energy and polarity, surface area covered, surface contamination, surface texture and roughness as well as the cohesive strength of the binder and/or coating.

In various embodiments, the contact between the binder particles and the coating material can be described as sticking or clinging. The contact between binder particle and coating may be due to for example, intermolecular interactions such as ionic forces, polar interactions, induced dipole interactions, London forces, and/or surface forces. The binder may deform and entrap the coating material. Some coating material may be located completely within the binder particles. In some embodiments, the coating material may form a chemical bond to the binder particles. Generally, a coated binder particle can comprise a substantially continuous layer of the coating material around the binder particle. For example, in particular embodiments, the coating material may cover at least about 90%, at least about 95%, or at least about 99% of the surface area of the binder particles. In preferable embodiments, more than 95% of the surface area of the binder particles is coated.

Generally, the coating can have a thickness suitable for ionically insulating a binder particle used in an electrode of an energy storage device. The thickness of the coating can vary over the surface of the binder particle, and can vary between various binder particles. In various embodiments, the thickness of the coating can be about 0.1 microns, about 0.5 microns, about 1 micron, about 2 microns, 5 microns, about 10 microns, about 20 microns, about 50 microns, about 100 microns, or values therebetween. In some embodiments, the thickness is selected to provide an ionically insulating coating such that degradation of the coated binder particles is not a failure mode of an energy storage device. In further embodiments, the thickness is selected to provide an ionically insulating coating such that the electrolyte does not make contact with the binder.

The binder particles and coating material may be combined in a particular mass ratio to achieve one or more of a desired coating thickness or a desired coated surface area of the binder particles. The mass of the coating material may be about 1-50% of the mass of the binder particles, or preferably 5-20%. For coatings with a high surface area, lesser amounts of coating material, for example 1-10% of the mass of the binder particles, and preferably 3-8%, are effective. An example of a high surface area coating material is conductive carbon sold under the Ketjenblack® trademark.

Depending on the surface area of the binder particles and coating material, different amounts of coating material may be appropriate. In various embodiments, the mass of the coating material may be about 1%, about 2%, about 3%, about 4%, about 5%, about 6%, about 7%, about 8%, about 10%, about 20%, about 30%, about 40%, or about 50%, or a range between any two of the preceding values, of the mass of the binder particles.

The coating should also be selected for compatibility with a binder fibrillization process. In some embodiments, the application process(es) results in binder particles coated such that a subsequent fibrillization process is unchanged from a fibrillization process effective for fibrillizing uncoated binder particles. In some embodiments, the coated binder particle is initially formed in a dry process and/or used in a dry electrode process to form a dry electrode, such as that described in U.S. Patent Publication No. 2015/0072234 and described further herein. In some embodiments, a dry electrode is provided, wherein the dry electrode is free from processing contaminants such as solvents, and wherein the dry electrode comprises the coated binder particle.

Generally, the coating can be applied to the binder particles by a method provided herein, or by any suitable method. Such methods are known to those of the art and include rolling, grinding, crushing, spraying, stretching, macerating, mixing, whipping, and chopping.

FIG. **1** shows a side cross-sectional schematic view of an example of an energy storage device **100** including an electrode having a coated binder. The energy storage device **100** may be classified as, for example, a capacitor, a battery, a capacitor-battery hybrid, or a fuel cell, depending on the composition of the electrodes **102** and **104**.

The device **100** can have a first electrode **102**, a second electrode **104**, and a separator **106** positioned between the first electrode **102** and second electrode **104**, wherein at least one of electrodes **102** and **104** includes a coated binder as provided herein. The first electrode **102** and the second electrode **104** may be placed adjacent to respective opposing surfaces of the separator **106**. The energy storage device **100** may include an electrolyte **118** to facilitate ionic communication between the electrodes **102**, **104** of the energy storage device **100**. For example, the electrolyte **118** may be in contact with the first electrode **102**, the second electrode **104** and the separator **106**. The electrolyte **118**, the first electrode **102**, the second electrode **104**, and the separator **106** may be received within an energy storage device housing **120**. One or more of the first electrode **102**, the second electrode **104**, and the separator **106**, or constituent thereof, may comprise porous material. The pores within the porous material can provide containment for and/or increased surface area for reactivity with an electrolyte **118** within the housing **120**. The energy storage device housing **120** may be sealed around the first electrode **102**, the second electrode **104** and the separator **106**, and may be physically sealed from the surrounding environment.

In some embodiments, the first electrode **102** can be an anode (the "negative electrode") and the second electrode **104** can be the cathode (the "positive electrode"), or vice versa. In some embodiments, the first electrode **102** may comprise a positive electrode of a lithium ion capacitor. In further embodiments, the second electrode **104** may comprise a negative electrode of a lithium ion capacitor. In some embodiments, the first electrode **102** may comprise a cathode of a lithium ion battery. In further embodiments, the second electrode **104** may comprise an anode of a lithium ion battery. In some embodiments the first electrode **102** and/or the second electrode **104** are free-standing and/or self-supporting dry electrode films.

The separator **106** can be configured to electrically insulate two electrodes adjacent to opposing sides of the separator **106**, such as the first electrode **102** and the second electrode **104**, while permitting ionic communication between the two adjacent electrodes. The separator **106** can comprise a suitable porous, electrically insulating material. In some embodiments, the separator **106** can comprise a polymeric material. For example, the separator **106** can comprise a cellulosic material (e.g., paper), a polyethylene (PE) material, a polypropylene (PP) material, and/or a polyethylene and polypropylene material.

