(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 December 2016 (29.12.2016)

(10) International Publication Number
WO 2016/209983 A1

(51) International Patent Classification:
H01M 4/136 (2010.01) *H01M 4/62* (2006.01) *H01M 4/46* (2006.01) *H01M 12/08* (2006.01) *H01M 4/58* (2010.01)

(21) International Application Number: PCT/US2016/038793

(22) International Filing Date: 22 June 2016 (22.06.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/182,978 22 June 2015 (22.06.2015) US

(71) Applicant: **ALLIANCE FOR SUSTAINABLE ENERGY, LLC** [US/US]; 15013 Denver West Parkway, Golden, CO 80401 (US).

(72) Inventors: **BAN, Chunmei**; National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401 (US). **SON, Seoung-bum**; National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401 (US).

(74) Agent: **MCINTYRE, Michael, A.**; 15013 Denver West Parkway, Golden, CO 80401 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

(54) Title: MAGNESIUM METAL DEVICES AND METHODS OF MAKING THE SAME

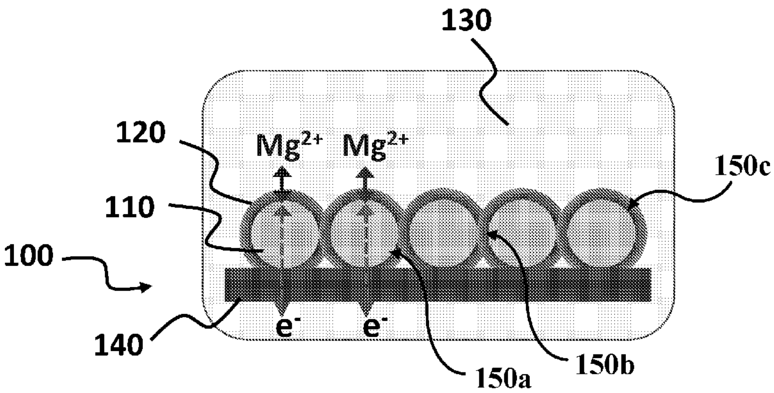

Figure 1a

(57) Abstract: The present disclosure relates to a device that includes a first electrode, where the first electrode includes magnesium metal having a first surface, and a first coating in physical contact with the first surface and covering substantially all of the first surface, where the first coating has a first thickness, and the first coating is configured to transport a plurality of magnesium ions through the first thickness, such that a first portion of the plurality of magnesium ions are reversibly depositable as elemental magnesium onto the first surface.

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MAGNESIUM METAL DEVICES AND METHODS OF MAKING THE SAME

CONTRACTUAL ORIGIN

The United States Government has rights in this invention under Contract No. DE-AC36-08GO28308 between the United States Department of Energy and the Alliance for Sustainable Energy, LLC, the Manager and Operator of the National Renewable Energy Laboratory.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S Provisional Application No. 62/182,978 filed June 22, 2015, the content of which is incorporated herein by reference in its entirety.

BACKGROUND

Current and historical incremental improvements to lithium-ion (Li-ion) batteries may not be sufficient to meet the anticipated demands of energy security, sustainability, and climate change. Magnesium metal may provide advantages relative to lithium, including increased abundance (5^{th} most abundant element on the earth) and improved environmentally-friendly physical properties. Therefore, magnesium metal batteries represent a new class of potentially ultrahigh-energy-density power sources useful for rechargeable batteries. However, magnesium metal presents numerous technical challenges including the inability for reversible deposition in most aprotic solvents containing currently commercial ionic salts, such as magnesium(II) bis(trifluoromethane sulfonyl) imide ($Mg(TFSI)_2$) and $MgClO_4$. Some success has been had with Grignard and magnesium organohaloaluminates-based electrolytes. However, the corrosive nature of these electrolytes has severely limited their usefulness in battery systems. Thus, there remains a need for improved magnesium metal-based battery components, batteries, battery systems, and methods of making such components, batteries and/or systems.

SUMMARY

An aspect of the present disclosure is a device that includes a first electrode, where the first electrode includes magnesium metal having a first surface, and a first coating in physical contact with the first surface and covering substantially all of the first surface, where the first coating has a first thickness, and the first coating is configured to transport a plurality of magnesium ions through the first thickness, such that a first portion of the plurality of magnesium ions are reversibly

depositable as elemental magnesium onto the first surface. In some embodiments of the present disclosure, the magnesium metal may be in the form of a particle, a film, a foil, a pellet, a cylinder, and/or a sphere. In some embodiments of the present disclosure, the first coating may include a first polymer. In some embodiments of the present disclosure, the first polymer may include at least one of a polyacrylonitrile (PAN), a cyclized polyacrylonitrile (cPAN), a polyimide, a polyamide, a polystyrene, a polyethylene, a polyether, poly(3,4-ethylenedioxythiophene), a polypyrrole, a polythiophene, a polyaniline, a polyacetylene, a polyparaphenylene, a polyethylene oxide, and/or a polyethylene glycol. In some embodiments of the present disclosure, the first polymer may be cPAN.

In some embodiments of the present disclosure, the first coating may further include a magnesium-ion salt. In some embodiments of the present disclosure, the magnesium-ion salt may include at least one of $MgClO_4$, $Mg(PF_6)_2$, $Mg(CF_3SO_3)_2$, $MgCO_3$, $Mg(BF4)_2$, $Mg(NO_3)_2$, and/or magnesium(II) bis(trifluoromethane sulfonyl) imide ($Mg(TFSI)_2$). In some embodiments of the present disclosure, the first coating may have a thickness between about 1 nm and about 500 nm. In some embodiments of the present disclosure, the device may further include an electrolyte, where the electrolyte may be in physical contact with the first coating. In some embodiments of the present disclosure, the electrolyte may include at least one of a nitrile and/or a carbonate. In some embodiments of the present disclosure, the electrolyte may include at least one of acetonitrile and/or propylene carbonate. In some embodiments of the present disclosure, the electrolyte may further include a magnesium-ion salt. In some embodiments of the present disclosure, the magnesium-ion salt may include at least one of $MgClO_4$, $Mg(PF_6)_2$, $Mg(CF_3SO_3)_2$, $MgCO_3$, $Mg(BF4)_2$, $Mg(NO_3)_2$, and/or magnesium(II) bis(trifluoromethane sulfonyl) imide ($Mg(TFSI)_2$). In some embodiments of the present disclosure, the first portion may be between about 80% and about 100% of the plurality of magnesium ions.

In some embodiments of the present disclosure, the first electrode may further include a first current collector, the first current collector may be in contact with the magnesium metal, and the magnesium metal may be positioned between the first current collector and the first coating. In some embodiments of the present disclosure, the device may further include a second electrode including V_2O_5, where a second portion of the plurality of magnesium ions may be reversibly intercalateable in the V_2O_5, and the second electrode may be in physical contact with the electrolyte. In some embodiments of the present disclosure, the device may further include a second electrode including magnesium metal having a second surface, and a second coating in physical contact with the second surface and covering substantially all of the second surface, where the second coating has a second thickness, and the second coating may be configured to transport a third portion of the plurality of magnesium ions through the second thickness, such that a fourth portion of the plurality of magnesium ions may be reversibly depositable as elemental magnesium onto the second surface.

An aspect of the present disclosure is an electrode including magnesium metal having a surface, and a coating in physical contact with the surface and covering substantially all of the surface, where the coating has a thickness, and the coating is configured to transport a plurality of magnesium ions through the thickness, such that a portion of the plurality of magnesium ions are reversibly depositable as elemental magnesium onto the surface.

An aspect of the present disclosure is a method for charging and discharging a battery, the method including, in a first electrode having a magnesium metal, converting a first portion of the first magnesium metal to a first plurality of Mg^{2+} ions, transferring a first portion of the first plurality of Mg^{2+} ions through a first coating substantially covering the magnesium metal, transferring the first portion of the first plurality of Mg^{2+} ions through an electrolyte in physical contact with the first coating, transferring first portion of the first plurality of Mg^{2+} ions through a second coating substantially covering a magnesium metal of a second electrode, and converting the first portion of the first plurality of Mg^{2+} ions to elemental magnesium on the magnesium metal of the second electrode, where the second coating is in physical contact with the electrolyte.

In some embodiments of the present disclosure, the method may further include converting the elemental magnesium on the magnesium metal of the second electrode to a second plurality of Mg^{2+} ions, transferring the second plurality of Mg^{2+} ions through the second coating, transferring the second plurality of Mg^{2+} ions through the electrolyte, transferring second plurality of Mg^{2+} ions through the first coating, converting the second plurality of Mg^{2+} ions to elemental magnesium on the magnesium metal of the first electrode.

DRAWINGS

Some embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than limiting.

Figure 1a illustrates an electrode that includes coated magnesium metal particles, according to some embodiments of the present disclosure.

Figure 1b illustrates an electrode that includes a coated magnesium metal foil, according to some embodiments of the present disclosure.

Figures 2a and 2b illustrate TEM images of coatings applied to magnesium metal foils, according to some embodiments of the present disclosure.

Figure 3 illustrates TEM images of coatings applied to a magnesium metal particle, according to some embodiments of the present disclosure.

Figure 4 illustrates an electrode constructed from a coated magnesium metal foil, according to some embodiments of the present disclosure.

Figure 5a illustrates experimental performance data collected from electrodes constructed using coated and uncoated magnesium metal powder, according to some embodiments of the present disclosure.

Figure 5b illustrates experimental performance data collected from electerodes constructed using coated and uncoated magnesium metal foils, according to some embodiments of the present disclosure.

Figure 6 illustrates detailed TEM observations of Mg^{2+}-conducting coatings, according to some embodiments of the present disclosure. Panel a illustrates a TEM image of magnesium metal with a Mg^{2+} conductive coating. A conformal coating thickness of about 100 nm is observed on the magnesium metal surface. Panel b illustrates HAADF mode observations of magnesium metal with a Mg^{2+} conductive coating. EDS mapping area is indicated within the rectangular box of Panel b. Panels c-h illustrate the corresponding EDS mapping results of carbon, nitrogen, magnesium, fluorine, oxygen, and sulfur respectively, in the coating.

Figure 7 illustrates the EDS signal of a Mg^{2+}-conducting coating of a coated magnesium metal electrode, according to some embodiments of the present disclosure.

Figure 8 illustrates XPS analysis of a Mg^{2+}-conducting coating, according to some embodiments of the present disclosure. XPS analysis of N_{1s} shows the structural change of cyanic group (N1) to pyridinic (N2) and substitutional graphite group (N3) after conversion of non-cyclic polyacrylonitrile (PAN) to cyclized polyacrylonitrile (cPAN).

Figure 9a illustrates a voltage versus time plot for symmetric magnesium metal cells, one having a cPAN Mg^{2+}-conducting coating and a second having a PAN Mg^{2+}-conducting coating, both with a current densities of about 0.01 mA cm^{-2}, according to some embodiments of the present disclosure.

Figure 9b illustrates an average plating voltage versus cycle numbers plot for symmetric magnesium metal cells, a first uncoated magnesium metal cell, a second magnesium metal cell having a PAN Mg^{2+}-conducting coating, and a third magnesium metal cell having a cPAN Mg^{2+}-conducting coating, all with a current densities of about 0.01 mA cm^{-2}, according to some embodiments of the present disclosure.

Figure 10 illustrates voltage versus time plot for symmetric magnesium metal cells with and without a coating under different electrolyte system, each having a current density of 0.01 mA cm^{-2}, according to some embodiments of the present disclosure.

Figure 11 illustrates TOF-SIMS and TGA analysis of Mg^{2+}-conducting coatings, according to some embodiments of the present disclosure. Panel a, TOF-SIMS spectra for positive Mg ions signals of cPAN and cPAN-$Mg(CF_3SO_3)_2$. Panels b and c, TOF-SIMS spectra for negative ions of cPAN and cPAN-$Mg(CF_3SO_3)_2$. Both signals for $CF_3SO_3^-$ and $[Mg(CF_3SO_3)_3]^-$ are only pronounced for cPAN-$Mg(CF_3SO_3)_2$. Panel d, TGA analysis of $Mg(CF_3SO_3)_2$, PAN and PAN-$Mg(CF_3SO_3)_2$. Weight losses (wt%) versus temperature (°C) for $Mg(CF_3SO_3)_2$, PAN and PAN-$Mg(CF_3SO_3)_2$ are shown as dashed line. In differentiated plots with solid line, each peak indicates where thermal decompositions of the samples occur. Panel e, illustrates a schematic of a magnesium metal powder electrode coated with a Mg^{2+}-conducting coating and the estimated structure of the cPAN-$Mg(CF_3SO_3)_2$ based on XPS, TOF-SIMS and TGA analysis.

Figure 12 illustrates the construction of a cell that includes a coated magnesium metal, according to some embodiments of the present disclosure.

Figure 13 illustrates conductivity measurements of a Mg^{2+}-conducting coating on a surface of a magnesium metal surface, according to some embodiments of the present disclosure. Panel a illustrates Nyquist plots resulting from EIS performed on a Mg^{2+}-

conducting coating. Panel b the results of a LSV test performed between -100 mV and 100 mV on a Mg^{2+}-conducting coating.

Figure 14 (Panels b-f) illustrates EDS data for a Mg^{2+}-conducting coating after 50 cycles in a symmetric cell, while Panels a and g illustrated HAADF TEM images of the same Mg^{2+}-conducting coating after 50 cycles in a symmetric cell, according to some embodiments of the present disclosure.

Figure 15 illustrates the electrochemical performance of a Mg/V_2O_5 system, according to some embodiments of the present disclosure.

Figure 16 illustrates a symmetric battery including two magnesium metal-containing electrodes, according to some embodiments of the present disclosure.

Figure 17 illustrates a method for charging and/or discharging a magnesium metal-containing battery, according to some embodiments of the present disclosure.

REFERENCE NUMBERS

100……………………electrode
110……………………magnesium metal
120……………………coating
130……………………electrolyte
140……………………current collector
150……………………surface
200……………………platinum layer
300……………………interface
400……………………cell
410……………………silver paste
420……………………carbon paper
430……………………ion-blocking electrode
500……………………battery
510……………………anode
520……………………cathode
530……………………circuit
600……………………method
610……………………first converting
620……………………first transferring

630……………………second transferring

640……………………third transferring

620……………………second converting

DETAILED DESCRIPTION

The present disclosure may address one or more of the problems and deficiencies of the prior art discussed above. However, it is contemplated that some embodiments as disclosed herein may prove useful in addressing other problems and deficiencies in a number of technical areas. Therefore, the embodiments described herein should not necessarily be construed as limited to addressing any of the particular problems or deficiencies discussed herein.

The use of magnesium metal provides a high specific capacity (2,205 mAh g^{-1} for Mg) and nearly doubles the volumetric capacity of lithium (Li) metal (3,832 mAh cm^{-3} for Mg vs. 2,061 mAh cm^{-3} for Li). A new concept is proposed here that takes advantage of these beneficial properties of magnesium metal by protecting a magnesium metal-containing electrode with a Mg^{2+}-conductive coating.

Figure 1a illustrates an exemplary electrode 100 utilizing magnesium metal 110 and a coating 120 positioned on a surface of the magnesium metal 110. The electrode 100 includes a current collector 140, upon which is deposited magnesium metal 110, in this example, in the form of solid magnesium metal particles, with a coating 120 applied to the outside surfaces of the magnesium metal particles. The electrode 100 may also be fabricated using a magnesium metal foil instead of, or in addition to the magnesium metal particles, as shown in Figure 1b, in which case, the current collector 140 is optional. Figure 1b shows a coating 120 applied to an outer surface 150 of the magnesium metal 110 foil. In addition, magnesium metal 110, may be substantially pure elemental magnesium (e.g. approaching 100% pure), and/or a magnesium-containing material, such as a magnesium alloy. The coating 120 may include a magnesium salt and a polymer such that the coating 120 may transport magnesium ions between an electrolyte 130 and the magnesium metal 110 (e.g. foil and/or particles). The coating 120 may be in physical contact with the electrolyte 130 to allow the reversible physical transport of magnesium ions (e.g. Mg^{2+} as shown in Figures 1a, 1b, and 4) to and from the electrolyte 130 and to and from the magnesium metal 110. In this example, the coated magnesium metal 110 may be in physical contact with the current collector 140 to allow the reversible physical transport of electrons (e.g. e as shown in figure 1a, 1b, and 4) to and from the circuit 530. Thus, by allowing the reversible transport of magnesium ions through the coating 120, the coating 120 may facilitate the reversible depositing and stripping of elemental magnesium onto and from the magnesium metal 110 (e.g. particles and/or foil), where the depositing of the elemental magnesium is represented by the reaction,

$$Mg^{2+} + 2e^{-} \rightarrow Mg,$$

and the stripping of the elemental magnesium is represented by the reaction,

$$Mg \rightarrow Mg^{2+} + 2e^{-}.$$

Without wishing to be bound by theory, it is believed that the stripping and depositing reactions occur on the outer surfaces (for example 150a-c) of the magnesium metal 110. Thus, referring again to Figure 1a, Mg^{2+} ions pass through the coating 120 to the outer surfaces (150a-c) of the magnesium metal 110 on which the Mg^{2+} ions are converted to elemental magnesium (not shown), and then, upon cycling of the battery, the elemental magnesium on the outer surfaces (150a-c) of the magnesium metal 110 is converted back to the Mg^{2+} ions. In some embodiments, cracks or fissures present in the magnesium metal 110 may provide additional surface area for the depositing and stripping reactions to occur.

