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(54) Title: PROTECTIVE LAYERS FOR METAL ELECTRODE BATTERIES

(57) Abstract: Rechargeable metal batteries are disclosed having a protective ionic membrane layer on a metal anode. The ionic membrane can be formed from ionomers in the electrolyte including polymerizable ionic liquid monomers or halogenated alkyl anion salts. Such ionic membranes can continuously supply ions near the anode electrode and stabilize the anode metal electrode.

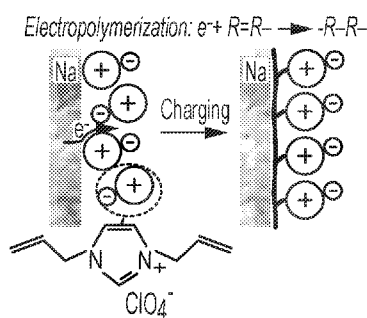


FIG. 1



PROTECTIVE LAYERS FOR METAL ELECTRODE BATTERIES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Nos. 62/436,248, filed 19 December 2016, 62/556,037 filed 8 September 2017, and 62/572,943, filed 16 October 2017, the entire disclosures of which are hereby incorporated by reference herein.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with government support under grant numbers DMR-1609125 and DMR-1120296 awarded by the National Science Foundation and grant numbers DE-AR0000750 and DE-FOA-001002-2265 awarded by the Department of Energy. The government has certain rights in the invention.

TECHNICAL FIELD

[0003] The present disclosure relates to protective layers for metal electrode batteries, methods of making the protective layers, and batteries comprising the protective layers.

BACKGROUND

[0004] High energy rechargeable batteries based on active metal (Li, Na, Al, Si, Sn, Zn, etc.) anodes are among the most important electrochemical energy storage devices to supply power for rapidly evolving technologies, including the fields of portable electronics, advanced robotics, electrification of transportation, etc. It has long been understood that such metal based anodes offer factors of 2-10 times higher specific capacity (e.g., 3860 mAh/g for Li), compared with the carbonaceous anode (360 mAh/g) used in lithium ion battery technology. Some metal anode batteries are also advantageous because they enable the development of high-energy unlithiated materials, such as sulfur, oxygen, and carbon dioxide as the active species in the cathode. This raises the prospect of multiple battery platforms that offer large improvements in specific energy on either a volumetric or mass basis.

[0005] Despite their promise, rechargeable batteries based on lithium (Li) metal, sodium (Na) metal, and aluminum (Al) anodes are not commercially viable today because the

metals are plagued by one or more instabilities. *Chemical instability* of the metal in contact with liquid and solid-state ceramic electrolyte depletes the electrolyte and electrode overtime, leading to run- away increases in cell resistance. At low current densities, spatial heterogeneities in the conductivity of spontaneously formed, fragile solid electrolyte interphases (SEIs) on Li lead to rough plating of the metal during battery recharge as electric field lines concentrate on thinner, more conductive SEI that provide faster growth leading to the *morphological instability* typically associated with mossy, high- surface-area deposits. At high current densities, depletion of ions from an electrochemically active surface leads to formation of the *hydrodynamic instability* termed electroconvection, which drives selective metal deposition at localized regions on the electrode to form diffusion limited fractal structures termed dendrites. Because the driving force for the last of these three instabilities is physical, all batteries based on charge storage by reduction of metal ions at the anode (e.g. Li, Na, Al) will fail by this mechanism at high currents.

[0006] Uncontrolled growth of metallic structures created as a result of morphological or hydrodynamic instabilities leads to battery failure by formation of internal shorts, which limits the cell lifetime. Even if this failure mode can be prevented through choice of electrolyte additives the chemical and physical fragility of the formed structures cause cell failure by other means, typically loss of active material in the anode, which manifests as a low charge utilization or Coulombic efficiency. Additionally, because Li-ion cells based on high-energy metallic anodes including Si, Sn, and Ge store Li by alloying reactions, which produce large cyclic volume change in the electrode and destroys the SEI formed on the electrode each cycle, the first of the three instabilities are common to Li-ion batteries based on any of these chemistries.

[0007] The main hurdles preventing large-scale deployment of batteries based on metal anodes stem from the uneven electrodeposition of metal ions during battery recharge and parasitic reactions between the metal anode and liquid electrolytes during all stages of battery operation. For example, batteries based on lithium or sodium are well-known to form rough, dendritic structures upon being reduced as a result of their intrinsic tendency to deposit on protrusions where the electric field lines are concentrated. Accumulated dendritic deposits can connect two electrodes, causing short-circuit and other safety-related hazards. In less extreme cases, dendrites promote the parasitic reaction of metal and the electrolyte which lowers the Coulombic efficiency and deteriorates the battery performance over time. This can be a more severe problem in a capacity balanced 'full cell' in which very limited amount of

the metal species are present, in contrast with lab-based 'half-cell' where usually excessive metal anodes are used.