Generally, the first electrode **102** and second electrode **104** each comprise a current collector and an electrode film. Electrodes **102** and **104** comprise electrode films **112** and **114**, respectively, wherein at least one of electrode films **112** and **114** includes a coated binder as provided herein. The electrode films generally comprise one or more porous carbon based materials. In some embodiments, electrode films **112** and **114**, can include mixtures comprising binder material and carbon material, wherein at least one of electrode films **112** and **114** includes a coated binder as provided herein.

The carbon based materials may be selected from activated carbon, carbon black, conductive carbon, graphene-containing carbon, graphite, and combinations thereof. Activated carbon can be derived from a steam process or an acid/etching process. In some embodiments, both the first electrode **102** and the second electrode **104** comprise a current collector, one or more porous carbon based materials, and a fibrillated binder. Electrode films **112** and **114** can have any suitable shape, size and thickness. For example, the electrode films can have a thickness of about 30 microns (μm) to about 250 microns, for example, about 50 microns, about 100 microns, about 150 microns, about 200 microns, about 250 microns, or values therebetween.

At least one of the first electrode film **112** and the second electrode film **114** will generally include coated binders as provided herein. In some embodiments, the binder can include one or more polymers. In some embodiments, the binder can include one or more fibrillizable binder components. The binder component may be fibrillized to provide a plurality of fibrils, the fibrils desired mechanical support for one or more other components of the film. It is thought that a matrix, lattice, or web of fibrils can be formed to provide mechanical structure to the electrode film. In some embodiments, a binder component can include one or more of a variety of suitable fibrillizable polymeric materials.

In some embodiments, one or more electrode films described herein can be fabricated using a dry fabrication process, for example, as described in U.S. Patent Publication No. 2005/0266298 and U.S. Patent Publication No. 2006/0146479. These, and any other references to extrinsic documents herein, are hereby incorporated by reference in their entirety. As used herein, a dry fabrication process can refer to a process in which no or substantially no solvents are used in the formation of an electrode film. For example, components of the electrode film, including carbon materials and binders, may comprise dry particles. The dry particles for forming the electrode film may be combined to provide a dry particle electrode film mixture. In some embodiments, the electrode film may be formed from the dry particle electrode film mixture such that weight percentages of the components of the electrode film and weight percentages of the components of the dry particles electrode film mixture are substantially the same. In some embodiments, the electrode film formed from the dry particle electrode film mixture using the dry fabrication process may be free from, or substantially free from, any processing additives such as solvents and solvent residues resulting therefrom. In some embodiments, the resulting electrode films are free-standing and/or self-supporting electrode films formed using the dry process from the dry particle mixture. A process for forming an electrode film can include fibrillizing the fibrillizable binder component such that the electrode film comprises fibrillized binder.

As shown in FIG. **1**, the first electrode **102** and the second electrode **104** include a first current collector **108** in contact with first electrode film **112**, and a second current collector **110** in contact with the second electrode film **114**, respectively. The first current collector **108** and the second current collector **110** may facilitate electrical coupling between each corresponding electrode film and an external electrical circuit (not shown). The first current collector **108** and/or the second current collector **110** can comprise one or more electrically conductive materials, and have any suitable shape and size selected to facilitate transfer of electrical charge between the corresponding electrode and an external circuit. For example, a current collector can include a metallic material, such as a material comprising aluminum, nickel, copper, rhenium, niobium, tantalum, and noble metals such as silver, gold, platinum, palladium, rhodium, osmium, iridium and alloys and combinations of the foregoing. For example, the first current collector **108** and/or the second current collector **110** can comprise an aluminum foil having a rectangular or substantially rectangular shape sized to provide transfer of electrical charge between the corresponding electrode and an external electrical circuit.

In some embodiments, the energy storage device may be configured to operate at about 2.5 to 4.5 V, or 3.0 to 4.2 V. In further embodiments, the energy storage device is configured to have a minimum operating voltage of about 2.5 V to about 3 V, respectively. In still further embodiments, the energy storage device is configured to have a maximum operating voltage of about 4.1 V to about 4.4 V, respectively. In some embodiments, secondary electrochemical reactions of the electrode and/or electrolyte components are reduced.

In some embodiments, an energy storage device is configured for operation at selected conditions of voltage and temperature. For example, an energy storage device can be configured for operation at 50° C., 55° C., 60° C., 65° C., 70° C., 75° C., 80° C., 85° C., 90° C., 95° C., 100° C., or greater temperatures. An energy storage device can be configured for continual operation at 2.7 V at 60 to 85° C., 2.8 V at 60 to 85° C., 2.9 V at 60 to 85° C., or 3 V at 60 to 85° C., or selected temperature values therebetween. In some embodiments, the conditions of voltage and temperature are about 2.7 V and about 85° C., about 2.8 V and about 80° C., about 2.9 V and about 75° C., about 3 V and about 70° C., or about 3.1 V and about 65° C.

In some embodiments, an energy storage device is configured for an operating voltage of about 2.7 to 3 volts at a temperature of at least about 65° C. for at least 500 k cycles.