In addition, the coating 120 may facilitate the reversible depositing and stripping of elemental magnesium (not shown) onto and from the surface 150 of the magnesium metal 110 without the electrolyte 130 interacting with the magnesium metal 110 to form an insulating passivation layer, for example on the outer surfaces of the magnesium metal 110. The magnesium metal 110 may be provided in any other suitable physical shape/form suitable for a particular electrode; e.g. the magnesium metal 110 need not be limited to particles or a foil. The magnesium metal 110 may contain impurities, and the magnesium metal 110 may be in the form of magnesium-based alloys, including magnesium-tin, magnesium-aluminum, magnesium-copper, magnesium-silicon, and or magnesium oxide.

As a result, an electrode 100 having a magnesium metal 110 with a coating 120 applied to at least a portion of the outer surfaces of the magnesium metal 110 may allow the use of both known magnesium electrolytes including Grignard reagents and hydride based anions in ethereal solvents, which tend to be vulnerable to oxidation, as well as other oxidation-resistant electrolytes such as $Mg(ClO_4)2$, $Mg(PF_6)_2$, $Mg(TFSI)_2$, $Mg(CF_3SO_3)_2$, $Mg(BF4)_2$, Mg(NO3)2 and/or $MgCO_3$ in propylene carbonate (PC), vinylene carbonate (VC), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and fluoroethylene carbonate (FEC), such that the coated magnesium metal 110 may result in better functioning magnesium metal-contained electrodes and battery systems. Thus, some of the embodiments described herein may enable the use of noncorrosive and commercially available electrolytes in nonaqueous Mg-metal batteries including Mg-ion, solid-state batteries, magnesium air, and/or sulfur batteries. In some cases, the coating 120 may include a hybrid coating composed of Mg-ion salts (e.g. $MgClO_4$, $Mg(PF_6)_2$, $Mg(TFSI)_2$, $Mg(CF_3SO_3)_2$, and/or $MgCO_3$, $Mg(BF4)_2$, Mg(NO3)2) and at least one polymer. Examples of suitable polymers include polyacrylonitrile (PAN), a cyclized polyacrylonitrile (cPAN), a polyimide, a polyamide, a polystyrene, a polyethylene, a polyether, poly(3,4-ethylenedioxythiophene), a polypyrrole, a polythiophene, a polyaniline, a polyacetylene, a polyparaphenylene, a polyethylene oxide, and/or a polyethylene glyco. Such coatings may address the mechanical, conductivity and stability requirements by protecting the magnesium metal 110, and as a result, enhance the short- and long-term performances of the magnesium metal-containing electrode 100 (and batteries utilizing such electrodes). A coating 120 may be applied to the magnesium metal 110 (e.g. particles and/or foil) by spin-coating, dip-coating, and/or any other suitable coating process, including wet processes and vapor deposition processes.

Figures 2a and 2b illustrate cross-section transmission electron microscopy (TEM) images of exemplary electrodes 100 that include magnesium metal 110, in the form of a magnesium foil, with a coating 120 applied to an outside surface 150 of the magnesium metal 110 foil. These figures also show a platinum layer 200, which was deposited on the coating 120 for purposes of the TEM method, and maintains the original morphology of the electrode 100. Therefore, the platinum layer 200 would not be included in an actual electrode used in a functioning battery. Figures 2a and 2b also indicate the areas where an electrolyte 130 would be positioned in a functioning battery and/or battery system. It should be understood, that for purposes of obtaining these TEM images, these areas were simply empty space, and electrolyte was not present during the imaging process. The coating 120 of Figure 2b was determined to have a thickness of about 500 nm. Figure 3 illustrates an example of an electrode 100 constructed from magnesium metal 110 with the magnesium metal 110 in powder form. In this case, the coating 120 was determined to have a thickness of about 100 nm. Figure 3 also shows a platinum layer 200, which again, was deposited on the coating for imaging purposes. An electrode 100 for use in a functioning battery would not include such a platinum layer 200.

Figures 2a, 2b, and 3 illustrate that the coatings 120 applied to the outside surfaces of the magnesium metal 110 (e.g. in the physical form of particles and a foil) demonstrated good adhesion at the magnesium metal/coating interfaces (see reference numeral 300 in Figure 3). The coverage of the magnesium metal 110 by the coating 120 and the adhesion of the coating 120 to the magnesium metal 110 are believed to protect the magnesium metal 110 from contacting the electrolyte 130. When magnesium metal is in direct contact with some noncorrosive, oxidation-resistant electrolytes, such as $Mg(TFSI)_2$ in acetonitrile (ACN) or $Mg(TFSI)_2$ in (PC) an/or analogous solvents, a passivation layer (not shown) may form on the outer surfaces 150 of the magnesium metal 110. Such passivation layers may prevent magnesium ion diffusion and the reversible depositing and stripping of magnesium in the magnesium metal 110 (e.g. particles, foil, and/or any other suitable form), resulting in decreased battery performance. The embodiments provided herein may protect the surface 150 of magnesium metal 110 of the electrodes 100 from reacting with the electrolyte 130, while maintaining the ability of magnesium ions to diffuse/migrate (e.g. as shown in Figures 1a, 1b, and 4), thus enabling the reversible stripping and depositing of magnesium in the magnesium metal 110, when using either non-ethereal-based electrolytes (e.g. $Mg(BH_4)_2$ in dimethoxyethane, diethylene glycol, triethylene glycol, and/or tetraethylene glycol) and/or more oxidation-resistant electrolytes, such as nitrile and/or carbonate electrolytes. Thus, oxidation-resistant electrolytes such as nitrile and/or carbonate electrolytes, may enable cathodes to operate at higher voltages, which may in turn enable the fabrication and use of high-energy rechargeable magnesium-metal based systems.

Referring again to Figures 2a, 2b, and 3, magnesium ions may be contained within the coating to provide ion conductivity that may enable the transport of magnesium ions from the electrolyte 130, through the coating 120, to at least the outer surfaces 150 of the magnesium metal 110, and vice versa (e.g. from the magnesium metal 110, through the coating 120, to the electrolyte 130). Without wishing to be bound by theory, isolating the magnesium metal 110 from the electrolyte 130 appears to allow this reversible transport of magnesium ions by preventing the side reaction between magnesium metal and the bulk electrolyte that typically results in the formation of one or more passivation layers. As illustrated in Figures 2a, 2b and 3, the magnesium metal 110 may be provided in any suitable shape or form, for example, as a substantially flat foil and/or in the form of particles, pellets, spheres, etc. Figure 4 illustrates another example of an electrode 100 that includes magnesium metal 110 in the form of a foil with a coating 120 placed on a surface 150 of the magnesium metal 110, with the electrode 100 immersed in an electrolyte 130. A current collector (not shown) may also be included, positioned in contact with a second surface of the magnesium metal 110 foil.

Reversible electrochemical stripping and depositing of magnesium in the magnesium metal foil and/or particles were performed to evaluate the Mg-ion conductivity and the chemical stability of the coatings described herein. Cell configurations consisting of two identical magnesium metal electrodes (referred to as "symmetric" cells) were used. The plots in Figure 5a illustrate the voltage profile as a function of reaction time for two symmetric cells tested. A first symmetric cell utilizing uncoated magnesium metal electrodes (e.g. both anode and cathode comprising uncoated magnesium metal) was tested and a second cell using coated magnesium metal electrodes (e.g. both anode and cathode comprising coated magnesium metal) was also tested. A Grignard electrolyte APC (all phenyl complex, or $(PhMgCl)_2$-$AlCl_3$/THF) was used as an electrolyte because this electrolyte is compatible with uncoated magnesium metal. Thus, this electrolyte choice allows a comparison of the two symmetric cells using, uncoated magnesium metal versus coated magnesium metal. Figure 5a shows that both the uncoated and coated magnesium metal electrodes allowed the reversible depositing and stripping of magnesium in the magnesium metal electrodes in both types of symmetric cells tested. The surface coating resulted in a magnesium metal electrode having a slightly higher potential than the uncoated magnesium metal electrode, at least initially. However, the overpotential of the coated magnesium metal electrode gradually decreased to the same level as the uncoated magnesium metal electrode for the later cycles. The reversibility of the stripping and depositing of magnesium in the coated magnesium metal electrode, as illustrated in Figure 5a, also supports the occurrence of the reversible transport of magnesium ions through the coating.

Other electrolytes may also be used. For example, an electrolyte that includes $Mg(TFSI)_2$ and (ACN) may form passivation layers on the surfaces of magnesium metal, with these layers potentially preventing the reversible stripping and depositing of magnesium in the magnesium metal electrode. Thus, such an electrolyte system was tested for two differenst symmetric cells, with the results illustrated in Figure 5b. Figure 5b illustrates the reversible stripping and depositing of magnesium in two cells using magnesium metal electrodes, both using an electrolyte of 0.5M $Mg(TFSI)_2$ in ACN. The cell using uncoated magnesium metal electrodes in an electrolyte of 0.5M $Mg(TFSI)_2$ in ACN failed to reversibly strip and deposit magnesium in the magnesium metal electrode because the conduction of magnesium ions into the magnesium metal electrode was in fact inhibited by the formation of a passivation layer on the magnesium metal electrode's surface. Contrary to the uncoated magnesium metal electrode, the coated magnesium metal electrode showed reversible magnesium ion stripping and depositing in the coated magnesium metal electrode, using the same electrolyte solution (0.5M $Mg(TFSI)_2$ in ACN), indicating that the surface of the magnesium metal did not form a passivation layer and continued to provide stable magnesium ion conduction through the coating, to and from the underlying magnesium metal surfaces. Thus, the protective and conductive nature of the coatings applied to the outside surfaces of the magnesium metal electrodes, enabled the use of an electrolyte of $Mg(TFSI)_2$ in ACN in a reversible magnesium metal battery system, whereas the same electrolyte was unsuccessful in battery systems utilizing uncoated magnesium metal electrodes due to the formation of a passivation layer(s) on the magnesium metal electrodes' surfaces.

Thus, in some embodiments described herein, reversible magnesium metal depositing and stripping may occur between the coating and the magnesium metal electrode, for example, on the outer surfaces of the magnesium metal electrode at the interface between the magnesium metal electrode and the coating (e.g. see reference numeral 300 of Figure 3).. By manipulating the coating composition and chemistry, coatings with suitable chemical stability, mechanical stability, and ionic conductivity may be developed to meet specific needs. Overall, this protective coating will have: 1) optimized mechanical properties; 2) the desired Mg-ion conductivity; and 3) chemical stability and compatibility in the magnesium ion-containing electrolytes.

In some cases, magnesium metal may be supplied in the form of a foil, ribbon, sheet, strip, particle, powder, and/or any other suitable form. When in the form of a foil, a magnesium metal foil may have a thickness between about 10 microns and about 1000 microns. In some cases a magnesium metal foil may have a thickness between about 80 and about 120 microns. When in the form of a particle and/or powder, a magnesium metal particle and/or powder having an average particle size between about 1 micron and about 100 microns. In other cases, a magnesium metal particle and/or powder may have an average particle size between about 30 micron and about 80 microns. In some cases, a magnesium metal powder may have particles that have a substantially irregular shape. In other cases, a magnesium metal powder may have particles with a substantially regular shape, including spherical, cylindrical, and/or any other suitable geometric shape.

Examples

The present disclosure relates to coatings applied to at least one surface of a magnesium metal electrode (e.g. anode and/or cathode) resulting in a coated magnesium metal electrode. The coatings are Mg^{2+}-conducting and enable the reversible depositing and stripping of magnesium in the magnesium metal electrode, as well as the reversible transport of magnesium ions through the coating itself, to and from the magnesium metal, and to and from the electrolyte. In addition, the coatings minimize and/or eliminate the reaction of magnesium present in the anode and/or cathode with the electrolyte present in the battery system, which enables the use of electrolyte solvents that are not ethereal-based and are more oxidation-resistant. Some embodiments demonstrated herein, include coated magnesium metal electrodes positioned in nitrile- and/or carbonate-based electrolytes containing magnesium salts (e.g. $Mg(TFSI)_2$ and/or $Mg(ClO_4)_2$), in both symmetric magnesium cells and magnesium batteries having a V_2O_5 cathode and a magnesium metal anode. Such examples demonstrate the viability of Mg^{2+}-conducting coatings and their viability as a solid-electrolyte-interface (SEI) on the surface of magnesium metal electrodes, which in turn, opens avenues for new magnesium electrolytes that may lead to high voltage (> 3.0 V) magnesium batteries.

In some embodiments of the present disclosure, a coating on a magnesium metal electrode may be constructed using a Mg^{2+}-conducting polymer such as a cPAN containing magnesium trifluoromethanesulfonate ($Mg(CF_3SO_3)_2$. For example, annealing PAN converts it to cPAN (see Panel e of Figure 11), which is a pyridine based conjugated polymer having excellent mechanical resiliency. Under high-resolution transmission electron microscopy (HRTEM), such a polymeric coating has a thickness of around 100 nm as shown in Panel a of Figure 6. Further microstructure observations were obtained using high angle annular dark field (HAADF, see Panel b of Figure 6) mode and energy dispersive spectroscopy (EDS, Panels c-h of Figure 6) mapping. HAADF shows the compositional difference between the coating and the magnesium metal particles as shown in weak contrast, while the latter maps the elemental distribution of carbon, nitrogen, magnesium, and fluorine, respectively, across the selected area of the coated magnesium metal electrode, which reflects the distribution of Mg^{2+} and $(CF_3SO_3)^-$ anions in the cPAN-matrix. EDS spectra of corresponding mapping area are also shown in Figure 7. The signal in Figure 7 clearly shows peaks matched with carbon, nitrogen, oxygen, fluorine, magnesium, and sulfur, respectively. Additional signals of copper are from the TEM sample holder and platinum is from the surface protective layer that is deposited during the focused ion beam (FIB) work. X-ray photoelectron spectroscopy (XPS) of N 1s domain in Figure 8 depicts the annealing-induced structural evolution of the polymeric coating. Cyanic group (N1, C≡N, at 400.4 eV) that was present in the pristine PAN (e.g. non-cyclic) matrix, prior to annealing, was found to gradually convert to the mixture of pyridinic group (N2, C-N=C, at 398.8 eV) and substitutional graphite group (N3, N coordinated with three C atoms, at 399.8 eV). Thus, as used herein, "annealing" refers to the thermal treatment of an electrode, magnesium, and/or coating, such that the electrode, magnesium, and/or coating are brought to an elevated temperature and maintained at that temperature for a period of time. Such an elastic polymeric component may accommodate the drastic volumetric changes during reversible depositing/stripping of magnesium. Figure 9 also compares reversible magnesium depositing/stripping performances of magnesium metal electrodes coated with cPAN versus magnesium metal electrodes coated with PAN. Panel a of Figure 9 illustrates reversible magnesium depositing/stripping using a 0.5M $Mg(TFSI)_2$ in PC electrolyte. Each half cycle was for a period of half an hour. A coated magnesium metal electrode having a cPAN Mg^{2+}-conducting coating improved cycle stability and showed stable reversible magnesium depositing/stripping up to 300 cycles, using the same electrolyte, relative to the magnesium metal electrode having a coating of non-cyclic PAN. A coated magnesium metal electrode having an uncylized Mg^{2+}-conducting coating showed an initial overpotential up to 0.8 V. A continuous increase of the overpotential up to 3.0 V was observed after 150 cycles of reversible magnesium depositing/stripping in the magnesium metal electrode. Panel b of Figure 9 illustrates the average magnesium depositing voltage versus cycle numbers for symmetric coated magnesium metal electrodes using 0.5M $Mg(TFSI)_2$ in PC electrolyte. The magnesium metal electrode having a cPAN Mg^{2+}-conducting coating demonstrated much lower average plating voltages during cycling than the uncoated magnesium metal electrode and magnesium metal electrodes having a non-cyclic PAN Mg^{2+}-conducting coating. Improved reversible magnesium depositing/stripping performances, with less overpotential build-up, emphasize the benefits attainable using cPAN.