[0008] It has been previously demonstrated that, elements such as Si, Sn, In, Mg, and Ge are able to reversibly form alloys with lithium (e.g., $\text{Li}_{4.4}\text{Sn}$), meaning these materials provide certain capacity in rechargeable lithium metal batteries. However, when used as stand-alone anodes, Si, Sn, In, Mg, and Ge undergo large volume changes (as high as 300%) upon lithiation, which destroys electrical connection with the current collectors and causes premature battery failure. The effects are even more severe for batteries based on sodium. This problem was previously addressed by two methods: creating composite anodes in which the metal is integrated with an inert metal or conductive carbon (e.g. graphene, graphite, carbon black, carbon nanotubes), or by fabricating the active materials (e.g. Si, Sn, In, Mg, Ge) nanostructures in various morphologies (e.g., nanowires, nanotubes, hollow particles) able to accommodate the volume expansion. The first method inevitably lowers the specific capacity as the inert metal or carbon materials used in the composites only serve as mechanical reinforcement for the active Si, Sn, In, Mg or Ge material and does not participate in the electrochemical reaction. Additionally, the alloying process is typically slow, and ideally requires higher temperature than those normally used in batteries for long-term stability. Fabricating the active material in the form of nanostructures does extend the anode lifetime, but comes at considerable costs in terms of the lower density of the active material, which reduces the specific energy on a volume basis of the electrode. The added costs of the processes required to create nanostructures in the desired shapes at scale and with high degrees of reproducibility for battery manufacturing also introduce new challenges that have so far proven to be stubborn roadblocks to commercialization of batteries employing metals as anodes.

[0009] Hence, there is a continuing need to develop high energy rechargeable batteries based on active metal anodes.

SUMMARY OF THE DISCLOSURE

[0010] An advantage of the present disclosure is a battery having a protected metal electrode, e.g., metal anodes that comprise substantially metallic lithium, metallic sodium, metallic aluminum, metallic zinc, etc. Advantageously, the battery is a rechargeable battery that can include a metal anode, a cathode and an electrolyte, in which the metal anode has an ionic membrane thereon. Advantageously, the ionic membrane can continuously supply ions

near the anode electrode by providing a halogenated salt at or near the anode-electrode interphase, for example. The ionic membrane can further protect the metal anode.

[0011] These and other advantages are satisfied, at least in part, by a rechargeable battery comprising a metal anode, a cathode and an electrolyte, wherein the metal anode has an ionic membrane thereon. The ionic membrane can be formed from ionomers including polymerizable ionic liquid monomers to form an ionic polymer membrane or from halogenated alkyl anion salts to form alkyl anions tethered to the metal anode.

[0012] In one aspect of the present disclosure, the ionic membrane can include an ionic polymer membrane directly on the metallic anode, e.g., a metallic sodium anode. Such ionic polymer membranes can be formed from one or more polymerizable ionomers, such as one or more polymerizable ionic liquids (IL) having one or more allyl or vinyl groups and having an anion. The polymerizable ionomers can be included with an electrolyte of a rechargeable battery.

[0013] In another aspect of the present disclosure, the ionic membrane can include alkyl anions tethered to the metal anode, e.g., a metallic lithium anode. Such ionic membranes can be formed from ionomers of halogenated alkyl anion salts, such as one or more halogenated alkyl sulfonate salts. The halogenated alkyl anion salts can be included with an electrolyte of a rechargeable battery.

[0014] Advantageously, the anodes protected with the ionic membrane of the present can be cycled stably with high Coulombic efficiency at high current densities. For example, metal anodes protected with ionic membranes of the present disclosure can exhibit coulombic efficiency exceeding 90% such as exceeding 95%. Such protected anodes can exhibit stable cycling of over 100 cycles such as over 150 cycles.

[0015] Other aspects of the present disclosure include processes for preparing ionic membranes on metallic anode electrodes, which can be used in a rechargeable battery. Such processes include electropolymerizing a polymerizable ionic liquid monomer onto the metal anode to form an ionic membrane thereon. Other processes include adsorbing halogenated alkyl anion salts onto a surface of the metal anode electrode to form an ionic membrane thereon. The IL monomer and the halogenated alkyl anion salts can be included with an electrolyte of the rechargeable battery. The addition of such ionomers in the electrolyte can help in the regeneration of the ionic membrane in repeated cycling of the battery.

[0016] Additional advantages of the present invention will become readily apparent to those skilled in this art from the following detailed description, wherein only the preferred

embodiment of the invention is shown and described, simply by way of illustration of the best mode contemplated of carrying out the invention. As will be realized, the invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, all without departing from the invention. Accordingly, the drawings and description are to be regarded as illustrative in nature, and not as restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Reference is made to the attached drawings, wherein elements having the same reference numeral designations represent similar elements throughout and wherein:

[0018] Figure 1 is a schematic representation of forming an ionic polymer membrane on a surface of a metal anode, e.g., a sodium anode, in accordance with an embodiment of the present disclosure.