An energy storage device may include one or more technologies described herein to enable the energy storage device to maintain a capacitance greater than about 80% of its initial capacitance, and/or less than 200% of its initial equivalent series resistance when operating at a voltage of about 2.7 to 3 volts over a period of about 1,500 hours, and/or at least 500 k cycles, and at a temperature of at least about 65° C. In other embodiments, the energy storage device is configured to maintain at least 75%, 85%, 90%, 95% or 99% of its initial capacity when operating for a period of at least 1500 hours, and/or at least 500 k cycles at about 65° C. or greater.

In some embodiments, no significant electrode decomposition occurs in an energy storage device following about 1500 hours of operation and/or at least 500 k cycles, where significance is determined by intervention of an adverse effect requiring operation under less than the rated conditions of the device.

Technologies described herein may be used separately or in combination in an energy storage device to enable operation under the selected conditions.

Lithium Ion Energy Storage Device

In some embodiments, energy storage device **100** can be a lithium ion energy storage device such as a lithium ion capacitor or a lithium ion battery. In some embodiments, the electrode film of a lithium ion energy storage device electrode can comprise one or more carbon materials, and a coated binder particle as provided herein. One or more of the carbon materials may be porous. The porous carbon may be, for example, activated carbon or a conductive carbon. In some embodiments, the porous carbon can include structured carbon nanotubes, structured carbon nanowires, structured carbon nanosheets, graphene sheets, or a combination thereof. In some embodiments, the porous carbon can be a surface treated carbon.

In some embodiments, the electrode film of a lithium ion energy storage device electrode comprises an electrode film mixture comprising carbon configured to reversibly intercalate lithium ions. In some embodiments, the lithium intercalating carbon is graphite, hard carbon, soft carbon, carbon nanotubes, porous carbon, conductive carbon, or a combination thereof. For example, the electrode film of the electrode can include a binder material, one or more of graphite, graphene-containing carbon, hard carbon and soft carbon, and an electrical conductivity promoting material. The electrical conductivity promoting material can be, for example, carbon black or other conductive carbon. The conductive carbon material may be, for example, carbon black such as that manufactured under the trademark Ketjenblack®. In some embodiments, an electrode is pre-doped with lithium ions.

In further embodiments, the energy storage device **100** is charged with a suitable lithium-containing electrolyte. For example, device **100** can include a lithium salt, and a solvent, such as a non-aqueous or organic solvent. Generally, the lithium salt includes an anion that is redox stable. In some embodiments, the anion can be monovalent. In some embodiments, a lithium salt can be selected from hexafluorophosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), lithium perchlorate ($LiClO_4$), lithium bis(trifluoromethansulfonyl)imide ($LiN(SO_2CF_3)_2$), lithium trifluoromethansulfonate ($LiSO_3CF_3$), and combinations thereof. In some embodiments, the electrolyte can include a quaternary ammonium cation and an anion selected from the group consisting of hexafluorophosphate, tetrafluoroborate and iodide. In some embodiments, the salt concentration can be about 0.1 mol/L (M) to about 5 M, about 0.2 M to about 3 M, or about 0.3 M to about 2 M. In further embodiments, the salt concentration of the electrolyte can be about 0.7 M to about 1 M. In certain embodiments, the salt concentration of the electrolyte can be about 0.2 M, about 0.3 M, about 0.4 M, about 0.5 M, about 0.6 M, about 0.7 M, about 0.8 M, about 0.9 M, about 1 M, about 1.1 M, about 1.2 M, or values therebetween.

In some embodiments, an energy storage device provided herein can include a liquid solvent. A solvent as provided herein need not dissolve every component, and need not completely dissolve any component, of the electrolyte. In further embodiments, the solvent can be an organic solvent. In some embodiments, a solvent can include one or more functional groups selected from carbonates, ethers and/or esters. In some embodiments, the solvent can comprise a carbonate. In further embodiments, the carbonate can be selected from cyclic carbonates such as, for example, ethylene carbonate (EC), propylene carbonate (PC), vinyl ethylene carbonate (VEC), vinylene carbonate (VC), fluoroethylene carbonate (FEC), and combinations thereof, or acyclic carbonates such as, for example, dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), and combinations thereof. In certain embodiments, the electrolyte can comprise $LiPF_6$, and one or more carbonates.

In some embodiments, an electrode film as provided herein includes at least one active material and at least one binder. The at least one active material can be any active material known in the art. The at least one active material may be a material suitable for use in the anode or cathode of a battery. Anode active materials can be comprised of, for example, an insertion material (such as carbon, graphite, and/or graphene), an alloying/dealloying material (such as silicon, silicon oxide, tin, and/or tin oxide), a metal alloy or compound (such as Si—Al, and/or Si—Sn), and/or a conversion material (such as manganese oxide, molybdenum oxide, nickel oxide, and/or copper oxide). The anode active materials can be used alone or mixed together to form multi-phase materials (such as Si—C, Sn—C, SiOx-C, SnOx-C, Si—Sn, Si-SiOx, Sn-SnOx, Si-SiOx-C, Sn-SnOx-C, Si—Sn—C, SiOx-SnOx-C, Si-SiOx-Sn, or Sn-SiOx-SnOx.). In some embodiments, an energy storage device cathode can include a metal oxide. The cathode active material, for example, a metal oxide, metal sulfide, or a lithium metal oxide. The lithium metal oxide can be, for example, a lithium nickel manganese cobalt oxide (NMC), a lithium manganese oxide (LMO), a lithium iron phosphate (LFP), a lithium cobalt oxide (LCO), a lithium titanate (LTO), and/or a lithium nickel cobalt aluminum oxide (NCA). In some embodiments, cathode active materials can be comprised of, for example, a layered transition metal oxide (such as $LiCoO_2$ (LCO), $Li(NiMnCo)O_2$ (NMC) and/or $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)), a spinel manganese oxide (such as $LiMn_2O_4$ (LMO) and/or $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO)) or an olivine (such as $LiFePO_4$).