The reversibility of magnesium depositing and stripping in a coated magnesium metal electrode was tested using a symmetric cell configuration consisting of two identical coated magnesium metal electrodes. Three electrolyte systems were tested, which include the highly corrosive Grignard electrolyte APC as reference, and two other electrolyte systems based on a stable magnesium salt (0.5M $Mg(TFSI)_2$ dissolved first in ACN and second in PC. The latter two electrolytes are non-corrosive (at least not corrodes metal current collectors such as aluminum, stainless steel) and highly oxidation-resistant (not oxidized at lower voltages < 3V vs Mg/Mg2+), but typically do not support reversible magnesium depositing and stripping in a magnesium metal electrode due to a reductive decomposition reaction on the magnesium metal surface(s). The magnesium depositing/stripping process was performed over half-hour or one-hour intervals with a cycling rate of 0.1 mA cm^{-2} and a voltage limit of 2 V for APC and ACN, or 3 V for PC system. Panel a of Figure 10 illustrates results for magnesium depositing and stripping in magnesium metal electrodes immersed in an APC electrolyte where each half cycle was for period of time of an hour. Panel b of Figure 10 illustrates results for magnesium depositing and stripping in magnesium metal electrodes immersed in 0.5M $Mg(TFSI)_2$ in ACN electrolyte, where each half cycle was for a period of time of half an hour. While the bare magnesium metal electrode system demonstrated a large over potential at the beginning and failed in 5 cycles, the system utilizing the coated magnesium metal electrodes demonstrated stable and reversible magnesium depositing and reversible magnesium stripping during all of the cycles of the test. Panel c of Figure 10 illustrates reversible magnesium depositing and reversible magnesium stripping in a magnesium metal electrode immersed in an electrolyte of 0.5M $Mg(TFSI)_2$ in PC, where each half cycle was performed for a period of time of half an hour. These data show that a Mg^{2+}-conducting coating on magnesium metal improves cycle stability with reversible magnesium depositing and stripping for up to at least about 300 cycles. Panel d of Figure 10 illustrates the average plating voltage versus cycle number for symmetric magnesium metal electrodes immersed in an electrolyte of 0.5M $Mg(TFSI)_2$ in PC. The coated magnesium metal electrode demonstrated a much lower average plating voltage than the uncoated magnesium metal electrode during cycling. This improved performance is attributed to the Mg^{2+}-conducting coating protecting the magnesium metal's surface from the electrolyte and preventing a passivation layer from forming.

Referring again to Panel a of Figure 10, reversible depositing/stripping of magnesium in the magnesium metal electrodes was observed in an APC electrolyte for both uncoated and coated magnesium metal electrodes. Slightly higher plating overpotential (~0.1 V) was observed for the coated magnesium metal electrodes, during the first 100 hours, as compared with the uncoated magnesium metal electrodes, probably due to a physical barrier on the coating (as described previously). The overpotential of the coated magnesium metal electrode gradually decreased to the same level as the uncoated magnesium metal electrode. Despite this difference, the APC electrolyte allowed reversible magnesium depositing/stripping, in the presence of a coating as well as in the absence of a coating. When the electrolyte was switched to 0.5M $Mg(TFSI)_2$ dissolved in either ACN or PC electrolytes, however, the uncoated magnesium metal electrode experienced an extremely high overpotential (> 1.0 V). Panel b of Figure 10 shows that the uncoated magnesium metal electrode failed in a nitrile-electrolyte after 5 hours, at which point the overpotential reached 2 V. Moreover, the coated magnesium metal electrode exhibited reversible depositing/stripping for more than 300 hours in the PC electrolyte, without a pronounced overpotential build-up during the extended cycles, as exhibited in Panel c of Figure 10. This observation agrees with the theory that reductive decomposition reactions occurred as a result of the nitrile or carbonate electrolytes, which produced a magnesium ion diffusion limiting layer on the magnesium metal surfaces.

Thus, for ACN and PC electrolytes, reversible magnesium depositing and stripping was only observed in magnesium metal electrodes having a polymeric coating. This is the first time that either nitrile- or carbonate-based electrolytes have been shown to support reversible magnesium depositing/stripping in a magnesium metal electrode. As shown in Panel d of Figure 10, the average plating voltage clearly reveals that the polymeric coating significantly reduced the magnesium metal electrode overpotentials, which enabled the reversible depositing/stripping of magnesium in the PC-based electrolyte, magnesium metal system. It appears that the polymeric coating successfully prevents the reductive magnesium surface from reacting with these solvents.

Further analysis of the structure of these polymeric coatings was conducted with time of flight secondary ion mass spectrometry (TOF-SIMS), which was collected from cPAN-based polymeric coatings with and without $Mg(CF_3SO_3)_2$, which are illustrated in Panels a-c of Figure 11. A conspicuous signal corresponding to positive ion Mg^+, which was generated by the interaction of Mg^{2+} with sputtering ions, appear at $m/z = 24$ only with cPAN with $Mg(CF_3SO_3)_2$, indicating that $Mg(CF_3SO_3)_2$ is the main source of Mg^+. Meanwhile, Mg^+ was still detected in cPAN containing no $Mg(CF_3SO_3)_2$ due to the magnesium metal underneath the polymeric coating (see Panel a of Figure 11). The negative ions $CF_3SO_3^-$ and $[Mg(CF_3SO_3)_3]^-$ are also most pronounced in intensity in the cPAN-$Mg(CF_3SO_3)_2$ coating. The above observations indicate that magnesium ions are multi-coordinated with $CF_3SO_3^-$ anions and the possible formation of a polymeric network of $CF_3SO_3^-$ and $[Mg(CF_3SO_3)_3]^-$ throughout the cPAN-$Mg(CF_3SO_3)_2$ coating. Therefore, it is speculated that structurally the polymeric coating may contain a cPAN matrix hybridized with a network of multi-coordinated Mg-($CF_3SO_3^-$) units, as illustrated in Panel e of Figure 11. This network facilitates the release of Mg^{2+} from a solvation cage and its diffusion through the coating. Thermogravimetric Analysis (TGA) (see Panel d of Figure 11 (4)) compares the thermal stabilities of $Mg(CF_3SO_3)_2$, PAN and PAN-$Mg(CF_3SO_3)_2$ coatings upon heating. While a PAN coating experienced an early and sluggish process of weight loss below 200 °C, the thermal decomposition of a $Mg(CF_3SO_3)_2$ coating showed a sudden onset at 400 °C, losing ~81 wt% of its original mass in a narrow range of 40 °C. A PAN-$Mg(CF_3SO_3)_2$ coating, however, illustrates a unique profile, probably indicating the existence of multi-coordinated Mg-($CF_3SO_3^-$) units in PAN-$Mg(CF_3SO_3)_2$ structure.

The ionic conductivity of a cPAN-$Mg(CF_3SO_3)_2$ coating was also measured by electrochemical impedance spectroscopy (EIS). The configuration of an example cell 400 is shown in Figure 12. The ionic conductivity of the Mg^{2+}-conducting coating 120 was measured using ion-blocking electrodes (430a and 430b) through electrochemical impedance spectroscopy. In this cell 400, a silver paste 410 was applied to provide intimate contact with the coating 120, and carbon paper was 420 used to avoid direct contact of the two stainless steel ion-blocking electrodes (430a and 430b). Panel a of Figure 13 illustrates a typical Nyquist plot along with its corresponding equivalent circuit, obtained for the exemplary cell illustrated in Figure 12. The Nyquist plot is composed of a semicircle, displaced by the quantity of the bulk resistance of the polymeric coating (R_b), whose impedance in a complex plane can be described as the combination of R_b, charge-transfer resistance (R_{ct}) and the Constant Phase Element (CPE). The ionic conductivity of the Mg^{2+}-conducting coating is then derived as:

$$\sigma = \frac{1}{Rb} \times \frac{l}{A} \quad (1)$$

where l is the thickness of the coating and A is the cross-sectional area of the cell. R_b was hence determined by the intercept of the semicircle with real axis of complex impedance plot. The average ionic conductivity of 1.19×10^{-6} S cm^{-1} was achieved according to results collected from three independent cells. The electronic conductivity was also detected due to the presence of conjugated sp2 C network formed in the cPAN. Note that the electronic conductivity is only about 1.04×10^{-7} S cm^{-1} as plotted in Panel b of Figure 13, which is 10 times less than ionic conductivity. Thus, the possibility of directly depositing onto the polymeric coating will be low. TEM images after deposition confirm that no magnesium deposition can be found on the outer surfaces of the polymeric coating, as indicated in Figure 14, which illustrates EDS line scanning results using a TEM (FEI Talos F200X). Panel a illustrates a HAADF TEM image of a Mg^{2+}-conducting coating on a magnesium metal electrode. Panel b illustrates EDS mapping results of carbon in the coating. Panel c illustrates EDS mapping results of magnesium in the coating. Panel d illustrates EDS mapping results of fluorine in the coating. Panel e illustrates EDS mapping results of nitrogen in the coating. Panel f illustrates EDS mapping results of sulfur in the coating. Panel g, HAADF TEM image of Mg^{2+}conducting coating with line scanning area with dashed line. Panel h illustrates EDS line scanning results for magnesium contained in the coating as a function of coating thickness.

These data show that negligible magnesium intensity was observed on the surface of coating and magnesium intensity began to increase in the Mg^{2+}-conducting coating. No evidence of magnesium plating on the surface of coating was observed from magnesium intensity variation in line scanning, which confirms the conduction of magnesium through the coating. To the best of our knowledge, this is the first ionic conductivity reported for a coated magnesium metal electrode coated with polymeric cPAN-$Mg(CF_3SO_3)_2$. It is comparable to the ion conductivities known for Li^+-polymer electrolytes. Considering that divalent ions are less mobile than their single-valent counterparts due to the much higher Coulombic drag, this ion conductivity is high. Combined with the mechanical strength, the ionically conductive polymeric coating ensures facile Mg^{2+} transport while accommodating the reversible depositing and stripping of magnesium in a magnesium metal electrode.

A complete cell was assembled to further prove the concept of a coated magnesium metal electrode using a Mg^{2+}-conducting coating. This cell's electrochemical performance results are illustrated in Figure 15. Panel a illustrates voltage profiles of cells constructed using an uncoated magnesium metal anode and a V_2O_5 cathode, and cells constructed using a coated magnesium metal anode and V_2O_5 cathode, for a voltage between 0.01 V and 3 V, and a current density of 29.4 mA g^{-1}. Voltage profiles of the 2nd, 10th, and 20th cycles are presented for both types of cells. The cells utilizing the uncoated magnesium metal anode and the V_2O_5 cathode demonstrated rapid capacity losses with cycling, while the cells utilizing the coated magnesium metal anode and the V_2O_5 cathode showed stable capacity retention with cycling. Panel b illustrates the CV profiles for the 2nd and 30th cycles of the uncoated Mg/V_2O_5 cell and coated Mg/V_2O_5 cell. The scan rate was 0.1 mV S^{-1}. Panel c illustrates a cycling performance comparison of the uncoated Mg/V_2O_5 cell, versus the coated Mg/V_2O_5 cell, both utilizing a 0.5M $Mg(TFSI)_2$ in PC electrolyte. The magnesium metal electrode having a Mg^{2+}-conducting coating dramatically improved the cell's cycling stability. Panel d illustrates XRD patterns of pristine V_2O_5 sample (that matches the standard structure of orthorhombic V_2O_5 based on Joint Committee on Power Diffraction Standards (JCPDS) card No. 41-1426), the Mg intercalated V_2O_5 sample (after intercalation of Mg ions into the V_2O_5) and the Mg deintercalated V_2O_5 sample (after deintercalation of Mg ions from the V_2O_5). The inset of Panel d magnifies peaks of (200) and (110) that shift to lower two theta degrees when intercalated and recover after deintercalation. Peaks newly appeared after intercalation are denoted as N and are diminished after deintercalation.

An orthorhombic V_2O_5 cathode, which can reversibly intercalate Mg^{2+}, was coupled with a magnesium metal anode with and without a coating, and the cells were galvanostatically cycled at a rate of 29.4mA g^{-1}. 0.5M $Mg(TFSI)_2$ in PC was used as the electrolyte. As displayed in Panels a and b of Figure 15, the cell made with a V_2O_5 cathode and a coated magnesium metal anode demonstrated significant improvement in terms of the operating voltage and discharge capacity. Thus, sustainable cycling performance was achieved in a carbonate-based electrolyte. In comparison, the cell made with a V_2O_5 cathode and an uncoated magnesium metal (e.g. in the absence of a coating) resulted in rapid capacity fading accompanied by a sharp rise in overpotential as shown in

Panel c of Figure 15. During the first discharg (magnesium intercalation into a V_2O_5 cathode), both cells delivered ~ 70 mAh g^{-1}, (71 mAh g^{-1} for the cell with an uncoated magnesium metal anode and 76 mAh g^{-1} for the cell with a coated magnesium metal anode), which corresponds to about ~ 0.24 moles of magnesium ions intercalated per mole of V_2O_5 cathode. The severe capacity decay observed in the cell with an uncoated magnesium metal anode was apparently caused by the formation of a passivation layer on the surface(s) of the uncoated magnesium metal anode, resulting in the inhibition of Mg^{2+} transfer and the reversible deposition of magnesium in the magnesium metal electrode. On the other hand, a sustainable cycling performance was obtained in the cell having a coated magnesium metal anode. XRD measurements provide structural evidence for the reversible intercalation/deintercalation chemistry of Mg^{2+} ion in the lattice of V_2O_5, where the main (200) and (110) peaks are shifted to the lower 2-θ values after initial intercalation of magnesium ions and recovered to their original positions after deintercalation releasing magnesium ions (see Panel d of Figure 15).

Figure 16 illustrates a battery 500 that includes an anode 510 and a cathode 520, with an electrolyte 130 positioned between the anode 510 and the cathode 520. In this embodiment, the battery 500 is a symmetric battery, where the anode 510 and the cathode 520 are substantially identical, with each having a current collector (140a and 140b), a coating (120a and 120b), with a magnesium metal (110a and 110b) foil positioned between the current collector (140a and 140b) and the coating (120a and 120b). Figure 16 also shows electrically connecting the cathode 520 to the anode 510 via a circuit 530. In the example shown in Figure 16, the battery is "charging". Thus, electrons are shown as flowing from the cathode 520 to the anode 510 and with Mg^{2+} ions flow from the cathode's magnesium layer 110b, through a separator positioned in the electrolyte 130, to the anode's magnesium layer 110a. The opposite occurs when "discharging" the battery: electrons flowing from the anode 510 to the cathode 520 and Mg^{2+} ions flow from the anode's magnesium layer 110a, through the separator positioned in the electrolyte 130, to the cathode's magnesium layer 110b.

Although Figure 16 illustrates a symmetric battery 500, other batteries may be envisioned, that utilize only one magnesium-containing electrode. For example, in some embodiments, the battery 500 may include a magnesium-containing anode 510 (as shown in Figure 16), however, include a non-magnesium-containing cathode. For example, in some embodiments a cathode may include at least one of V_2O_5, MoO_3, MnO_2, TiO_2,

TiS_2, and/or sulfur. A separator 540 may be constructed of glass, polypropylene, polyethylene, and/or any other suitable Mg^{2+}-permeable material. In some embodiments of the present disclosure, the electrolyte 130 positioned between the cathode 520 and the anode 510 may be a solid that is Mg^{2+}-permeable. For example, a solid electrolyte 130 may be constructed of at least one of polyacrylonitrile (PAN), a cyclized polyacrylonitrile (cPAN), a polyimide, a polyamide, a polystyrene, a polyethylene, a polyether, poly(3,4-ethylenedioxythiophene), a polypyrrole, a polythiophene, a polyaniline, a polyacetylene, a polyparaphenylene, a polyethylene oxide, and/or a polyethylene glycol. In such an embodiment, the solid electrolyte replaces the liquid electrolyte and is in physical contact with the magnesium metal 110a of the anode 510 and the magnesium metal 110b of the cathode 520. Alternatively, if the solid electrolyte is constructed of a material that is different than the material used to construct the coating 120a of the anode 510 and/or the material used to construct the coating 120b of the cathode 520, the solid electrolyte may be in physical contact with both coatings (120a and 120b). Such embodiments may be suitable for use in solid-state batteries, such as coin batteries.

Figure 17 illustrates a method for charging and/or discharging a symmetric magnesium metal-containing battery. The method 600 includes converting 610 elemental magnesium from a first magnesium metal-containing electrode to Mg^{2+} ions. The method 600 continues with transferring 620 the Mg^{2+} ions through a first coating positioned on the outside surface of the first magnesium metal-containing electrode. Next, the method 600 proceeds with transferring 630 the Mg^{2+} ions through an electrolyte. Next, the method 600 proceeds with transferring 640 the Mg^{2+} ions through a second coating positioned on a second magnesium metal-containing electrode. Finally, the method 600 concludes with converting 650 at least a portion of the transferred Mg^{2+} ions to elemental magnesium on the surface of the second magnesium metal-containing electrode. For example, if the steps described above were completed during charging of the battery, the reverse process would occur in a subsequent discharging step.