[0019] Figure 2 is a plot showing cell failure time at various current densities derived from constant current polarization test of Na/Na symmetric cell with and without 20 wt% DAIM in the electrolyte.

[0020] Figure 3A shows cycling performance of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cells with and without protected sodium metal anode at 100 mA/g of the active material in the cathode.

[0021] Figure 3B shows cycling performance of Na-SPAN cells with and without protected sodium metal anode at 0.2 C ($1\text{C} = 1675 \text{ mAh/g}$) based on sulfur in the cathode.

[0022] Figure 4 is a schematic representation of forming an ionic membrane on a surface of a metal anode, e.g., a lithium anode, in accordance with an embodiment of the present disclosure.

[0023] Figure 5 is a plot comparing interfacial and bulk impedance values for ionomer-based and control electrolytes as a function of time. The circles denote results with the control electrolyte (1 M LiNO_3 - *N,N*-dimethylacetamide (DMA)), whereas the squares and triangles represent batteries with 10 and 5% (by weight) ionomer additive, respectively, with the same electrolyte (open symbols represent bulk impedance and solid symbols represent interfacial impedance).

[0024] Figure 6 is a voltage profile of the Li||SS cell plotted over time. In this experiment, Li^+ ions were deposited onto the stainless steel side at a current density of 1 mA/cm^2 for 10 hours, after which the cell was kept at rest for an additional 10 hours, as shown in the current-versus-time curve. In the voltage-versus-time graph, the red line

represents the profile of the control electrolyte (1 M LiNO₃-DMA), whereas the black line is for the same electrolyte enriched with 10% (by weight) ionomer additive. The dashed line in the current-versus-time graph is the applied current for both cases.

[0025] Figure 7 is a plot of cycle number associated with divergence of voltage against respective current densities for a Li/SS cell in which lithium with 10-mAh/cm² capacity is deposited onto SS, and the battery was charged and discharged consecutively at various current densities.

[0026] Figure 8 shows end voltage of charging cycle for the control and the ionomer-added electrolyte plotted as function of cycle number.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0027] In the following description, reference is made to the accompanying drawings that form a part hereof, and in which is shown by way of illustration specific embodiments which may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the disclosure, and it is to be understood that other embodiments may be utilized and that structural, logical, and/or other changes may be made without departing from the scope of the present disclosure. The following description of example embodiments is, therefore, not to be taken in a limited sense.

[0028] Ranges of values are disclosed herein. The ranges set out a lower limit value and an upper limit value. Unless otherwise stated, the ranges include all values to the magnitude of the smallest value (either lower limit value or upper limit value) and ranges between the values of the stated range.

[0029] The present disclosure provides protective layers for electrodes (e.g., anodes) of batteries. The present disclosure also provides methods of making protective layers for the electrodes of batteries, and devices comprising same. Various embodiments and examples, describe providing safe, stable, air-insensitive metal anodes (e.g., lithium or sodium metal anode) by protecting the surface with an ionic membrane layer through in situ or ex situ facile wet chemistry reaction, with no harmful byproducts generated. The ionic membrane provides desirable (e.g., low) surface impedance and protects metallic anodes from parasitic reaction with the electrolyte. The methods disclosed herein can be readily incorporated into large-scale manufacturing.

[0030] In this disclosure, a metallic anode is protected by an ionic membrane directly on a surface of the anode exposed to electrolyte. The protected anode can be part of a

rechargeable battery including the metal anode, a cathode and an electrolyte. The ionic membranes of the present disclosure can be formed from ionomers. As used herein an ionomer is a compound that has ionizable or ionic groups, or both and that can either polymerize to form an ionic membrane on a surface of a metallic anode or can adsorb on the surface of the metallic anode to form an ionic membrane thereon. Advantageously, the ionomers form thin conformal coatings directly on the anode surface exposed to the electrolyte. Ionic membranes prepared from ionomers of the present disclosure can continuously supply ions near the anode electrode and stabilize anode metal. In certain embodiments, the ionic membrane can have a thickness in the range of a monolayer to micron scale, e.g., from about 5 nm to about 500 microns.

[0031] In one aspect of the present disclosure, the ionic membrane can include an ionic polymer membrane directly on the metallic anode. Such ionic polymer membranes can be formed from polymerizable ionomers, which can be included with an electrolyte of a rechargeable battery. Useful polymerizable ionomers of the present disclosure include, for example, polymerizable ionic liquids (IL) having one or more allyl or vinyl groups and a corresponding anion. Such IL monomers include 1,3-diallyl imidazolium perchlorate (DAIM), 1-allyl-3-vinyl imidazolium perchlorate (AVIM), 1,3-diallyl piperidinium hexafluorophosphate, 1,3-diallyl piperidinium bis(trifluoroethanesulfonyl)imide, 1,3-diallyl imidazolium bis(fluorosulfonyl)imide, etc. Preferably, the IL monomer has more than one polymerizable group and a corresponding anion.