In some embodiments, a cathode electrode film can include about 70 weight % to about 98 weight % of the at least one active material, including about 70 weight % to about 92 weight %, or about 70 weight % to about 96 weight %. In some embodiments, the cathode electrode film can comprise up to about 10 weight % of the porous carbon material, including up to about 5 weight %, or about 1 weight % to about 5 weight %. In some embodiments, the cathode electrode film comprises up to about 5 weight %, including about 1 weight % to about 3 weight %, of the conductive additive. In some embodiments, the cathode electrode film comprises up to about 20 weight % of the binder, for example, about 1.5 weight % to 10 weight %, about 1.5 weight % to 5 weight %, or about 1.5 weight % to 3 weight %. In some embodiments, the cathode electrode film comprises about 1.5 weight % to about 3 weight % binder.

In some embodiments, an anode electrode film may comprise at least one active material, a binder, and optionally a conductive additive. In some embodiments, the conductive additive may comprise a conductive carbon additive, such as carbon black. In some embodiments, the at least one active material of the anode may comprise synthetic graphite, natural graphite, hard carbon, soft carbon, graphene, mesoporous carbon, silicon, silicon oxides, tin, tin oxides, germanium, lithium titanate, mixtures, or composites of the aforementioned materials. In some embodiments, an anode electrode film can include about 80 weight % to about 98 weight % of the at least one active material, including about 80 weight % to about 98 weight %, or about 94 weight % to about 97 weight %. In some embodiments, the anode electrode film comprises up to about 5 weight %, including about 1 weight % to about 3 weight %, of the conductive additive. In some embodiments, the anode electrode film comprises up to about 20 weight % of the binder, including about 1.5 weight % to 10 weight %, about 1.5 weight % to 5 weight %, or about 3 weight % to 5 weight %. In some embodiments, the anode electrode film comprises about 4 weight % binder. In some embodiments, the anode film may not include a conductive additive.

In some embodiments, the energy storage device **100** is a lithium ion battery. In some embodiments, the lithium ion battery is a lithium-cobalt, lithium-manganese, lithium iron phosphate, lithium nickel manganese cobalt oxide, lithium nickel cobalt aluminum oxide or lithium titanate, or lithium sulfur battery. In some embodiments, the lithium ion battery is configured to operate at about 3 to 4 V, or 3.6 to 3.7 V.

The binder can include polytetrafluoroethylene (PTFE), a polyolefin, polyalkylenes, polyethers, styrene-butadiene, co-polymers of polysiloxanes and polysiloxane, branched polyethers, polyvinylethers, co-polymers thereof, and/or admixtures thereof. The binder can include a cellulose, for example, carboxymethylcellulose (CMC). In some embodiments, the polyolefin can include polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), co-polymers thereof, and/or mixtures thereof. For example, the binder can include polyvinylene chloride, poly(phenylene oxide) (PPO), polyethylene-block-poly(ethylene glycol), poly(ethylene oxide) (PEO), poly(phenylene oxide) (PPO), polyethylene-block-poly(ethylene glycol), polydimethylsiloxane (PDMS), polydimethylsiloxane-coalkylmethylsiloxane, co-polymers thereof, and/or admixtures thereof. In some embodiments, the binder comprises a fibrillizable polymer. In certain embodiments, the binder comprises, consists essentially, or consists of PTFE. One or more electrode films may include coated PTFE binder as described herein.

In some embodiments, the binder may comprise PTFE and optionally one or more additional binder components. In some embodiments, the binder may comprise one or more polyolefins and/or co-polymers thereof, and PTFE. In some embodiments, the binder may comprise a PTFE and one or more of a cellulose, a polyolefin, a polyether, a precursor of polyether, a polysiloxane, co-polymers thereof, and/or admixtures thereof. An admixture of polymers may comprise interpenetrating networks of the aforementioned polymers or co-polymers.

The binder may include various suitable ratios of the polymeric components. For example, PTFE can be up to about 98 weight % of the binder, for example, from about 20 weight % to about 95 weight %, about 20 weight % to about 90 weight %, including about 20 weight % to about 80 weight %, about 30 weight % to about 70 weight %, about 30 weight % to about 50 weight %, or about 50 weight % to about 90 weight %.

In some embodiments, the electrode film mixture may include binder particles having selected sizes. In some embodiments, the binder particles may be about 50 nm, about 100 nm, about 150 nm, about 200 nm, about 250 nm, about 300 nm, about 350 nm, about 400 nm, about 450 nm, about 500 nm, about 1 μm, about 2 μm, about 3 μm, about 4 μm, about 5 μm, about 10 μm, about 50 μm, about 100 μm, or values therebetween.

As provided herein, an energy storage device can be a capacitor, a lithium ion capacitor (LIC), an ultracapacitor, or a battery. The energy storage device can be characterized by an operating voltage. In some embodiments, an energy storage device described herein can have an operating voltage of about 2.2 V to about 3.8 V. In further embodiments, the operating voltage can be about 2.7 V to about 3 V, about 3.6 to about 3.7 V, or values therebetween.