Fabrication of magnesium metal electrodes. Coated magnesium metal electrodes were constructed using magnesium powder (Alfa Aesar, -325 mesh), carbon black, PAN and $Mg(CF_3SO_3)_2$ in weight ratio of 77 % - 10 % - 10 % - 3%. Prepared mixture was dissolved in dimethylformamide (DMF) solution and then stirred for 5 hours. The achieved slurry was coated on stainless steel foil and then heat-treated at 300 °C for 1 hour under argon to convert the PAN to cPAN in the electrode. Bare magnesium metal electrodes were constructed of 80 % of magnesium, 10 % of carbon black (CB), and 10 % of polyvinylidene fluoride (PVDF) binder. A predetermined amount of N-methylpyrrolidone (NMP, Sigma Aldrich) was added and the resultant slurry was thoroughly mixed. An applicator was used to blade the slurry onto a stainless steel current collector, after which the slurry was heated to remove residual liquid. The processes for fabrication of magnesium metal electrodes were conducted in the glove box filled with argon.

Electrochemical test. Coin cells with 2032 type were used for cyclic voltammetry and galvanostatic cycling measurements. Biologic and Arbin were used for both cyclic voltammetry and galvanostatic cycling measurements.

Preparation of V_2O_5 electrode. A V_2O_5 cathode was prepared by using micro-sized particles, purchased from Aldrich. Three grams of V_2O_5 powders (Alfa Aesar) were ball-milled for 50 hours and then heat-treated at 650 °C for 5 minutes before mixing with the electrode additives. The V_2O_5 electrodes used here were comprised of 70 % of V_2O_5, 15 % of CB, and 15 % of PVDF binder.

Microstructure and XRD analysis. A FIB (FEI, NOVA200 dual beam system) was used for TEM sample preparation and Pt deposition was applied to protect the surface of desired observation area. The Pt deposition was applied with electron beam first to minimize the damage on the coating layer and then Pt deposition with Ga^+ ion was applied. Ga ion source was used for FIB sectioning. The microstructure of Mg^{2+}-conducting coating structure was investigated by analytical TEM (TECNAI F20 and FEI Talos F200X equipped with EDS) operating at 200 keV. XRD data for phase determination was collected with X-ray diffractometer (XRD, Rigaku DMax) with Cu-Kα radiation.

Secondary Ion Mass Spectrometry (SIMS) measurement. An ION-TOF TOF-SIMS V spectrometer was utilized to determine the composition of the specimens. Surface spectra were acquired utilizing a Bi^{3+} primary-ion beam (operated in bunched mode; 21 ns pulse width, analysis current 0.6 pA), scanned over a 50 x 50 μm area, utilizing a low energy electron flood gun for charge-compensation. A 150 μs cycle time was utilized, yielding mass spectra with a range of 1 to 2,000 amu. All spectra were collected at a primary ion dose density of $1x10^{12}$ ions cm^{-2} to remain under the static-SIMS limit.

XPS measurement. Samples were transferred without air exposure to an N_2 atmosphere glove box connected to the XPS system. XPS experiments were performed using a Physical Electronics (PHI) 5600 photoelectron spectrometer. Excitation was provided with a monochromatized Al anode (Kα radiation at 1486.6 eV) operating at 25 mA and 15 kV. Core level spectra were collected at analyzer pass energy of 11.75 eV. The XPS binding energies were calibrated by comparing centroid positions of clean Cu $2p_{3/2}$, Ag $3d_{5/2}$, and Au $4f_{7/2}$ from measured and accepted values. The spectra were fit and analyzed in Multipak software. No charging of the samples was observed.

TGA analysis. TGA was performed using a TA Instruments SDT Q600 Simultaneous TGA/DSC system. 5 mg of the sample was placed in a platinum crucible and then into the TGA/DSC for analysis. The sample was heated to 500 °C under nitrogen flow at a ramping rate of 1 °C per minute.

Conductivity measurement. The ionic conductivity of the Mg^{2+}-conducting coating was measured using ion-blocking electrodes through electrochemical impedance spectroscopy. To ensure good electrical contact a silver paste or a conductive carbon tape was first coated on top of the polymer. For the example illustrated in Figure 12, a Mg^{2+}-conducting coating 120 was applied to magnesium metal 110, which was sandwiched between two stainless steel disks, which performed as the ion blocking electrodes (100a and 100b). Silver paste 410 was used to enhance the electronic contact between the Mg^{2+}-conducting coating 120 and the first stainless steel electrode 100a. EIS was conducted on this set-up with AC amplitude of 50 mV and frequency of 10^6-0.01 Hz. The obtained results were plotted on a Nyquist diagram and the high frequency intercept with the real axis was used as the ionic resistance of the polymer electrolyte.

The foregoing disclosure has been set forth merely to illustrate the invention and is not intended to be limiting. Since modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed to include everything within the scope of the appended claims and equivalents thereof.

Example 1. A device that includes a first electrode, where the first electrode includes magnesium metal having a first surface, and a first coating in physical contact with the first surface and covering substantially all of the first surface, where the first coating has a first thickness, and the first coating is configured to transport a plurality of magnesium ions through the first thickness, such that a first portion of the plurality of magnesium ions are reversibly depositable as elemental magnesium onto the first surface.

Example 2. The device of Example 1, where the magnesium metal may be in the form of a particle, a film, a foil, a pellet, a cylinder, and/or a sphere.

Example 3. The device of Examples 1 or 2, where the first coating may include a first polymer.

Example 4. The device of Example 3, where the first polymer may include at least one of a polyacrylonitrile (PAN), a cyclized polyacrylonitrile (cPAN), a polyimide, a polyamide, a polystyrene, a polyethylene, a polyether, poly(3,4-ethylenedioxythiophene), a polypyrrole, a polythiophene, a polyaniline, a polyacetylene, a polyparaphenylene, a polyethylene oxide, and/or a polyethylene glycol.

Example 5. The device of Examples 3 or 4, where the first polymer may be cPAN.

Example 6. The device of any one of Examples 1-5, where the first coating may further include a magnesium-ion salt.

Example 7. The device of Example 6, where the magnesium-ion salt may include at least one of $MgClO_4$, $Mg(PF_6)_2$, $Mg(CF_3SO_3)_2$, $MgCO_3$, $Mg(BF4)_2$, $Mg(NO_3)_2$, and/or magnesium(II) bis(trifluoromethane sulfonyl) imide ($Mg(TFSI)_2$).

Example 8. The device of any one of Examples 1-7, where the first coating may have a thickness between about 1 nm and about 500 nm.

Example 9. The device of any one of Examples 1-8, where the device may further include an electrolyte, where the electrolyte may be in physical contact with the first coating.

Example 10. The device of Example 9, where the electrolyte may include at least one of a nitrile and/or a carbonate.

Example 11. The device of Example 10, where the electrolyte may include at least one of acetonitrile and/or propylene carbonate.

Example 12. The device of any one of Examples 9-11, where the electrolyte may further include a magnesium-ion salt.

Example 13. The device of Example 12, where the magnesium-ion salt may include at least one of $MgClO_4$, $Mg(PF_6)_2$, $Mg(CF_3SO_3)_2$, $MgCO_3$, $Mg(BF4)_2$, $Mg(NO_3)_2$, and/or magnesium(II) bis(trifluoromethane sulfonyl) imide ($Mg(TFSI)_2$).

Example 14. The device of any one of Examples 1-13, where the first portion may be between about 80% and about 100% of the plurality of magnesium ions.

Example 15. The device of any one of Examples 1-14, where the first electrode may further include a first current collector, the first current collector may be in contact with the magnesium metal, and the magnesium metal may be positioned between the first current collector and the first coating.

Example 16. The device of any one of Examples 9-15, where the device may further include a second electrode including V_2O_5, where a second portion of the plurality of magnesium ions may be reversibly intercalateable in the V_2O_5, and the second electrode may be in physical contact with the electrolyte.

Example 17. The device of any one of Examples 9-15, where the device may further include a second electrode including magnesium metal having a second surface, and a second coating in physical contact with the second surface and covering substantially all of the second surface, where the second coating has a second thickness, and the second coating may be configured to transport a third portion of the plurality of magnesium ions through the second thickness, such that a fourth portion of the plurality of magnesium ions may be reversibly depositable as elemental magnesium onto the second surface.

Example 18. The device of Example 17, where the magnesium metal of the second electrode may be in the form of a particle, a film, a foil, a pellet, a cylinder, and/or a sphere.

Example 19. The device of Examples 17 or 18, where the second coating may include a second polymer.

Example 20. The device of Example 19, where the second polymer may include at least one of a polyacrylonitrile (PAN), a cyclic polyacrylonitrile (cPAN), a polyimide, a polyamide, a polystyrene, a polyethylene, a polyether, poly(3,4-ethylenedioxythiophene), a polypyrrole, a polythiophene, a polyaniline, a polyacetylene, a polyparaphenylene, a polyethylene oxide, and/or a polyethylene glycol.

Example 21. The device of Examples 19 or 20, where the second polymer may include cPAN.

Example 22. The device of any one of Examples 17-21, where the second coating may include a magnesium-ion salt.

Example 23. The device of Example 22, where the magnesium-ion salt of the second coating may include at least one of $MgClO_4$, $Mg(PF_6)_2$, $Mg(CF_3SO_3)_2$, $MgCO_3$, and/or magnesium(II) bis(trifluoromethane sulfonyl) imide ($Mg(TFSI)_2$).

Example 24. The device of any one of Examples 17-23, where the second coating may have a thickness between about 1 nm and about 500 nm.

Example 25. The device of any one of Examples 17-24, where the electrolyte may be in physical contact with the second coating.

Example 26. The device of any one of Examples 17-25, where the electrolyte may include at least one of a nitrile and/or a carbonate.

Example 27. The device of any one of Examples 17-26, where the fourth portion may be between about 80% and about 100% of the plurality of magnesium ions.

Example 28. The device of Example 17, where the electrolyte may include a third polymer, and the third polymer may be in physical contact with the first coating and the second coating.

Example 29. The device of any one of Examples 17-28, where the second electrode may further include a second current collector, the second current collector may be in contact with the magnesium metal of the second electrode, and the magnesium metal of the second electrode may be positioned between the second current collector and the second coating.

Example 30. An electrode including magnesium metal including a surface, and a coating in physical contact with the surface and covering substantially all of the surface, where the coating has a thickness, and the coating is configured to transport a plurality of magnesium ions through the thickness, such that a portion of the plurality of magnesium ions are reversibly depositable as elemental magnesium onto the surface.

Example 31. The electrode of Example 30, where the magnesium metal may be in the form of a particle, a film, a foil, a pellet, a cylinder, and/or a sphere.

Example 32. The electrode of Example 30 or 31, where the coating may include a polymer.

Example 33. The electrode of claim 32, where the polymer may include at least one of a polyacrylonitrile (PAN), a cyclized polyacrylonitrile (cPAN), a polyimide, a polyamide, a polystyrene, a polyethylene, a polyether, poly(3,4-ethylenedioxythiophene), a polypyrrole, a polythiophene, a polyaniline, a polyacetylene, a polyparaphenylene, a polyethylene oxide, and/or a polyethylene glycol.

Example 34. The electrode of Examples 32 or 33, where the polymer may be cPAN.

Example 35. The electrode of any one of Examples 31- 33, where the polymer may further include a magnesium-ion salt.

Example 36. The device of Example 35, where the magnesium-ion salt may include at least one of $MgClO_4$, $Mg(PF_6)_2$, $Mg(CF_3SO_3)_2$, $MgCO_3$, $Mg(BF4)_2$, $Mg(NO_3)_2$, and/or magnesium(II) bis(trifluoromethane sulfonyl) imide ($Mg(TFSI)_2$).

Example 37. The electrode of any one of Examples 30-36, where the coating may have a thickness between about 1 nm and about 500 nm.

Example 38. A method for charging and discharging a battery, the method including, in a first electrode having a magnesium metal, converting a first portion of the first magnesium metal to a first plurality of Mg^{2+} ions, transferring a first portion of the first plurality of Mg^{2+} ions through a first coating substantially covering the magnesium metal, transferring the first portion of the first plurality of Mg^{2+} ions through an electrolyte in physical contact with the first coating, transferring first portion of the first plurality of Mg^{2+} ions through a second coating substantially covering a magnesium metal of a second electrode, and converting the first portion of the first plurality of Mg^{2+} ions to elemental magnesium on the magnesium metal of the second electrode, where the second coating is in physical contact with the electrolyte.

Example 39. The method of Example 38, further including converting the elemental magnesium on the magnesium metal of the second electrode to a second plurality of Mg^{2+} ions, transferring the second plurality of Mg^{2+} ions through the second coating, transferring the second plurality of Mg^{2+} ions through the electrolyte, transferring second plurality of Mg^{2+} ions through the first coating, converting the second plurality of Mg^{2+}

ions to elemental magnesium on the magnesium metal of the first electrode.

CLAIMS

What is claimed is:

1. A device comprising:

a first electrode comprising:

magnesium metal comprising a first surface; and

a first coating in physical contact with the first surface and covering substantially all of the first surface, wherein:

the first coating has a first thickness, and

the first coating is configured to transport a plurality of magnesium ions through the first thickness, such that a first portion of the plurality of magnesium ions are reversibly depositable as elemental magnesium onto the first surface.

2. The device of claim 1, wherein the magnesium metal is in the form of a particle, a film, a foil, a pellet, a cylinder, or a sphere.

3. The device of claim 1, wherein the first coating comprises a first polymer.

4. The device of claim 3, wherein the first polymer comprises at least one of a polyacrylonitrile (PAN), a cyclized polyacrylonitrile (cPAN), a polyimide, a polyamide, a polystyrene, a polyethylene, a polyether, poly(3,4-ethylenedioxythiophene), a polypyrrole, a polythiophene, a polyaniline, a polyacetylene, a polyparaphenylene, a polyethylene oxide, or a polyethylene glycol.

5. The device of claim 4, wherein the first polymer is cPAN.

6. The device of claim 3, wherein the first coating further comprises a magnesium-ion salt.

7. The device of claim 6, wherein the magnesium-ion salt comprises at least one of $MgClO_4$, $Mg(PF_6)_2$, $Mg(CF_3SO_3)_2$, $MgCO_3$, $Mg(BF4)_2$, $Mg(NO_3)_2$, or magnesium(II) bis(trifluoromethane sulfonyl) imide ($Mg(TFSI)_2$).

8. The device of claim 1, wherein the first coating has a thickness between about 1 nm and about 500 nm.

9. The device of claim 1, further comprising an electrolyte, wherein the electrolyte is in physical contact with the first coating.

10. The device of claim 9, wherein the electrolyte comprises at least one of a nitrile or a carbonate.

11. The device of claim 10, wherein the electrolyte comprises at least one of acetonitrile or propylene carbonate.

12. The device of claim 9, wherein the electrolyte further comprises a magnesium-ion salt.

13. The device of claim 12, wherein the magnesium-ion salt comprises at least one of $MgClO_4$, $Mg(PF_6)_2$, $Mg(CF_3SO_3)_2$, $MgCO_3$, $Mg(BF4)_2$, $Mg(NO_3)_2$, or magnesium(II) bis(trifluoromethane sulfonyl) imide ($Mg(TFSI)_2$).

14. The device of claim 1, wherein the first portion is between about 80% and about 100% of the plurality of magnesium ions.

15. The device of claim 1, wherein:

the first electrode further comprises a first current collector,

the first current collector is in contact with the magnesium metal, and

the magnesium metal is positioned between the first current collector and the first coating.

16. The device of claim 9, further comprising:

a second electrode comprising V_2O_5, wherein:

a second portion of the plurality of magnesium ions are reversibly intercalateable in the V_2O_5, and

the second electrode is in physical contact with the electrolyte.

17. The device of claim 9, further comprising:

a second electrode comprising:

magnesium metal comprising a second surface; and

a second coating in physical contact with the second surface and covering substantially all of the second surface, wherein:

the second coating has a second thickness, and the second coating is configured to transport a third portion of the plurality of magnesium ions through the second thickness, such that a fourth portion of the plurality of magnesium ions are reversibly depositable as elemental magnesium onto the second surface.

18. An electrode comprising:

magnesium metal comprising a surface; and

a coating in physical contact with the surface and covering substantially all of the surface, wherein:

the coating has a thickness, and

the coating is configured to transport a plurality of magnesium ions through the thickness, such that a portion of the plurality of magnesium ions are reversibly depositable as elemental magnesium onto the surface.