[0032] In another aspect of the present disclosure, the ionic membrane can include alkyl anions tethered to the metal anode. Such ionic membranes can be formed from ionomers of halogenated alkyl anion salts, e.g., halogenated alkyl sulfonate salt, which can be included with an electrolyte of a rechargeable battery. Useful halogenated alkyl anion salts of the present disclosure include, for example, those with the following formula:



[0033] wherein X represents a halogen such as a chlorine, bromine, iodine; alkyl represents a C_{1-12} , e.g., C_{2-6} divalent alkyl group; and A represents a anion salt such as a sulfonate metal ion salt, e.g., lithium sulfonate, where the metal ion is preferably a metal ion corresponding to the metal of the anode. Examples of ionomers that can adsorb onto a metal anode include 2-bromoethanesulfonate lithium salt, 2-bromoethanesulfonate sodium salt, 2-chloro-ethane sulfonate sodium salt, 2-bromoethane-bis (fluorosulfonyl) imide lithium salt.

Such halogenated alkyl anion salts form alkyl anions tethered to the metal anode, i.e., $M\text{-alkyl-A}^{-+}M$ where M is the metallic anode electrode surface and $A^{-+}M$ is the anion salt.

[0034] Another aspect of the present disclosure is processes for preparing ionic membranes on metallic anode electrodes, which can be used in a rechargeable battery. Such processes include electropolymerizing a polymerizable ionic liquid monomer onto the metal anode to form an ionic membrane thereon. Other processes include adsorbing halogenated alkyl anion salts onto a surface of the metal anode electrode to form an ionic membrane thereon. The IL monomer and the halogenated alkyl anion salts can be included with an electrolyte of the rechargeable battery. The addition of such ionomers in the electrolyte can help in the regeneration of the ionic membrane in repeated cycling of the battery. In an embodiment, the ionomer, e.g., polymerizable ionic liquid monomer or halogenated alkyl anion salts or both, can be included as an additive in the electrolyte of a rechargeable battery at concentration of about 1% to about 30 % by weight such as of about 5% to about 20% by weight based on the total weight of the electrolyte.

[0035] Advantageously, the anodes protected with the ionic membrane of the present can be cycled stably with high Coulombic efficiency at high current densities. For example, metal anodes protected with ionic membranes of the present disclosure can exhibit coulombic efficiency exceeding 90% such as exceeding 95%. Such protected anodes can exhibit stable cycling of over 100 cycles such as over 150 cycles.

[0036] Metal anodes that can benefit from the present disclosure include metal anodes that comprise substantially metallic lithium, metallic sodium, metallic aluminum, metallic zinc, etc. Forming an ionic membrane on the surface of such anodes according to the present disclosure provides a solid electrolyte interface (SEI) that offers desirable (e.g., fast) ion transport between a bulk liquid electrolyte and a metal anode (e.g., Li or Na), or optionally an intercalating or conversion cathode, but at the same time protects the electrodes from physical contact with the liquid, which provides an important route towards creation of reactive metal anodes able to overcome chemical instability of the metal anode. Thus, the advantages of a metal anode (e.g., metallic lithium or sodium anodes) such as, for example, high energy density and low voltage, are not compromised, while its cycle life and/or safety can be enhanced.

[0037] Various embodiments and examples of the present disclosure are provided below.

[0038] In one aspect of the present disclosure, an ionic membrane can be prepared as an SEI film formed directly on a metallic anode, e.g., a metallic sodium anode, through electropolymerization of a polymerizable ionic liquid monomer in a liquid electrolyte. It was found that such membranes markedly increase the stability of anodes to failure. We also found that unlike Li anodes, which can fail by any of the processes discussed in the Background section above, Na anodes almost always fail as result of electrolyte degradation. The ionic membrane of the present disclosure advantageously can exhibit exceptional chemical and electrochemical stability in contact with reactive metals and in certain environments stabilize lithium and sodium metal anodes against dendrite formation such as with aprotic liquid electrolytes. Theoretical work suggests that the tethered anions in an ionic liquid can improve the stability of Li plating during the battery recharge by acting as a supporting electrolyte. This has been verified by the experimental studies which show that dendrite free electrodeposition can be achieved by uniforming ion distribution by contacting lithium to functional glass fiber or solid polymer electrolyte. An ionic liquid additive is believed to reduce the magnitude of destabilizing electric fields near the anode by providing a localized supply of anions able to support a high cation flux at the electrode. This effect is quite general and is not limited to Li. Carbonate based electrolyte containing around 5 to 10 vol% 1-methyl-3-propylimidazolium-chlorate tethered to SiO₂ nanoparticles were shown to enhance the stability and cycle life for both Na-S and Na-O₂/CO₂ cells. (*Nat Commun*, 2016, 7, 11722 and *ChemSusChem* **2016**, 9, 1600-1606).