An energy storage device includes one or more electrodes. An electrode generally includes an electrode film and a current collector. The electrode film can be formed from a mixture of one or more binders and active electrode material. It will be understood that an electrode binder, and an electrode including a binder provided herein, can be used in various embodiments with any of a number of energy storage devices and systems, such as one or more batteries, capacitors, capacitor-battery hybrids, fuel cells, or other energy storage systems or devices, and combinations thereof. In some embodiments, a coated electrode binder, and an electrode including coated binder particles described herein may be a component of a lithium ion capacitor, a lithium ion battery, or an ultracapacitor.

An energy storage device as provided herein can be of any suitable configuration, for example planar, spirally wound, button shaped, or pouch. An energy storage device as provided herein can be a component of a system, for example, a power generation system, an uninterruptible power source systems (UPS), a photo voltaic power generation system, an energy recovery system for use in, for example, industrial machinery and/or transportation. An energy storage device as provided herein may be used to power various electronic device and/or motor vehicles, including hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and/or electric vehicles (EV).

In some embodiments, energy storage device **100** is an ultracapacitor configured to operate at about 2.7 V, 2.8 V, 2.9 V, 3 V, or greater than 3 V.

In some embodiments, the lithium ion capacitor includes one or more lithium ion intercalating components, as described in U.S. Patent Publication No. 2015/0287546.

In some embodiments, the ultracapacitor includes a positive electrode or a negative electrode comprising a treated carbon material, where the treated carbon material includes a reduction in a number of hydrogen-containing functional groups, nitrogen-containing functional groups and/or oxygen-containing functional groups, as described in U.S. Patent Publication No. 2014/0098464. In further embodiments, the ultracapacitor includes an electrolyte comprising a quaternary ammonium salt with a concentration of less than one molar, as described in U.S. Patent Publication No. 2014/0104752. In still further embodiments, the ultracapacitor includes a protective coating disposed on an inner housing surface, as described in U.S. Patent Publication No. 2014/0098463. In yet further embodiments, the ultracapacitor includes a positive electrode or a negative electrode comprising a carbon based layer having a selected porosity, for example, mesoporosity or microporosity, as described in U.S. Patent Publication No. 2014/0098465. In some embodiments, the ultracapacitor includes electrolyte in an amount that is selected to correspond to the saturation quantity of components of the ultracapacitor as described in U.S. Patent Publication No. 2014/0368973.

Definitions

As used herein, the terms "battery" and "capacitor" are to be given their ordinary and customary meanings to a person of ordinary skill in the art. The terms "battery" and "capacitor" are nonexclusive of each other. A capacitor or battery can refer to a single electrochemical cell that may be operated alone, or operated as a component of a multi-cell system.

As used herein, the voltage of an energy storage device is the operating voltage for a single battery or capacitor cell. Voltage may exceed the rated voltage or be below the rated voltage under load, or according to manufacturing tolerances.

As provided herein, a "self-supporting" electrode film is an electrode film that incorporates binder matrix structures sufficient to support the film or layer and maintain its shape such that the electrode film or layer can be free-standing. When incorporated in an energy storage device, a self-supporting electrode film or active layer is one that incorporates such binder matrix structures. Generally, and depending on the methods employed, such electrode films or active layers are strong enough to be employed in energy storage device fabrication processes without any outside supporting elements, such as a current collector or other film. For example, a "self-supporting" electrode film can have sufficient strength to be rolled, handled, and unrolled within an electrode fabrication process without other supporting elements. A dry electrode film, such as a cathode electrode film or an anode electrode film, may be self-supporting.

As provided herein, a "solvent-free" electrode film is an electrode film that contains no detectable processing solvents, processing solvent residues, or processing solvent impurities. A dry electrode film, such as a cathode electrode film or an anode electrode film, may be solvent-free.

A "wet" electrode, "wet process" electrode, or slurry electrode, is an electrode prepared by at least one step involving a slurry of active material(s), binder(s), and optionally additive(s). A wet electrode may include processing solvents, processing solvent residues, and/or processing solvent impurities.

Methods

In some embodiments, a method for constructing an energy storage device is provided. In further embodiments, the method comprises selecting a binder material, selecting a coating material, coating the binder particles, optionally, fibrillating the coated binder particles and an electrode active material to form an electrode composition, and optionally applying the electrode composition to a current collector to form an electrode.

FIG. **6** depicts an embodiment of a method for coating binder particles as raw material to be used in an electrode film for an energy storage device. In step **200**, select a binder, a suitable binder is selected. The binder selected may be a binder as described herein. In some embodiments, the binder selected comprises a fluorinated polymer. In further embodiments, the binder is selected from polytetrafluoroethylene (PTFE), ultra-high molecular weight polyethylene (UHMWPE), polyvinylidene fluoride (PVDF), a PVDF copolymer, poly(ethylene oxide) (PEO), or combinations thereof. In some embodiments, the binder selected is a single binder. In some embodiments, the binder is dry. In some embodiments, the binder is in powder form.

In some embodiments, the binder selected is a fibrillizable binder, wherein the fibrillizable binder is as provided herein. In preferable embodiments, the binder selected is PTFE. In certain embodiments, the binder consists of or consists essentially of PTFE or any one of the aforementioned binder materials.