19. A method for charging and discharging a battery, the method comprising:

in a first electrode comprising a magnesium metal, converting a first portion of the first magnesium metal to a first plurality of Mg^{2+} ions;

transferring a first portion of the first plurality of Mg^{2+} ions through a first coating substantially covering the magnesium metal;

transferring the first portion of the first plurality of Mg^{2+} ions through an electrolyte in physical contact with the first coating;

transferring first portion of the first plurality of Mg^{2+} ions through a second coating substantially covering a magnesium metal of a second electrode; and

converting the first portion of the first plurality of Mg^{2+} ions to elemental magnesium on the magnesium metal of the second electrode, wherein:

the second coating is in physical contact with the electrolyte.

20. The method of claim 19, further comprising:

converting the elemental magnesium on the magnesium metal of the second electrode to a second plurality of Mg^{2+} ions;

transferring the second plurality of Mg^{2+} ions through the second coating;

transferring the second plurality of Mg^{2+} ions through the electrolyte;

transferring second plurality of Mg^{2+} ions through the first coating;

converting the second plurality of Mg^{2+} ions to elemental magnesium on the magnesium metal of the first electrode.

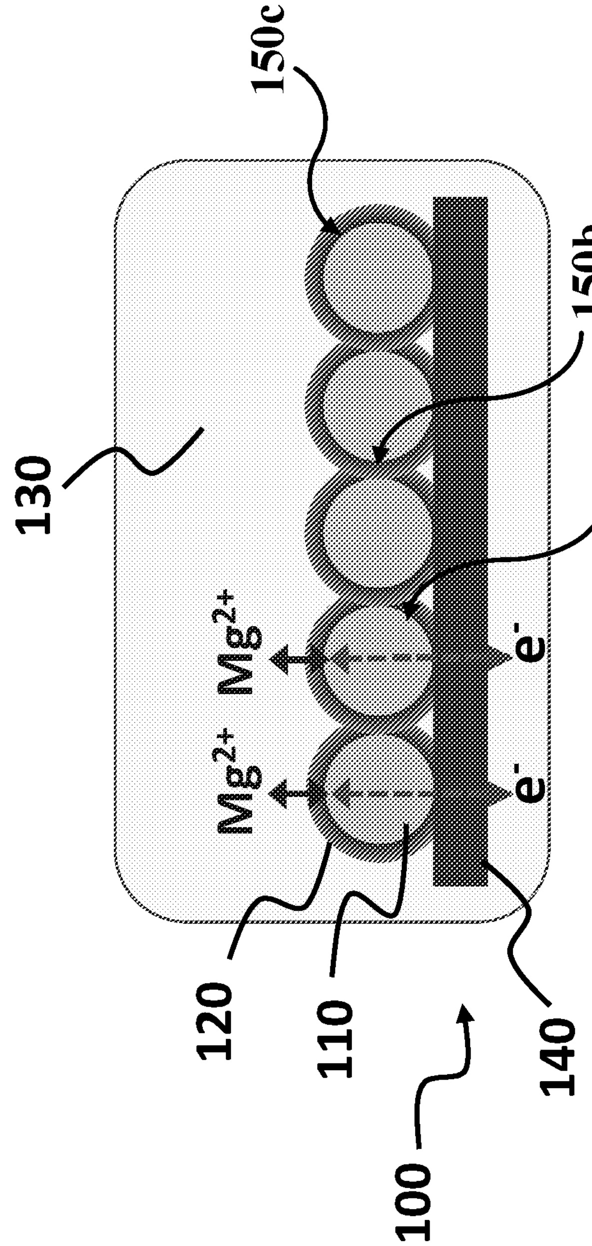

Figure 1a

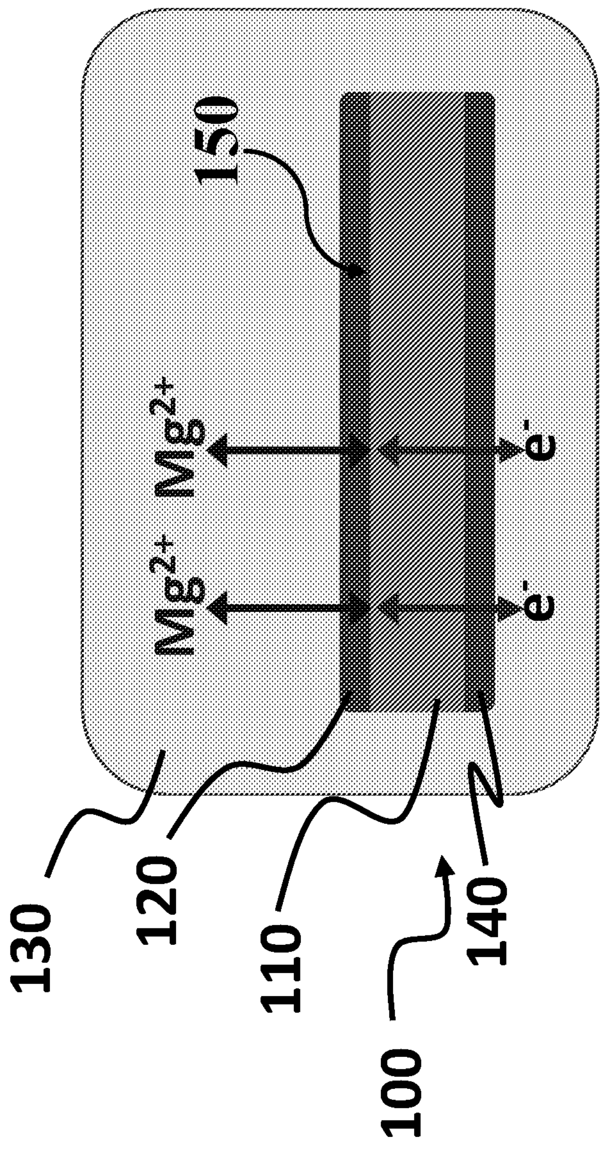

Figure 1b

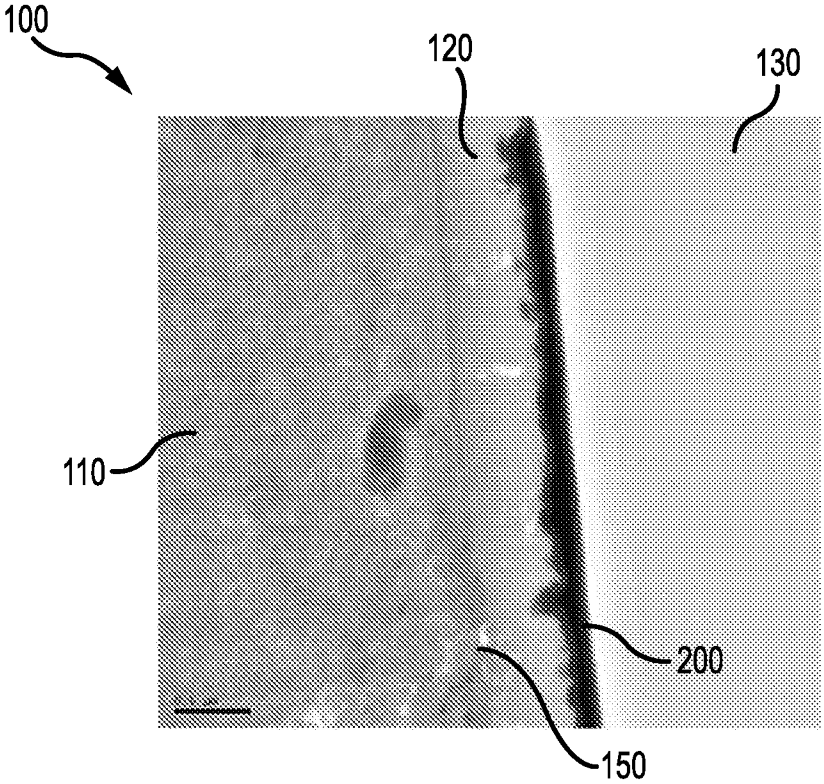

FIG.2a

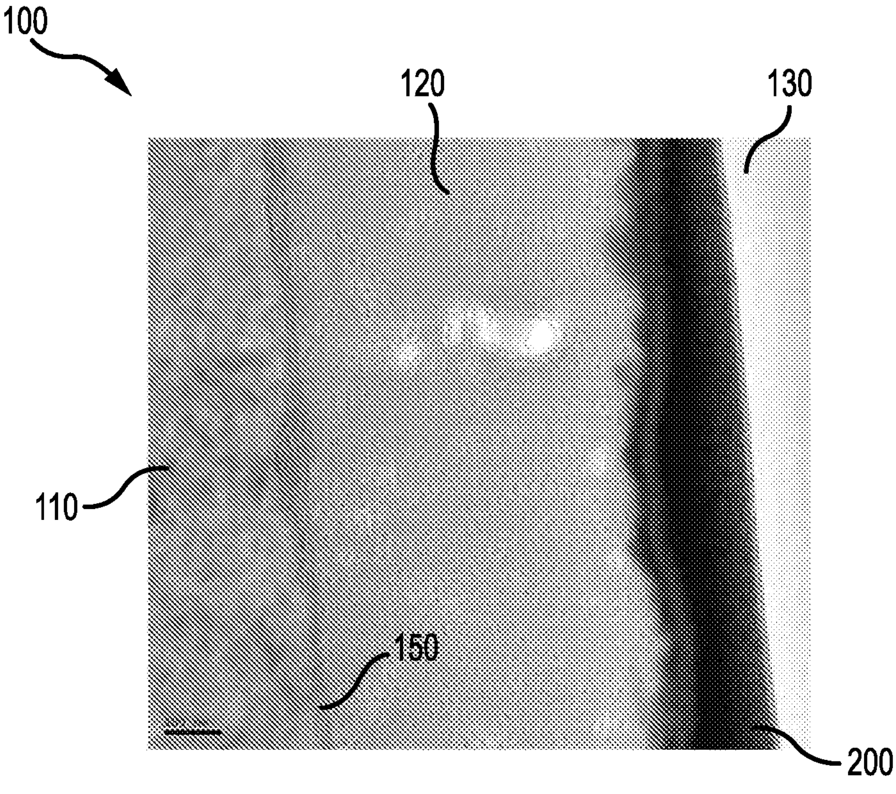

FIG.2b

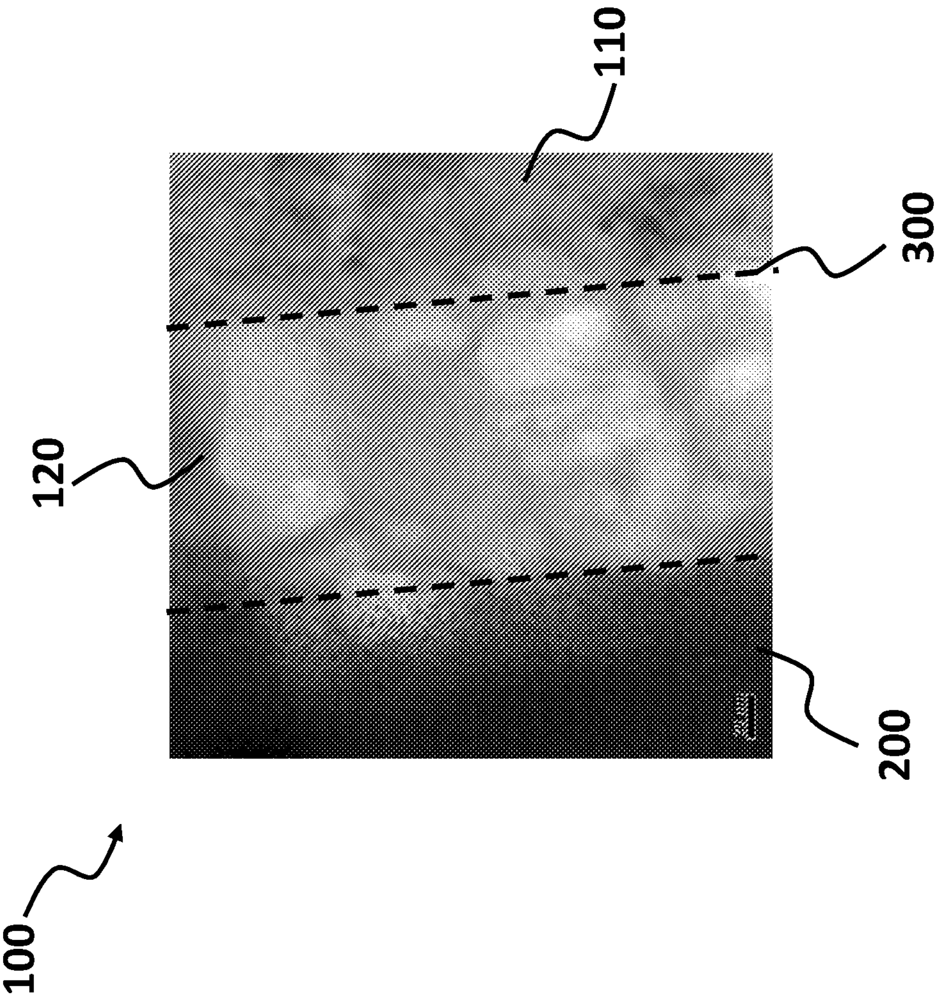

Figure 3

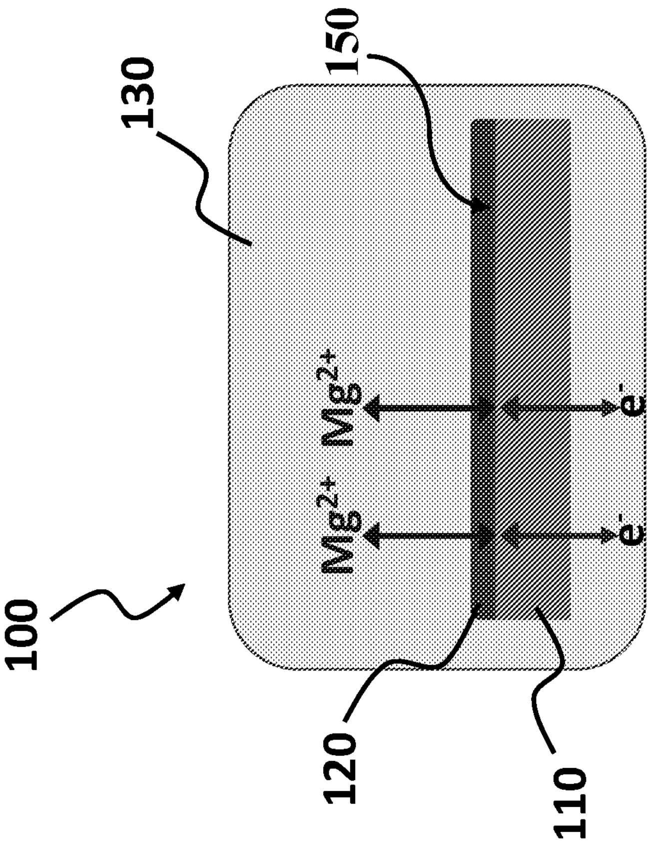

Figure 4

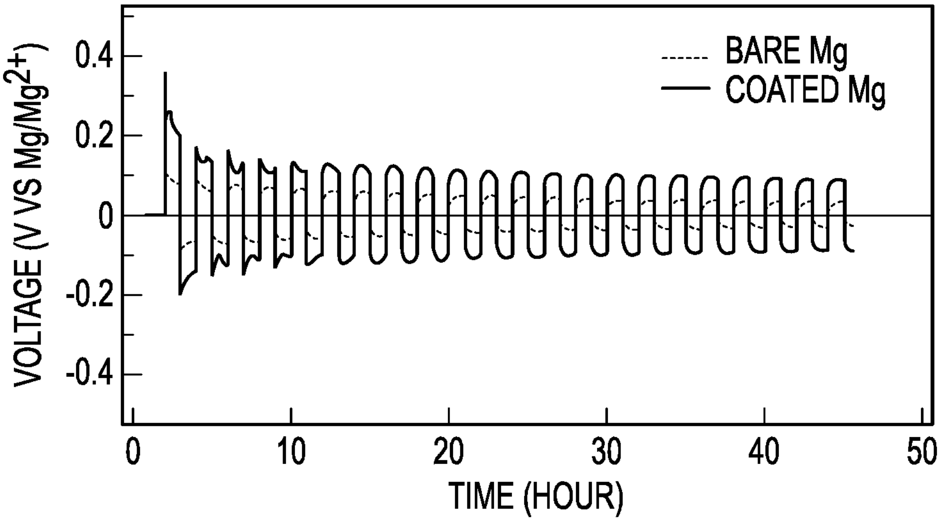
BARE Mg
COATED Mg
VOLTAGE (V VS Mg/Mg2+)
0.4
0.2
0
-0.2
-0.4
0
10
20
30
40
50
TIME (HOUR)