[0039] Secondary sodium-ion and sodium-metal batteries offer multiple advantages over their lithium counterparts for portable storage in electric vehicles and locomotives as well as for stationary storage in power stations. Among the motivations for interest in these batteries include the low cost and high natural abundance of sodium, the high theoretical capacity (1166 mAh/g) and moderate redox potential (-2.71 V versus the standard hydrogen potential) of the sodium anode, and the fact that high-temperature sodium-sulfur (Na-S) and Na-metal chloride (Na/MeCl₂) batteries have already been demonstrated to be commercially viable technologies for grid storage and for electrification of transportation. On-field accidents and difficult maintenance of these batteries due to their high operating temperature are a concern for broader deployment in portable devices, robotics, and electric vehicles. Room-temperature sodium batteries based on high-voltage intercalation cathodes or energetic conversion cathodes (e.g. Na-S or Na-O₂/CO₂ cells) have already been reported to overcome some of these difficulties, however the focus on improvements afforded by ambient-

temperature operation, typically gloss over fundamental challenges associated with long term stability of a sodium metal anode in liquid electrolytes.

[0040] Recharge of any battery utilizing a sodium metal anode requires repetitive stripping and plating of the metal surface. The size difference between sodium ions and sodium atoms subjects the anode to large volumetric and morphological changes during normally battery cycling, which makes the batteries unstable to failure by multiple processes. First, because of its high reactivity, metallic sodium rarely forms stable solid electrolyte interphases, rather it is corroded continuously by aprotic liquid electrolytes upon cycling, which lowers the Coulombic efficiency (CE) and lifetime of the cells. Second, the uncontrolled nature of the SEI formation reactions lead to significant spatial variations in SEI conductivity, which drives spatial variations in Na deposition during battery recharge making the metal particularly unstable towards the morphological instability known as dendritic electrodeposition. Finally, because of the metal's softness and low melting point, dendrite induced short circuits either end in thermal run-away or in sodium dendrites breaking away from the metal electrode to become electrochemically disconnected from the metal substrate, which shorten the lifetime of the cell.

[0041] Ionic membranes formed directly on metallic sodium anodes can mitigate the stability problems of such anodes. The following provides an example of preparing such an ionic membrane from a polymerizable ionic liquid (IL) monomer.

[0042] Polymeric ionic liquid film formation and characterization

[0043] Electrochemical polymerization of reactive monomers on metallic surfaces is a well-established method to fabricate functional polymer thin films for protecting metals and electronic devices, including sensors. The approach offers several advantages over other polymerization techniques that may also be used to create coatings on metals, including: (i) it combine polymer synthesis with thin film formation; (ii) it eliminates the need for exogenous oxidants to initiate the polymerization; and (iii) properties of the membrane, including its thickness, morphology, and porosity are controlled by transport processes in the film itself. Although the method has not been previously studied to protect reactive alkali metals for battery applications, it is well suited to this application because the transport processes that control film thickness and morphology are related to those that control access of ions to/from the metal surface during charge/discharge processes in a battery. Figure 1 is a schematic representation of the process, showing how it can be used to create an ionic polymer membrane on the surface of a metal anode, e.g., a sodium anode. The polymerization reaction

is believed to progress via the usual steps (initiation, propagation, and termination) that govern free radical polymerization processes. Initiation occurs during charging, wherein the unsaturated ionic liquid monomers accept electrons to form reactive radical species. These species react with monomers to increase the size of the radicals, propagating the polymerization process and creating a thin, porous membrane in conformal contact with the anode.

[0044] The molecular structure of the ionic liquid (IL) monomer was found to be a factor in regulating the structure and morphology of the polymer membrane as well as in controlling the degree of polymerization achieved. It was reported that polymerization of IL molecules may result in degradation of properties of the monomers, including ionic conductivity, due to elevation of the glass transition temperature and reduced number of mobile ions after covalent bonding of the component ions. In order to achieve optimized adhesion and ionic conductivity, different functional imidazolium cation- based ionic liquid monomers bearing allyl or vinyl group and perchlorate anion, namely 1-allyl-3-methylimidazolium perchlorate (AMIM), 1,3-diallyl imidazolium perchlorate (DAIM), 1-allyl-3-vinyl imidazolium perchlorate (AVIM) were synthesized, and their electroinitiated polymerization process on the electrode surface was investigated. To characterize the polymeric film formed on the electrode, the monomers were dropped on a polypropylene separators sandwiched by two stainless steel electrodes in a coin cell. A constant current of 1 mA/cm² was applied to the cells to initiate polymerization until the voltage goes diverging with no current passing through the cell, at which point the electrodes are probably covered by the films and completely insulated. The morphology of the polymer film was examined by scanning electron microscopy (SEM). Both DAIM and AVIM monomers are able to polymerized by charges with good adhesion and contact to the stainless steel electrode, while AMIM barely forms a film on the surface likely due to limited unsaturated components on the ionic liquid. A uniform thin, membrane was found to cover the rough and scratched surface of the stainless steel electrode by polymerizing DAIM monomer. The surface topography of the film formed by DAIM was further characterized by atomic force microscopy (AFM) in tapping mode. A smooth and uniform height/topography image was seen from a DAIM prepared film on stainless steel, which was comparable with an SEM image. To assess the thickness of the film formed on the electrode, a scratch was made to expose the stainless steel and allow measurement of the height from the stainless steel surface to the upper polymer, giving a thickness of about 80 nm.