In step **210**, select a coating material, a suitable coating material is selected. Generally, the coating material is an ionic insulator. In some embodiments, the coating material is an electrical conductor. In further embodiments, the coating material can comprise a carbon material, for example, carbon black, conductive carbon, graphene-containing carbon, graphite, and combinations thereof. In yet further embodiments, the coating material can comprise a plurality of carbon materials. In still further embodiments, the coating material can comprise a ductile metal. The ductile metal can be, for example, Cu, Sn or Sb. Preferably, the coating material comprises conductive carbon. The conductive carbon can be, for example, a commercial carbon such as Super P, Acetylene black (AB), Shwanigan, black (SB), and a number of other carbons compatible with battery operation. In some embodiments, other conductive materials, including metals, semi-metals and semi-conductors may be suitable. In some embodiments, the coating material consists of or consists essentially of conductive carbon, or any one of the aforementioned coating materials.

The coating material should be in a suitable form for application to the binder particles. The coating material can be dry. The coating material may change form during processing such that appropriate coated binder particles result. Generally, the coating material can be in powder form, however, other forms are contemplated, for example, flakes. In certain embodiments, the coating material may be amorphous prior to processing.

In step **220**, coat the binder particles, the coating material is applied to the surface of the binder particles. The coating material can be applied to the binder particles by any suitable method or methods. Some, most, or substantially all of the surface of a binder particle can be coated. Generally, substantially all of the surface of a binder particle is coated following the application process or processes. The thickness of the coating can be selected for a particular application, and can be a thickness provided herein. Preferably, the binder particles are completely coated with the coating material following the application process(es). In some embodiments, substantially all of the surface of a binder particle is coated following the application process(es). In some embodiments, 80 to 90% of the binder particle surface is coated. For example, in particular embodiments, 70%, 80%, 90%, 95%, or 99%, or a range between two of these values, of the surface area of the binder particles is coated. Preferably the coating material forms an ionically insulating layer on the surface of the binder particles. In preferable embodiments, more than 95% of the surface area of the binder particles is coated. In some embodiments, the binder particles are insulated from passage by lithium ions.

Step **220** may comprise steps of combining and mixing the binder particles and the coating material. Combining may comprise combining binder particles and coating material in a particular mass ratio. Generally, the amount of coating material used for a particular amount of binder particles can be such that substantially all of the coating material coats the surface of the binder particles. Mixing may comprise mechanical fusion and/or milling as described below. Mixing may be carried out under conditions that do not fibrillize the binder particles. The combining and mixing steps may be started, performed, or completed sequentially or concurrently. In some embodiments, the combining and mixing steps are performed in a single apparatus. In some embodiments, combining and/or mixing can include processing materials that consist essentially of or consist of the binder particles and the coating material. In further embodiments, the binder particles combined and/or mixed consist essentially or consist of PTFE, and the coating material combined and/or mixed consists essentially or consists of conductive carbon. The mass of the coating material may be about 1-50% of the mass of the binder particles, or preferably 5-20%. For coatings with a high surface area, lesser amounts of coating material, for example 1-10% of the mass of the binder particles, and preferably 3-8%, are effective. An example of a high surface area coating material is conductive carbon sold under the Ketjenblack® trademark. Depending on the surface area of the binder particles and coating material, different amounts of coating material may be appropriate.

The coating step can comprise a mechanical fusion step, wherein the surface of a binder particle is coated with the coating material to provide a coated binder particle as provided herein. Generally, the mechanical fusion step will be any combining process sufficient to adhere the chosen coating material to the binder. Generally, the mechanical fusion is accomplished by imparting mechanical energy to the binder and coating materials. Without wishing to be limited by theory, it is thought that the mechanical energy may lead to chemical reactions between binder and coating particles. In some embodiments, the mechanical fusion can comprise a lower-velocity milling or other tumbling process with lower velocities than would be sufficient to fibrillize a binder, for example, jet milling or other high-velocity blending. Generally, high shear milling, or high velocity milling, refers to milling conducted at sufficient velocities to fibrillize PTFE or another fibrillizable binder.

The coating process may include either or both mixing and milling steps. The mixing and/or milling steps may be performed in a milling apparatus including media. The media may be fixed or free. Either or both of the mixing and milling may be conducted in an inert atmosphere, for example, comprising nitrogen or argon. The coating process may be a dry process conducted in the absence of solvents or other additives.

In certain embodiments, the coating process may include a mixing step. The mixing step may comprise a mechanical fusion performed in a mixing apparatus having a fixed media, such as a fixed press element. FIG. **7** depicts a mixing apparatus having a fixed press element. As a specific example, the mixing apparatus may be a MECHANO FUSION™ system of Hosokawa Micron Corp., Japan. In such embodiments, feed material comprising coating material and binder particles is charged into a rotor with a fixed press head. Thus, compressive forces are applied to the mixture of binder and coating materials while a rotor presses the mixture against the rotor wall by centrifugal force. Multiple compression cycles may be used.

In some embodiments, a milling process can be performed to ensure that the coated binder particles have a sufficient surface coating, for example, to create a coating covering at least about 70%, at least about 80%, at least about 90%, at least about 95%, or at least about 99% of the surface of the binder particles. In preferable embodiments, more than 95% of the surface area of the binder particles is coated. For example, the coating process may include a milling step performed by processing the binder and coating particles in a jar roller mill. The roller may be, for example, a one-tier jar mill. In some embodiments, the jar mill be a high-capacity laboratory jar mill including a 13" roller, and operating at 115 VAC/60 Hz A specific example is a U.S. Stoneware jar variable speed roller mill, Model 755RMV1.