FIG.5a

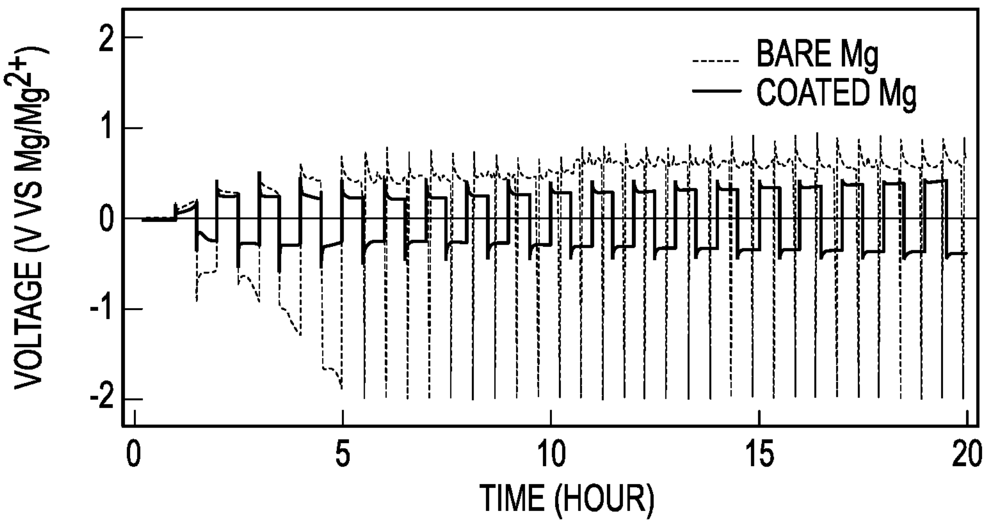
BARE Mg
COATED Mg
VOLTAGE (V VS Mg/Mg2+)
2
1
0
-1
-2
0
5
10
15
20
TIME (HOUR)

FIG.5b

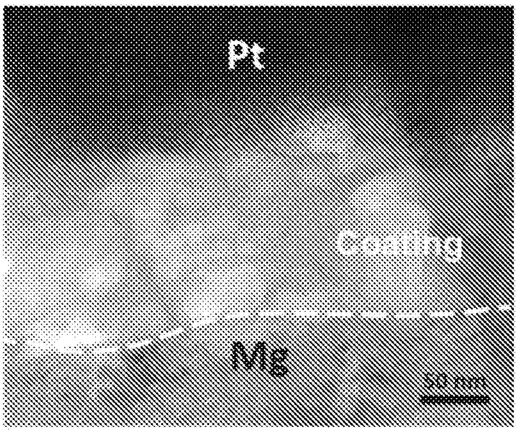

FIG.6a

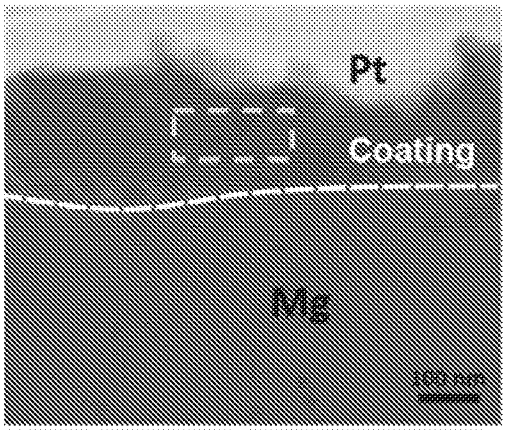

FIG.6b

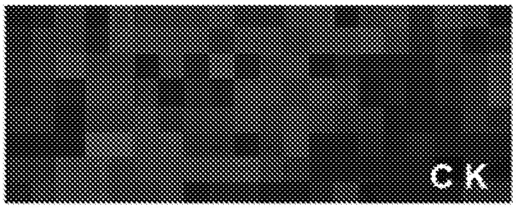

FIG.6c

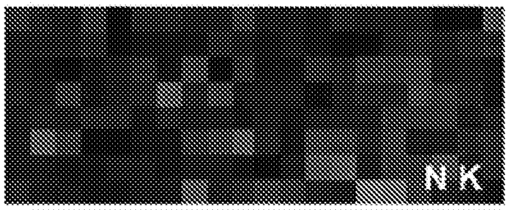

FIG.6d

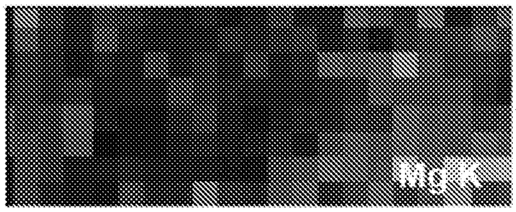

FIG.6e

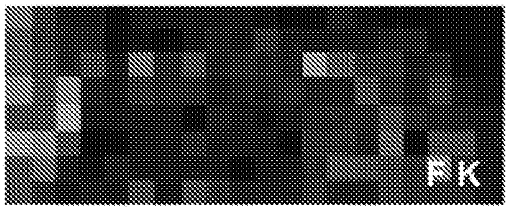

FIG.6f

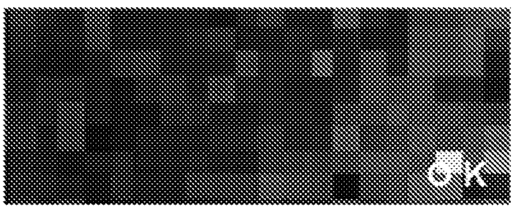

FIG.6g

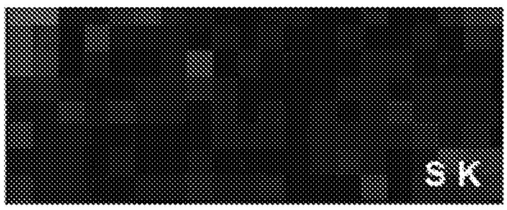

FIG.6h

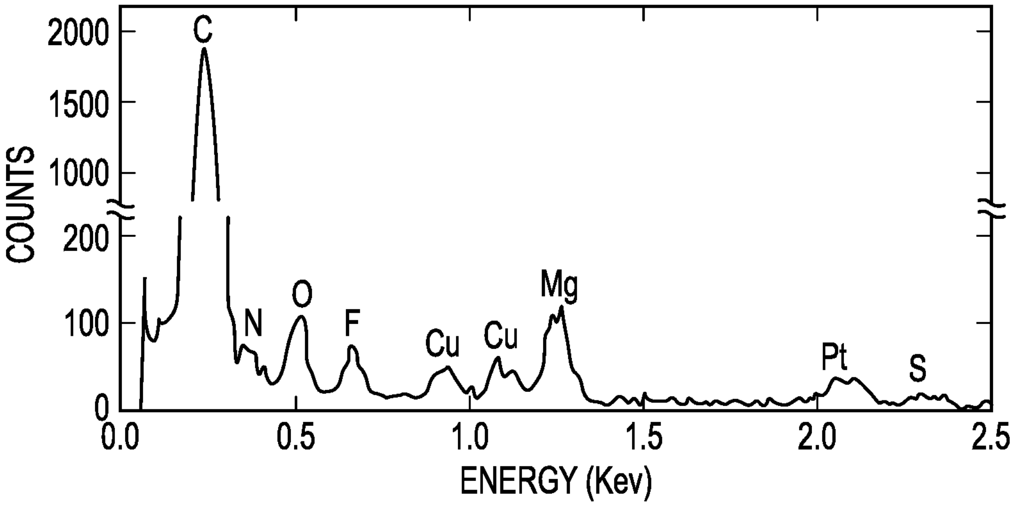
C
N
O
F
Cu
Cu
Mg
Pt
S
COUNTS
2000
1500
1000
200
100
0
0.0
0.5
1.0
1.5
2.0
2.5
ENERGY (Kev)

FIG.7

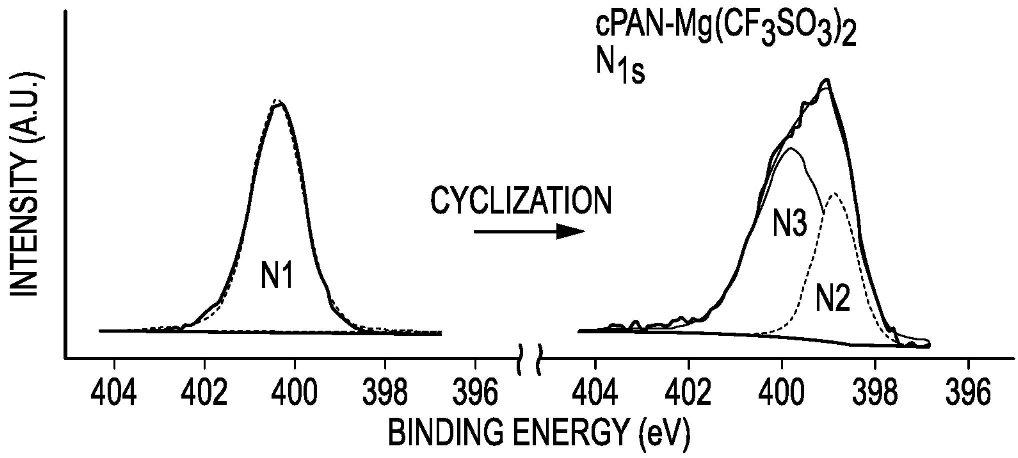
cPAN-Mg(CF3SO3)2
N1s
INTENSITY (A.U.)
N1
CYCLIZATION
N3
N2
404
402
400
398
396
404
402
400
398
396
BINDING ENERGY (eV)

FIG.8

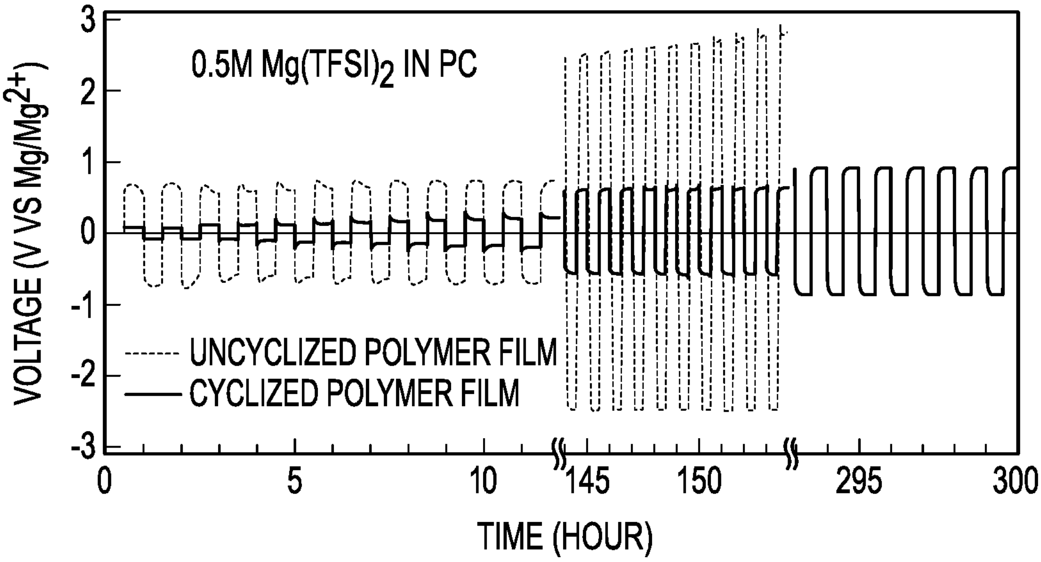
0.5M Mg(TFSI)2 IN PC
VOLTAGE (V VS Mg/Mg2+)
UNCYCLIZED POLYMER FILM
CYCLIZED POLYMER FILM
TIME (HOUR)
3
2
1
0
-1
-2
-3
0
5
10
145
150
295
300

FIG.9a

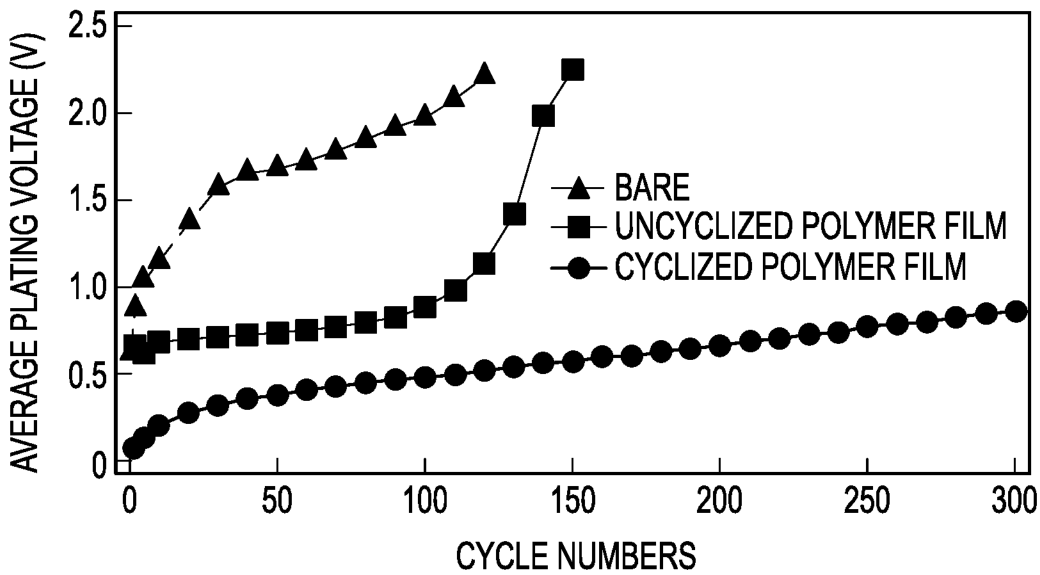
AVERAGE PLATING VOLTAGE (V)
BARE
UNCYCLIZED POLYMER FILM
CYCLIZED POLYMER FILM
CYCLE NUMBERS
2.5
2.0
1.5
1.0
0.5
0
0
50
100
150
200
250
300