[0045] The molecular weight (M_w) and polydispersity index (PDI) of the electropolymerized IL films were determined by means of gel permeation chromatography (GPC) in dimethylformamide. It was seen that AMIM forms oligomers (M_w of about 896 g/mol) (possibly due to the limited unsaturated double bonds), while DAIM and AVIM monomers were capable of forming large molecular weight polymer films (M_w of 58,540 g/mol and 122,100 g/mol, respectively) consistent with the film morphologies characterized by SEM. The existence of sp^2 hybridized vinyl group in AVIM makes it more reactive and self-polymerizable in the presence an initiating moiety, leading to much larger M_w and denser membrane films than produced by electropolymerization of DAIM. Thus, while membranes formed by DAIM are rubber-like with softer consistency and more open morphologies, those based on AVIM have molecular weight about twice as large and less open morphologies. Based on the morphology and stability of the film formed, DAIM was selected for further evaluation. To create membranes suitable for electrochemical studies, DAIM monomer was used as additives in liquid electrolytes to form ionic membranes in a variety of configurations on sodium metal anodes. For brevity, we here focus on membranes created in-situ on metallic sodium using 20 wt% of the IL monomer as an additive in an electrolyte comprised of 1 M sodium perchlorate in ethylene carbonate/propylene carbonate (EC/PC- $NaClO_4$).

[0046] Sodium metal stability

[0047] To evaluate the stability of the sodium metal anodes passivated with our ionic polymer membrane SEI prepared with polymerizable ionomers, the Coulombic efficiency (CE) for sodium stripping and plating processes was determined from galvanostatic experiments in a Na/stainless steel cell. Initially, a predetermined amount of sodium (1 mAh/cm²) was plated on the stainless steel electrode at a constant current of 1 mA/cm². In the following cycle, a fraction (1/6) of the sodium was stripped and plated from the stainless steel repeatedly at the same current density. Under these conditions, the CE can be calculated based on the simple formula proposed by Aurbach (*J. Electrochem. Soc.* 1989, 136, 3198-3205). Control cells that do not contain IL monomer in the electrolyte, or which contain the unpolymerizable IL monomer 1-methyl-3-propylimidazolium chlorate (MPIM), were evaluated in the same manner and found to yield very low CE values around 16.7% and to fail within the first cycle for the cells with no IL in the electrolyte. This result is expected as the unpassivated sodium metal is expected to vigorously and irreversibly react with liquid electrolyte during electrochemical cycling. The low CE is also consistent with previous reports in cycling experiments in carbonate electrolytes in which all of the plated sodium was

stripped from the stainless steel electrode each cycle. Consistent with the discussion in the introduction, the authors explain the low CE for sodium metal anodes in terms of formation of non-uniform solid electrolyte interphase as well as dendritic growth.

[0048] In contrast, electrolytes containing DAIM as an additive exhibit markedly improved Coulombic efficiency with values as high as 95.0 % measured at a current density of 1 mA/cm². Additionally, cells containing DAIM exhibit vastly improved stability in long-term cycling measurements and lower overpotential compared with those containing MPIM. It is important here to note that while MPIM additives in carbonate electrolytes were reported previously to prevent dendrite formation in lithium metal batteries, the material only has a limited effect in improving the CE of the sodium metal anode, with only a 60 % CE being achieved. As the surface of the neat stainless steel electrode is relatively rough, this experiment tentatively confirms our previous finding that DAIM monomer helps form a uniform ion conducting polymeric membrane that not only protects the sodium metal surface, but facilitates transport at the anode.

[0049] A more detailed assessment of the membranes was performed using an aggressive galvanostatic polarization experiment in Na/Na symmetric cells in order to study the role played by the as prepared membranes over a wider range of current densities. Figure 2 reports the cell lifetimes at various current densities in the two cases, with and without DAIM additive in the electrolyte. It is seen that the cell lifetime doubles at low current density and improves by at least a factor of three at higher current densities (≥ 1 mA/cm²). As important is our observation that unlike typical lithium metal anodes, wherein cell failure by internal short-circuit is evidenced by a large voltage drop during galvanostatic polarization, failure of sodium anodes is almost always evidenced by a diverging voltage, indicative of electrolyte degradation. Comparison of the voltage profiles at 0.1 mA/cm² shows a higher polarization voltage with fluctuations for the cells in neat electrolyte, indicative of severe side reaction between sodium and electrolyte. The results reported here are to our knowledge the first to show that sodium metal cells are more likely to fail by electrolyte depletion than by dendrite-induced short circuits. This observation is believed to derive from the relative softness of metallic sodium (room-temperature hardness: 0.5 MPa and shear modulus: 3.3 GPa) relative to Li. It indicates that dendrite induced short-circuiting and associated phenomena such as thermal runaway are not as important for sodium metal battery technology as they are for Li metal cells, and provides insights into the role the IL membranes may play in stabilizing the sodium anode.