A Jar-Roller mill generally includes a ceramic jar pre-loaded with the feed materials and media, which is placed on two rotating rollers. The speed of rotation can be varied, any can be, for example, from 5 to 200 rpm. Where blending only is desired (no attrition or size reduction effects), it is preferable to use lower rpm, below 100 and preferably below 50 rpm. In some embodiments, such as that discussed with reference to the Example below, an additional media can be included within the mill during the coating step, to improve the efficiency of the coating process. The media can be separated from the coated binder material, upon completion of the coating step, to allow the coated binder to be further processed into an electrode film. The media can comprise any of a number of materials that are inert relative to the binder and coating. The media can be configured as a plurality of balls, beads, cylinders, or any of a number of different regular or irregular shapes. The media can be any of a number of different sizes, but is generally significantly larger than the binder and coating material. Typical sizes of the media may be 0.1 mm to about 30 mm in diameter for spherical media, and 5 mm to 20 mm in diameter for cylindrical media. In preferable embodiments, the media is a cylindrical media having a length of about 0.5 cm to 1.5 cm. FIGS. **8**A-**8**C depict cross sections of a jar roller mill including ball shaped media at various rotational speeds, with polymeric binder materials and coating materials.

In some embodiments, the application process(es) results in binder particles coated such that a subsequent fibrillization process is unchanged from a fibrillization process for uncoated binder particles. In some embodiments, the coating process provides a reduction of the electrostatic attractive forces between binder particles. In further embodiments, the coating process(es) result in binder particles having no tendency to agglomerate, or a decreased tendency to agglomerate relative to uncoated binder mixed with carbon or other materials used in electrode film formation. The coated binder particles may appear as those depicted in FIG. **5**. The binder particles in FIG. **5** do not display the original (off white) color of the binder particles, and appear black to the naked eye.

Optionally, in step **230**, fibrillize the coated binder particles, the coated binder particles and electrode active materials are fibrillized, for example, by jet milling. Persons of skill in the art have the knowledge to perform such a fibrillizing process. Such processes are discussed in, for example, U.S. Patent Publication No. 2015/0072234.

In some embodiments, a milling apparatus is provided. The milling apparatus may include a media, binder particles and a coating material. The media may be a fixed media, such as a press tip or element, or a moveable media, such as balls. The milling apparatus may include a container forming an inner volume, and a media. The inner volume may further contain binder particles and a coating material. The media and container may be configured to move relative to each other to coat the binder particles with the coating material to form coated binder particles. The media may be a fixed media or a moveable media. For example, in some embodiments, the media may be a fixed press head adjacent to a rotor as depicted in FIG. **7**. The milling apparatus may be configured to carry out one or more steps of the method of FIG. **6**.

In further embodiments, the media may be ball media. The apparatus may be configured for rotation of the inner volume. For example, when ball media are contained in the inner volume, rotation of the inner volume may lead to various modes of milling, as depicted in FIGS. **8**A-**8**C. FIG. **8**A depicts a roller mill including ball media operating well below critical speed and below a speed at which cascading of media occurs. FIG. **8**B depicts a roller mill operating at a speed above which cascading occurs. FIG. **8**C depicts a roller mill including ball media operating above critical speed.

EXAMPLE

PTFE binder powder was coated with a conductive carbon including graphite and carbon black (Super P®) using a Jar roller mill. The Jar roller mill used zirconia media (½ in diameter) to facilitate the coating process, by smearing the carbon particles on the white PTFE binder particles. The coated binder particles are depicted in FIG. **5**. Following coating, the white color of the binder particles was no longer visible, and the agglomerating properties of the PTFE particles to each other was eliminated. The coated PTFE binder particles had a flake shape of approximately 2 to 3 mm in the longest dimension.

While certain embodiments of the inventions have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the disclosure. Indeed, the novel methods and systems described herein may be embodied in a variety of other forms. Furthermore, various omissions, substitutions and changes in the systems and methods described herein may be made without departing from the spirit of the disclosure. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the disclosure. Accordingly, the scope of the present inventions is defined only by reference to the appended claims.

Features, materials, characteristics, or groups described in conjunction with a particular aspect, embodiment, or example are to be understood to be applicable to any other aspect, embodiment or example described in this section or elsewhere in this specification unless incompatible therewith. All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. The protection is not restricted to the details of any foregoing embodiments. The protection extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

Furthermore, certain features that are described in this disclosure in the context of separate implementations can also be implemented in combination in a single implementation. Conversely, various features that are described in the context of a single implementation can also be implemented in multiple implementations separately or in any suitable subcombination. Moreover, although features may be described above as acting in certain combinations, one or more features from a claimed combination can, in some cases, be excised from the combination, and the combination may be claimed as a subcombination or variation of a subcombination.

Moreover, while operations may be depicted in the drawings or described in the specification in a particular order, such operations need not be performed in the particular order shown or in sequential order, or that all operations be performed, to achieve desirable results. Other operations that are not depicted or described can be incorporated in the example methods and processes. For example, one or more additional operations can be performed before, after, simultaneously, or between any of the described operations. Further, the operations may be rearranged or reordered in other implementations. Those skilled in the art will appreciate that in some embodiments, the actual steps taken in the processes illustrated and/or disclosed may differ from those shown in the figures. Depending on the embodiment, certain of the steps described above may be removed, others may be added. Furthermore, the features and attributes of the specific embodiments disclosed above may be combined in different ways to form additional embodiments, all of which fall within the scope of the present disclosure. Also, the separation of various system components in the implementations described above should not be understood as requiring such separation in all implementations, and it should be understood that the described components and systems can generally be integrated together in a single product or packaged into multiple products. For example, any of the components for an energy storage system described herein can be provided separately, or integrated together (e.g., packaged together, or attached together) to form an energy storage system.