FIG.9b

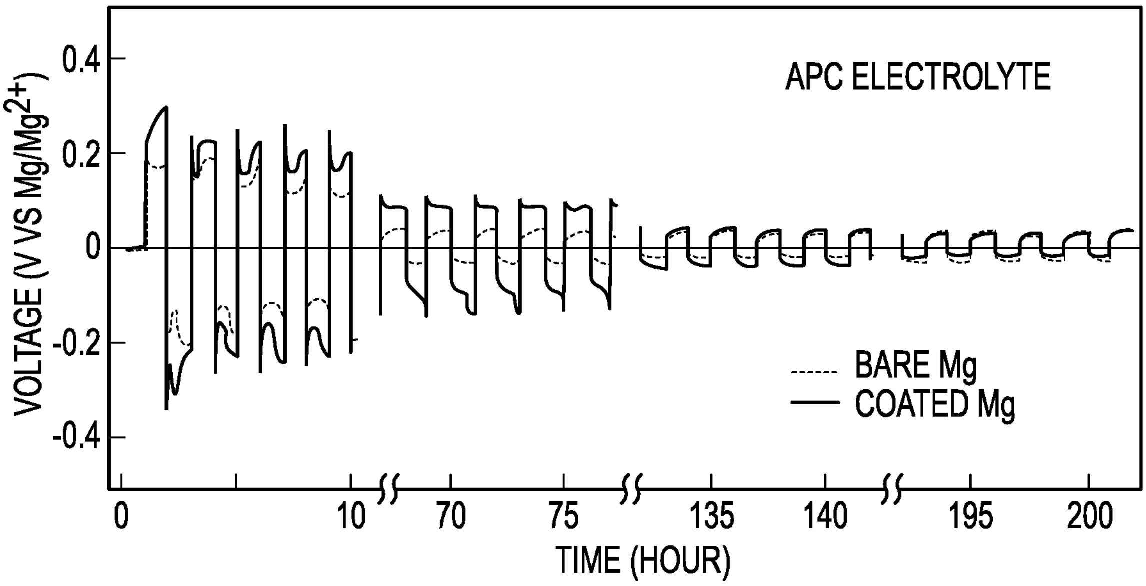

FIG.10a

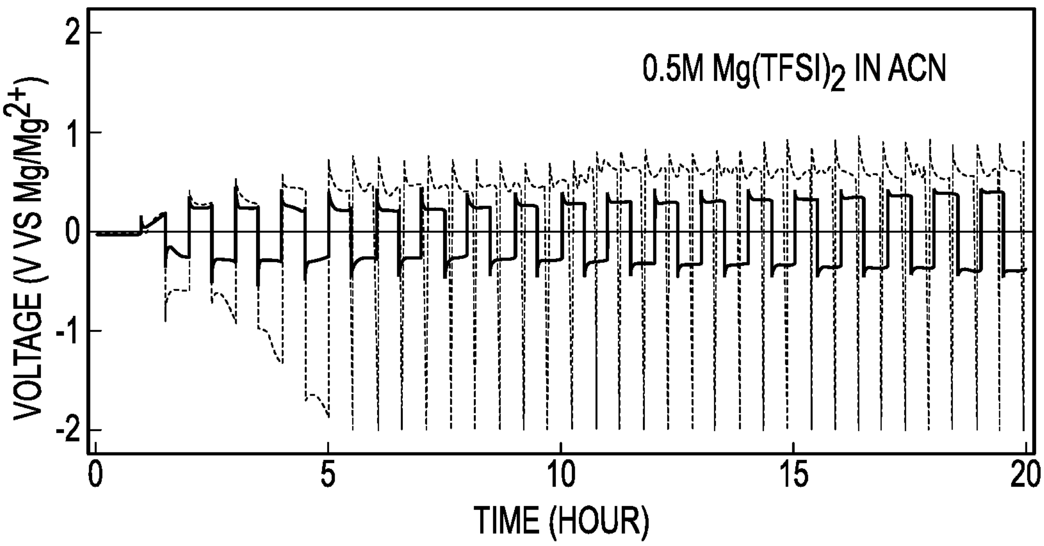

FIG.10b

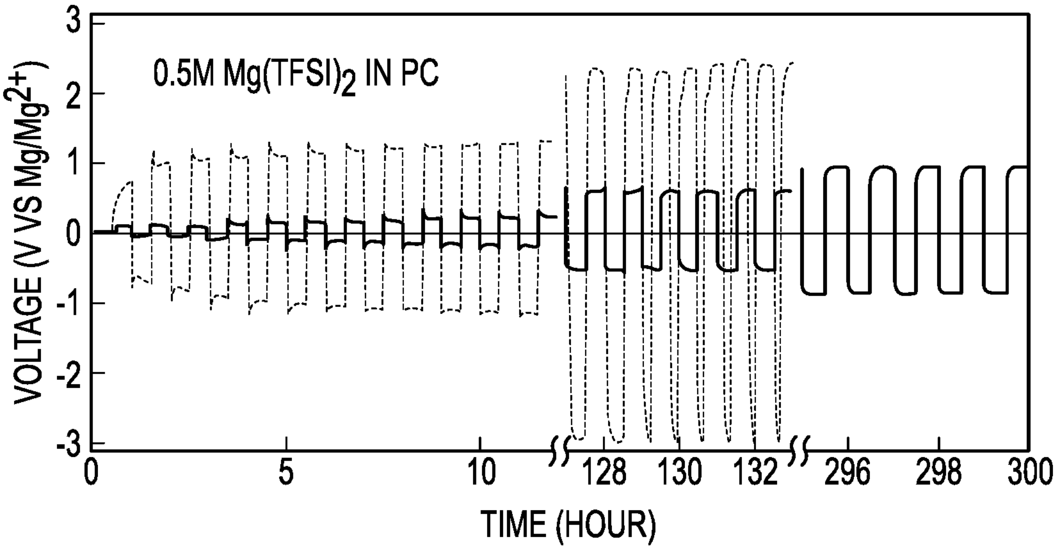

FIG.10c

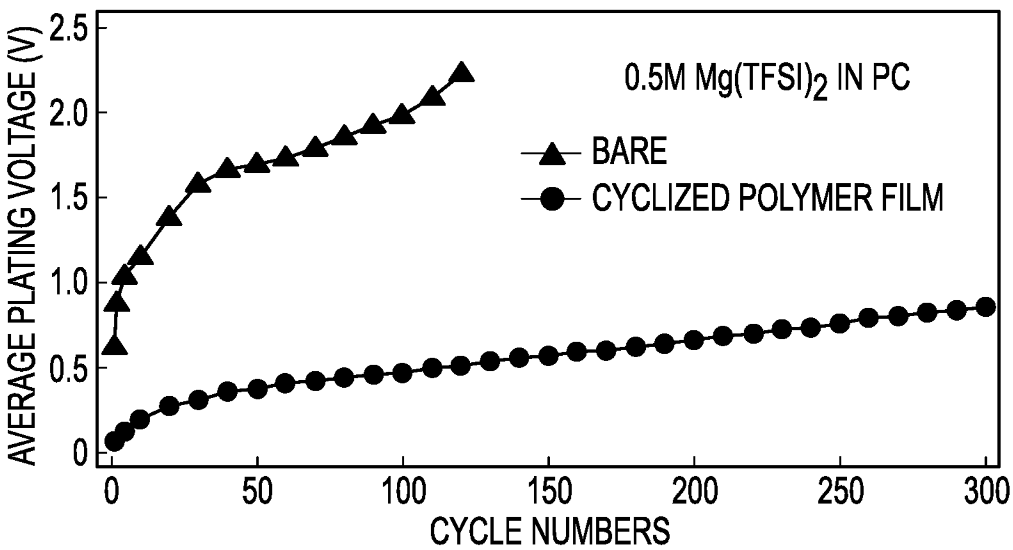

FIG.10d

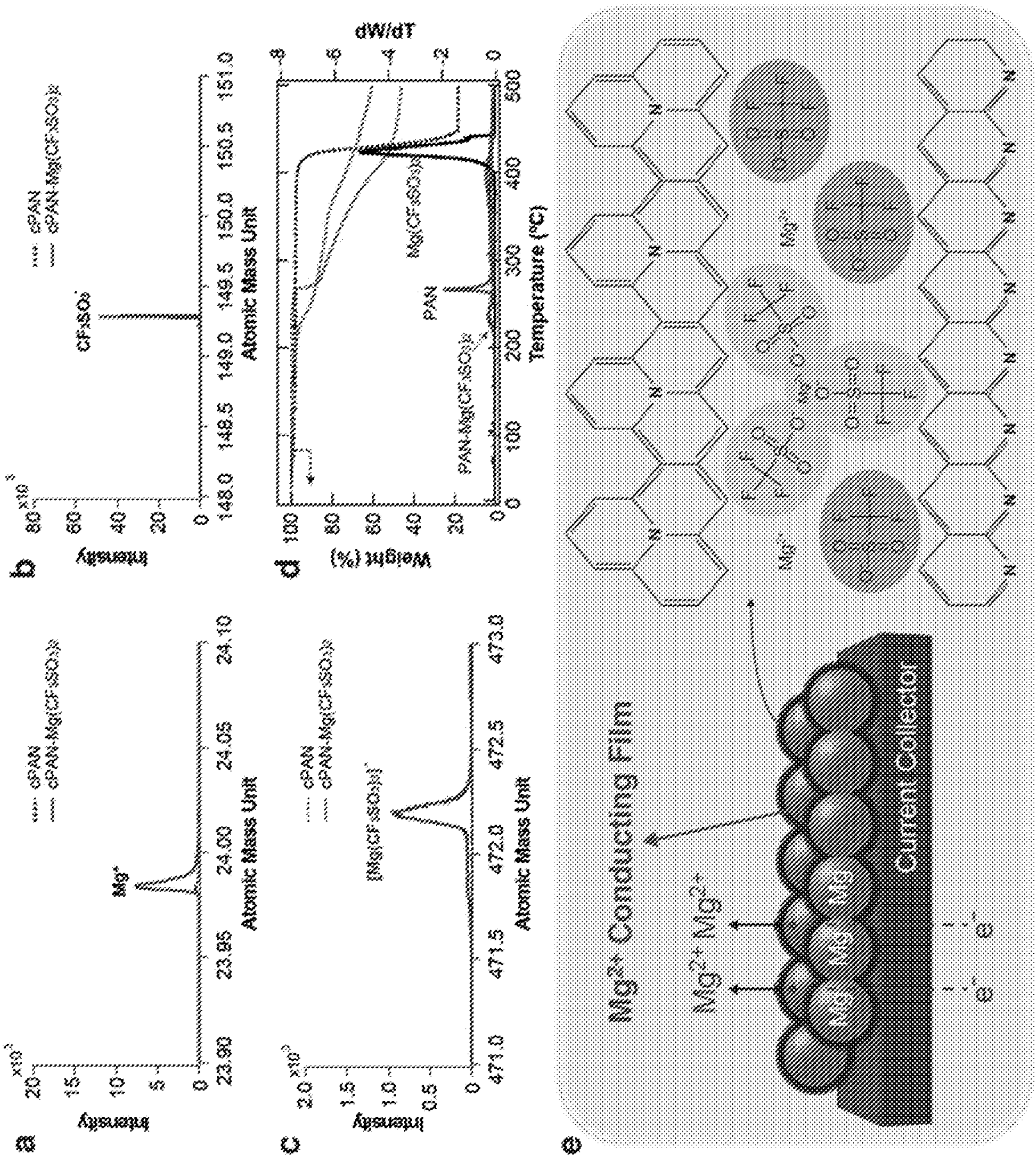
a
Intensity
Mg+
cPAN
cPAN-Mg(CF3SO3)2
Atomic Mass Unit
b
CF3SO3-
c
[Mg(CF3SO3)2]+
d
Weight (%)
dW/dT
PAN
Mg(CF3SO3)2
PAN-Mg(CF3SO3)2
Temperature (°C)
e
Mg2+ Conducting Film
Mg2+ Mg2+
Mg
Current Collector
e- e-