[0050] The stability of the Na/Na symmetric cell containing DAIM monomer additives in the electrolyte was also investigated by electrochemical impedance spectroscopy (EIS) experiments. To evaluate the interfacial reactivity of the sodium metal surface during polarization, impedance of the cells containing 0 or 20 wt% DAIM was measured as a function of time following intervals of two-hour charging at 1 mA/cm^2 . The interfacial resistance was found to be unstable for the control cell, displaying erratic values and transients from measurement to measurement. In contrast, in the 20 wt% DAIM case, the interfacial resistance steadily increases, indicative the formation of a stable SEI layer by the ionic membrane. The electrochemical initiated polymerization process in the presence of sodium anode and electrolyte was further investigated by linear-sweep voltammetry. The oxidation currents after the breakdown voltage are seen to be much lower for IL containing electrolytes than for the control electrolyte, indicating that the IL containing electrolytes have better electrochemical stability than the neat liquid electrolytes. It is also noted that small oxidization peaks were observed between 2 to 4 V for the electrolytes containing DAIM and AVIM, possibly indicative of an electron-transfer-induced polymerization process. The peak current increases linearly with the increase of the root mean square of the scan rate, indicating a diffusion-limited controlled polymerization process.

[0051] Sodium surface characterization

[0052] To further verify that an ionic polymeric membrane prepared from IL monomers helps stabilize sodium metal and prevent side reaction between electrode and aprotic electrolyte, an in-situ optical microscopy technique was applied to directly visualize how sodium deposits in a quartz cuvette optical Na/Na symmetric cell. A constant current of 1 mA/cm^2 was applied to polarize one electrode and we choose this current to make the study consistent with our previous test in coin cells. Light microscopic images of the sodium electrode at different deposition times in a 1M EC/PC- NaClO_4 electrolyte were obtained. Due to the softness of sodium metal, the pristine sodium electrode surface was not perfectly smooth. As the deposition process continued, the electrode was gradually covered by two types of deposits-thin fiber-like and bulky mushroom-like, which were formed in a dynamically swinging movement manner. Both types of deposits grow not in a specific direction but spark randomly, which probably was due to the unevenness and defects of the electrode surface. The shinning fiber-like deposit was discovered previously on sodium metal surface at a very low current density of $57 \text{ } \mu\text{A/cm}^2$ and on lithium electrodeposition as well. The bulky black sodium deposit was first discovered to the best of our knowledge, we

tentatively attribute its formation to the uncontrolled side reaction with electrolyte. This type of deposit grows faster and seems to be more detrimental to the electrode as it quickly withdraws from the electrodes and floats randomly in the electrolyte, eventually becomes 'dead sodium' which lowers the coulombic efficiency. When DAIM was added in the electrolyte, a big improvement was observed during sodium deposition at the same current density. It is apparent that the big black mushroom-like deposit was completely eliminated during the whole process of deposition, which indicates that the in-situ formed ionic polymeric membrane protects sodium and eliminate the side reaction with liquid electrolyte. Though the needle-like deposits still exist, it is seen that the quantity of this type of dendrite is much smaller than that of the control and the growth rate is less than half than that of the bulky dendrites. The grows of the needle deposits may related to the effective pore size ($\sim 1 \mu\text{m}$) of the polymer membrane, which was approximated from the storage modulus ($4.05 \times 10^{-3} \text{ Pa}$) of the polymeric DAIM. As the effective pore is in the similar length scale to that of the needles and much smaller than mushroom deposits, it can successfully block the growing pathway of the mushroom deposits while some of the needles may penetrate through the film and continue to grow.

[0053] As the condition and environment are quite different between coin cells and optical cell due to assembling pressure and the existence of separators in the coin cells. We hypothesize with the help of mechanical pressure and separator, sodium can be engineered into an effective anode once the side reaction is eliminated and sodium surface is protected based on a recent theory study on lithium dendrite growth. To verify our believe, the morphology of the sodium metal anode after galvanostatic polarization and after 10 cycles of stripping and plating in coin cells were examined by SEM. As we expected, sodium anode polarized in the existence of DAIM in electrolyte exhibits uniform and flat surface morphology with a film formed on top, indicative of dendrite free electrode deposition with the help of pressure and separator, however, the control sodium electrode was quickly oxidized when transferring it to the SEM sample holder. Though the MPIM and AVIM additives in the electrolyte are beneficial compared with electrolyte with no such no additives, they are not as effective as the DAIM additive which is probably due to the non-contact protection of the sodium metal and the reactivity of the vinyl group. C 1s based on X-ray photoelectron spectroscopy (XPS) analysis on the control sodium metal and sodium electrode deposited in the prescience of DAIM in the electrolyte verifies the existence of IL components on the sodium surface after one-minute sputtering on the sodium metal surface.