For purposes of this disclosure, certain aspects, advantages, and novel features are described herein. Not necessarily all such advantages may be achieved in accordance with any particular embodiment. Thus, for example, those skilled in the art will recognize that the disclosure may be embodied or carried out in a manner that achieves one advantage or a group of advantages as taught herein without necessarily achieving other advantages as may be taught or suggested herein.

Conditional language, such as "can," "could," "might," or "may," unless specifically stated otherwise, or otherwise understood within the context as used, is generally intended to convey that certain embodiments include, while other embodiments do not include, certain features, elements, and/or steps. Thus, such conditional language is not generally intended to imply that features, elements, and/or steps are in any way required for one or more embodiments or that one or more embodiments necessarily include logic for deciding, with or without user input or prompting, whether these features, elements, and/or steps are included or are to be performed in any particular embodiment.

Conjunctive language such as the phrase "at least one of X, Y, and Z," unless specifically stated otherwise, is otherwise understood with the context as used in general to convey that an item, term, etc. may be either X, Y, or Z. Thus, such conjunctive language is not generally intended to imply that certain embodiments require the presence of at least one of X, at least one of Y, and at least one of Z.

Language of degree used herein, such as the terms "approximately," "about," "generally," and "substantially" as used herein represent a value, amount, or characteristic close to the stated value, amount, or characteristic that still performs a desired function or achieves a desired result.

The scope of the present disclosure is not intended to be limited by the specific disclosures of preferred embodiments in this section or elsewhere in this specification, and may be defined by claims as presented in this section or elsewhere in this specification or as presented in the future. The language of the claims is to be interpreted broadly based on the language employed in the claims and not limited to the examples described in the present specification or during the prosecution of the application, which examples are to be construed as non-exclusive.

What is claimed is:

1. A method for fabricating an energy storage device electrode film, comprising:

mixing binder particles and an ionically insulating coating material to form coated binder particles, wherein mixing does not fibrillize the binder particles, and wherein mixing coats at least about 70% of an average surface of the binder particles with the ionically insulating coating material;

combining the coated binder particles with active material particles to form a first mixture;

milling at least some of the first mixture to form an electrode film mixture; and

calendering the electrode film mixture to form a free-standing electrode film.

2. The method of claim **1**, wherein the polymeric binder particles comprise a binder selected from the group consisting of polytetrafluoroethylene (PTFE), ultra-high molecular weight polyethylene (UHMWPE), polyvinylidene fluoride (PVDF), a PVDF co-polymer, poly(ethylene oxide) (PEO), and combinations thereof.

3. The method of claim **1**, wherein the active material particles comprise a material selected from the group consisting of graphite, hard carbon, soft carbon, graphene, mesoporous carbon, silicon, a silicon oxide, tin, a tin oxide, germanium, lithium titanate, combinations thereof, and composites thereof.

4. The method of claim **1**, wherein the coated binder particles comprise composite particles of binder and ionically insulating coating material.

5. The method of claim **1**, wherein the ionically insulating coating material comprises a material selected from the group consisting of carbon black, conductive carbon, graphene-containing carbon, graphite, and combinations thereof.

6. The method of claim **1**, wherein the ionically insulating coating material comprises an electrically conductive material.

7. The method of claim **1**, wherein mixing comprises pre-milling.

8. The method of claim **7**, wherein the pre-milling is conducted in a mill comprising media.

9. The method of claim **8**, further comprising removing the media prior to forming the electrode film.

10. The method of claim **8**, wherein the media comprises a material shape selected from the group consisting of balls, beads, cylinders, and combinations thereof.

11. The method of claim **7**, wherein the pre-milling is performed in a jar roller mill.

12. The method of claim **1**, wherein milling at least some of the first mixture is a high shear process at a shear velocity sufficient to fibrillize the binder particles.

13. The method of claim **12**, wherein the high shear process comprises jet-milling.

14. The method of claim **1**, wherein surface color of the binder particles is not visible to the naked eye following the mixing step.

15. The method of claim **1**, wherein the coated binder particles do not aggregate.

16. The method of claim **1**, wherein the coated binder particles comprise binder particles covering about 80% to 90% of an average surface of the coated binder particles.

17. The method of claim **1**, wherein during the mixing step the mass of the coating material is about 1-50% the mass of the binder particles.

18. The method of claim **1**, wherein the mixing step consists essentially of mixing the binder particles and the ionically insulating coating material to form the coated binder particles.

19. The method of claim **1**, wherein the mixing step comprises mechanically fusing the binder particles and the ionically insulating coating material to form the coated binder particles.

20. The method of claim **19**, wherein mechanically fusing comprises a process selected from the group consisting of low-velocity milling, tumbling, and combinations thereof.

21. The method of claim **1**, wherein the ionically insulating coating material further comprises a ductile metal.

22. The method of claim **21**, wherein the ductile metal is selected from the group consisting of Cu, Sn, Sb, and combinations thereof.

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