Figure 11

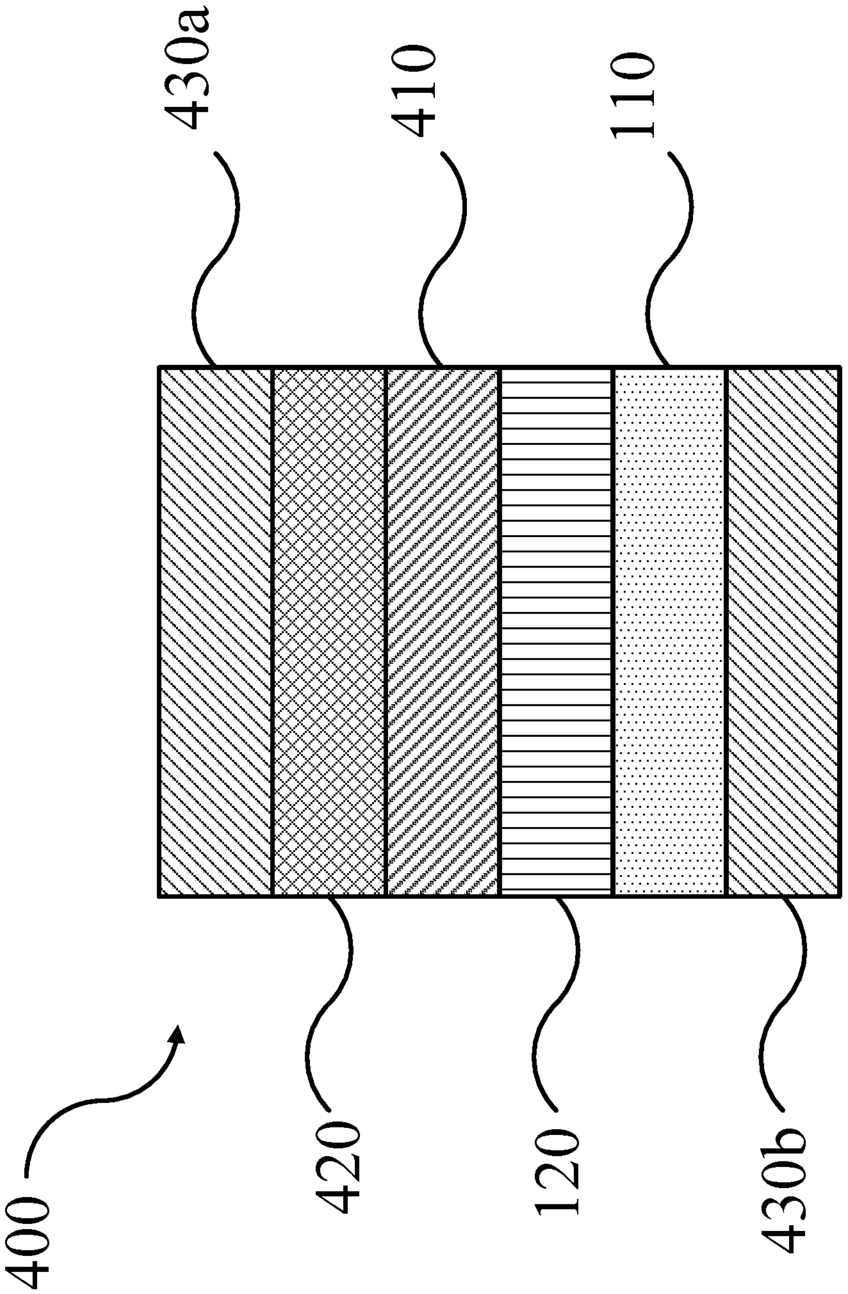

Figure 12

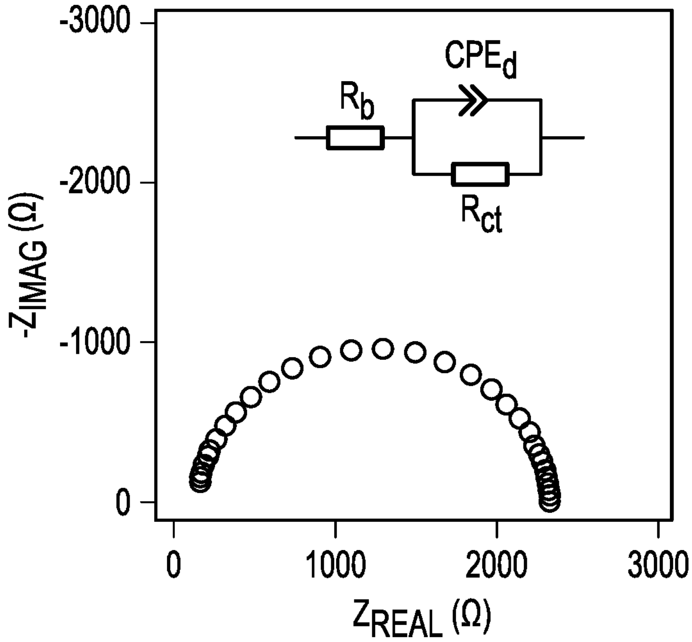

FIG.13a

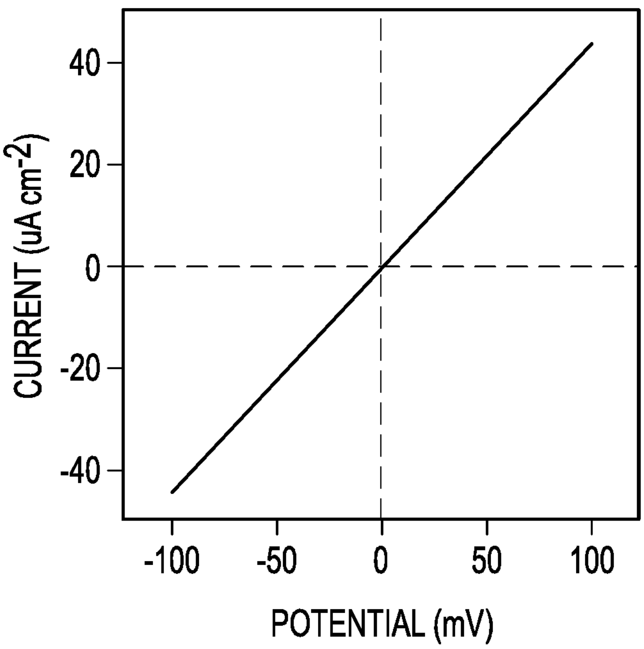

FIG.13b

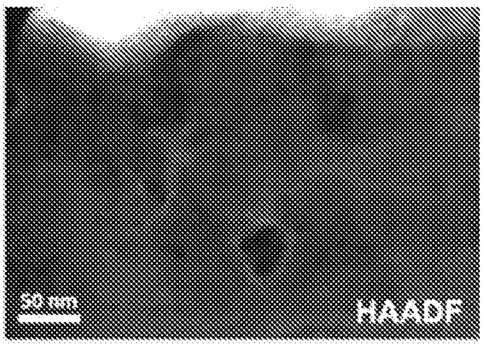

FIG.14a

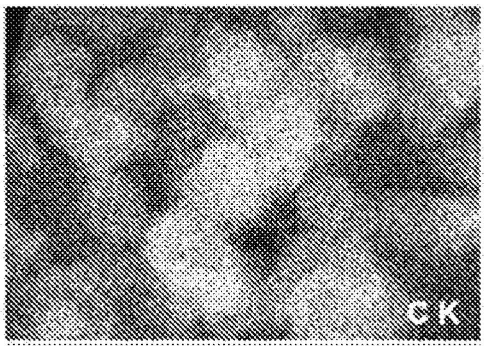

FIG.14b

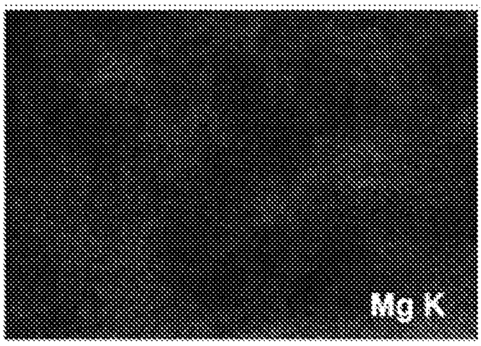

FIG.14c

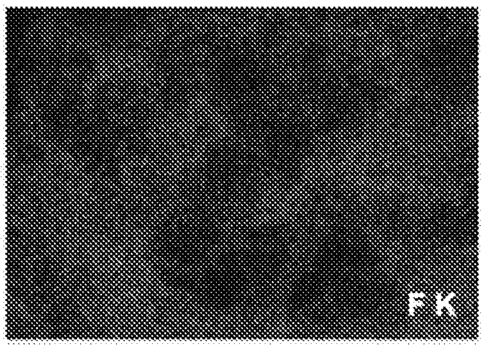

FIG.14d

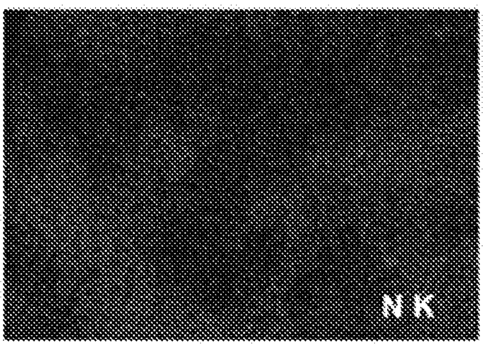

FIG.14e

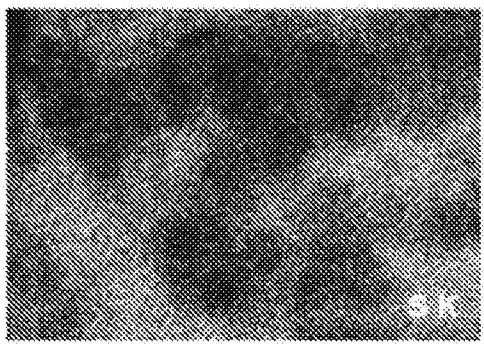

FIG.14f

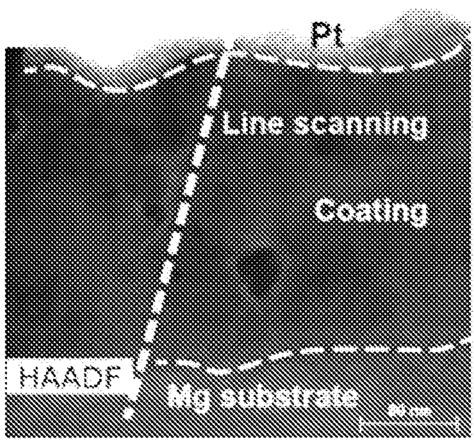

FIG.14g

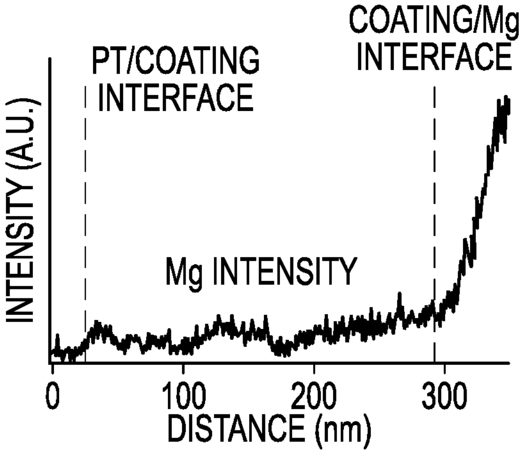

FIG.14h

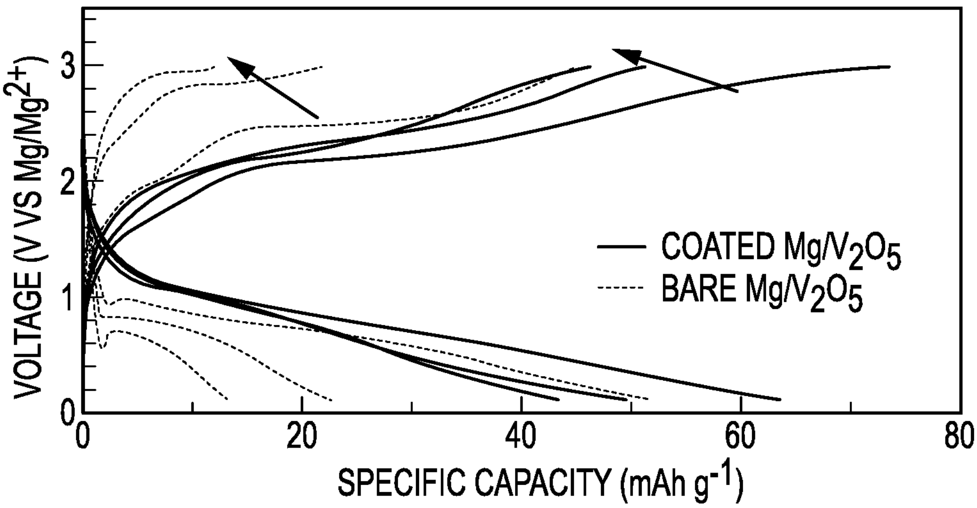

FIG.15a

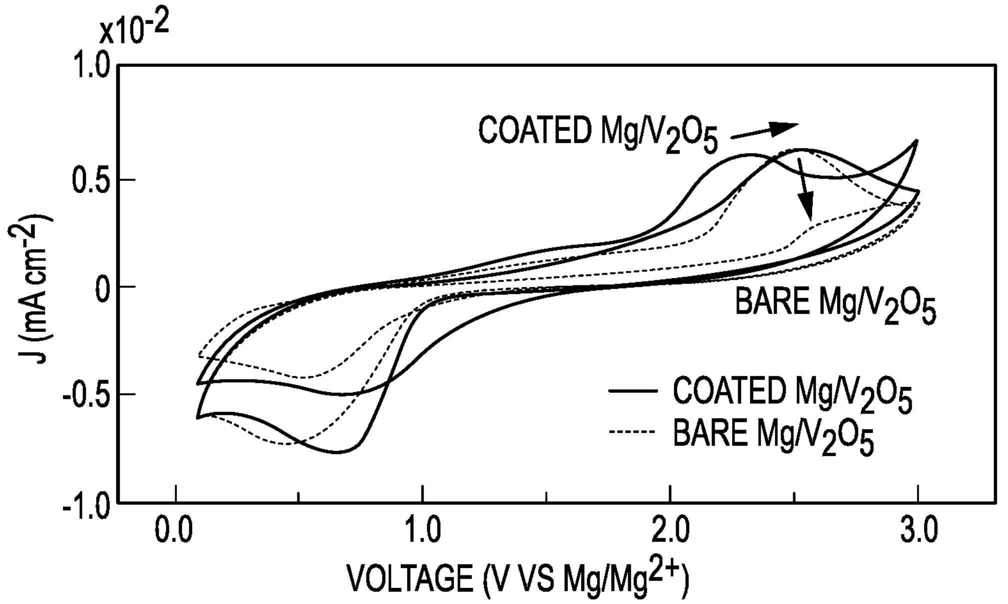

FIG.15b

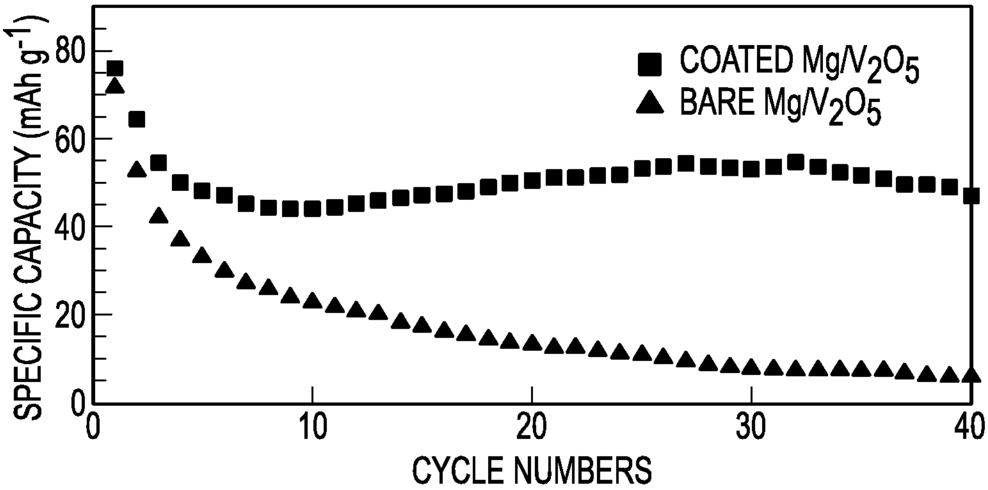

FIG.15c

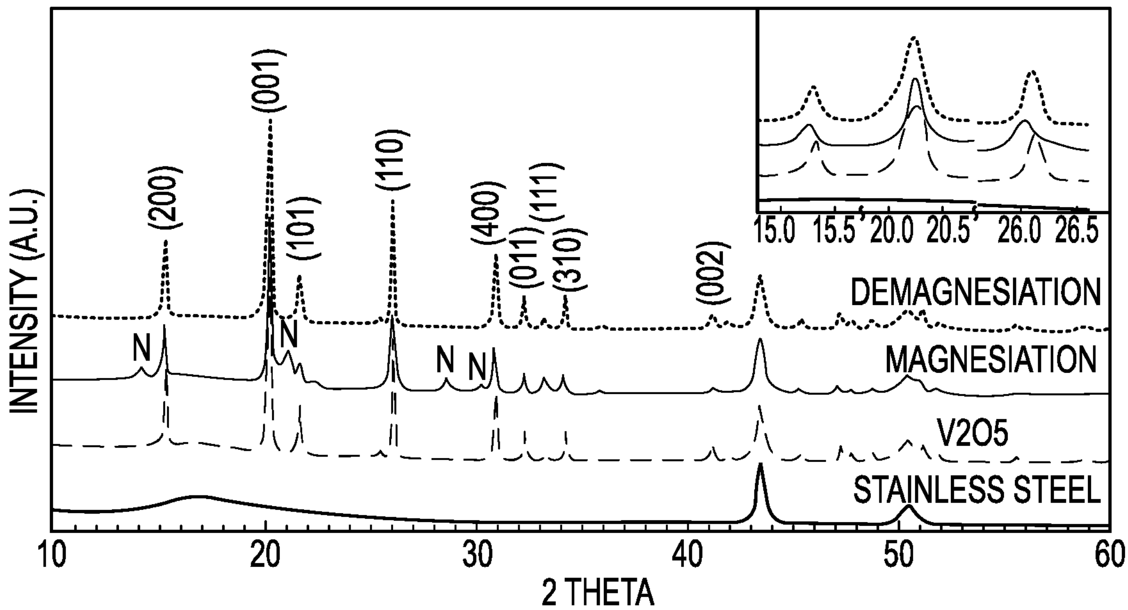

FIG.15d

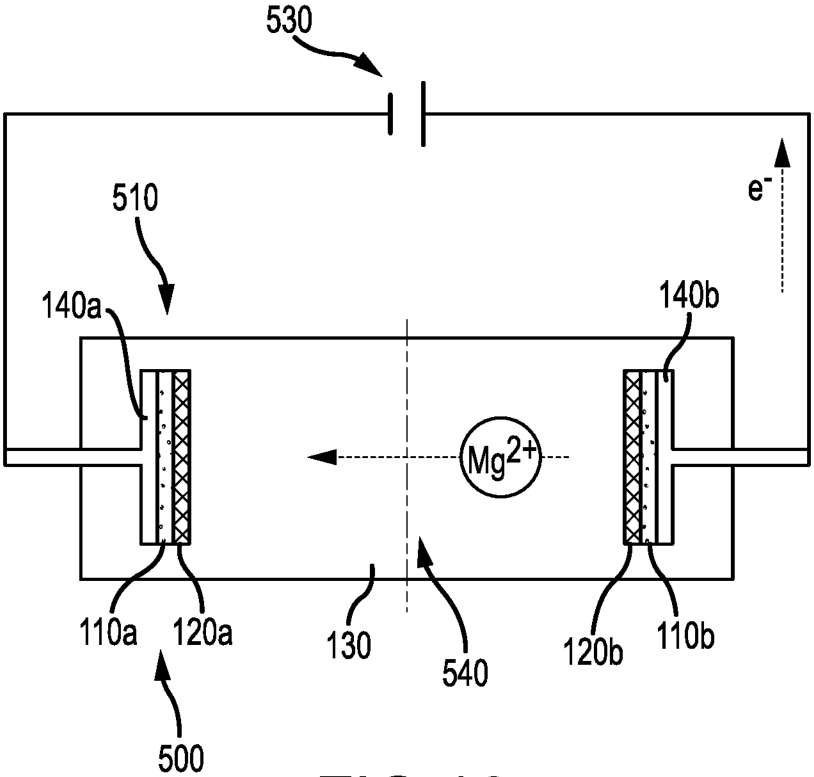
530
510
e-
140a
140b
Mg2+
110a
120a
130
540
120b
110b
500

FIG.16

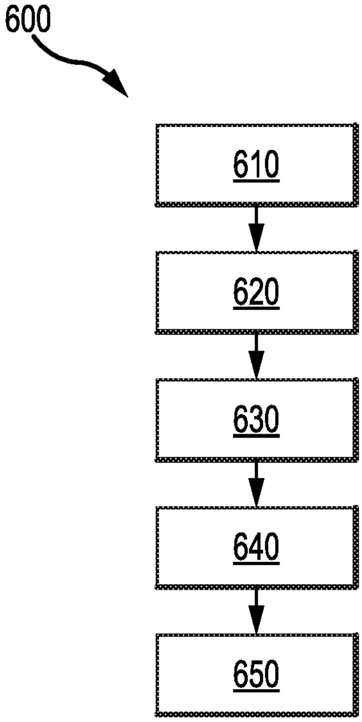
600
610
620
630
640
650

FIG.17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US16/38793

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - H01M 4/136, 4/46, 4/58, 4/62; 12/08 (2016.01)
CPC - H01M 4/136, 4/381, 4/485, 10/054, 10/0568, 10/0569, 12/08
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8): H01M 4/136, 4/46, 4/58, 4/62; 12/08 (2016.01)
CPC: H01M 4/136, 4/381, 4/485, 10/054, 10/0568, 10/0569, 12/08, 2300/0025, 2300/0028, Y02E 60/12; USPC: 429/224, 231.9

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, RU, AT, CH, TH, BR, PH, SE, NO, DK, FI, BE, NL, LU, MX, INPADOC Data); EBSCO; PatentsGoogle; Google Scholar; sciencedirect.com; magnesium, electrode, polymer, coating, reversibly depositable, magnesium ion salt, electrolyte

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 8,361,661 B2 (DOE, RE et al.) 29 January 2013; figures 5, 7; column 6, lines 5-40; column 7, lines 60-67; column 8, lines 1-20, 40-60; column 9, lines 5-45; column 10, lines 30-65; column 11, lines 10-55; column 12, lines 15-20; claims 1, 11	1-20
Y	US 3,343,995 A (REID, RW et al.) 26 September 1967; column 4, lines 60-70; column 5, lines 57-60	1-20
Y	(Wang, H et al.) A novel type of one-dimensional organic selenium-containing fiber with superior performance for lithium–selenium and sodium–selenium batteries. Royal Socity of Chemistry Advances. 2014. vol 4. no. 106; page 2, lines 35-80; page 5, lines 10-25	4-5
Y	US 2015/0050554 A1 (ZEON CORPORATION) 19 February 2015; paragraphs [0082]-[0083], [0101], [0129], [0141]-[0142], [0144]	6-7, 16
Y	US 8,211,578 B2 (JIANG, Z et al.) 3 July 2012; column 6, lines 15-30; claims 1-2	10-11, 13
A	WO 2011/029058 A2 (MOLECULAR NANOSYSTEMS, INC.) 10 March 2011; entire document	1-20
A	US 2014/0205904 A1 (SASAKI, T) 24 July 2014; entire document	1-20
A	US 2012/0315466 A1 (ABRAMI, S et al.) 13 December 2012; entire document	1-20
A	US 2015/0010832 A1 (UNIVERSITY OF PITTSBURGH OF THE COMMONWEALTH SYSTEM OF HIGHER EDUCATION) 8 January 2015; entire document	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search
17 August 2016 (17.08.2016)

Date of mailing of the international search report
19 SEP 2016

Name and mailing address of the ISA/
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
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Authorized officer
Shane Thomas
PCT Helpdesk: 571-272-4300
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