[0054] Electrochemical performance for sodium storage

[0055] In order to evaluate the suitability of the protected sodium anode for room-temperature sodium metal batteries, the sodium anode after 10 hour's deposition in the presence of 20 wt% DAIM in the electrolyte in Na/Na symmetric cell was investigated under galvanostatic conditions with $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and polyacrylonitrile-sulfur (SPAN) composite, respectively, as electrodes. $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ is attractive because it exhibits high intercalation potential of around 3.4 V (vs Na^+/Na), which makes $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ a good candidate for next generation cathode materials for electrical energy storage, however, due to the larger ionic radius of sodium, it is a challenge to allow stable Na ion extraction and insertion. Previous work usually applied fluoroethylene carbonate (FEC) as electrolyte additive to stabilize the passivation layer between electrode and electrolyte interphases, however FEC is known to decompose and forms hazardous HF gas during electrochemical process. Therefore, it is urgent to develop alternative methods to stabilize this type of cell. SPAN composite cathode was capable of delivering high capacity and cycle stability in lithium metal batteries, and it is compatible with carbonate electrolyte. For these reasons, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and SPAN serve as good candidates for investigating the electrochemical stability of the protected sodium anode in rechargeable batteries.

[0056] Figure 3A reports the electrochemical characteristics of Na- $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cells based on the DAIM treated Na metal anodes. A floating point test from 3 V to 5 V gives a time dependent current response for the cell with protected sodium electrode up to 4.8 V, while an irregular and noisy current response was observed for the control cell at almost entire voltage ranges. The improved cell stability over different voltage ranges directly relates to the reduced side reaction between sodium anode and aprotic electrolyte. This enhanced cell stability also reduces the overpotential during galvanostatic cycling test, which results in higher cycling stability and coulombic efficiency (Figure 3A). When the anode is protected by the ionic polymeric membrane, both the capacity and efficiency rise, with the coulombic efficiency exceeding 96 % and capacity maintaining at 97 mAh/g after 160 cycles, while the control cell exhibit a variation of coulombic efficiency and a quick decrease of discharge capacity to below 20 mAh/g in 30 cycles. We believe this direct benefit of dramatic improvements stems from the tethered and uniform polymeric film that continuously supply ions near the electrode and prevent sodium metal from reacting with liquid electrolyte.

[0057] We also evaluate the application of the ion-rich sodium anode in Na-SPAN batteries. As SPAN has a high theoretical capacity, more coulombs will be applied to the cell

during cycling. Therefore, it is effective to evaluate the effect of the sodium anode protection in the system. As we expected, the protected cell gives rise to an almost 100 % coulombic efficiency and a reversible discharge capacity for over 100 cycles, however, the control cell bears random coulombic efficiency and the capacity drops to 200 mAh/g after 100 cycles (Figure 3B). The failure in the Na-SPAN cell, more likely be the same with the Na- $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cell, could be attributed to the side reaction with the electrolyte during cell charging, as the voltage profile is noisy and the efficiency is very low. Those results clearly indicate that the importance of protecting sodium anode in sodium metal batteries and their widely applications.

[0058] In summary, we report an example of fabricating an ionic membrane from polymerizable ionic liquids to protect metal anodes such as a sodium metal anode. The protected anode can be cycled stably with high Coulombic efficiency at high current densities. The ionic membrane on the anode was prepared by electroinitiated-polymerizing unsaturated functional IL monomer in electrolyte in-situ. We use both spectroscopic and analytical tools to show that such polymeric IL films provide sufficient amount of immobile ions on the electrode surface to prevent sodium anode from reacting with aprotic electrolyte and reduce uneven sodium electrodeposition. Electron and optical microscopy as well as electrochemical analysis indicate that IL monomer form a protective film on the Na anode and stabilize deposition of sodium by at least two mechanisms. First, they form an ionic polymeric SEI layer that protects sodium metal from parasitic side reactions with the liquid carbonate electrolyte. Second, they appear to utilize a previously reported tethered anion effect to stabilize deposition of Na. Our finding underscores the benefits of protecting sodium metal anode in the application of inexpensive rechargeable sodium metal batteries bearing high voltage or high specific capacity.

[0059] Another aspect of the present disclosure includes ionic membranes that form stable solid electrolyte interphases between a metal anode and electrolyte based on a halogenated alkyl anion salt, e.g., a bromide ionomer, which can adsorb onto the metal anode, e.g., a Li anode. Such ionic membranes can advantageously exhibit three attributes required for stable anode operation such as Li- O_2 cell operation.

[0060] First, they protect the Li anode against parasitic reactions and also stabilize Li electrodeposition during cell recharge. Second, halogen (bromine) species liberated during the anchoring reaction function as a redox mediator for the recharge reaction at the cathode, reducing the charge overpotential. Finally, such ionic membranes form an exceptionally

stable interphase with Li, which is shown to protect the metal in high Gutmann donor number liquid electrolytes. Such electrolytes have been reported to exhibit rare stability against nucleophilic attack by Li_2O_2 and other cathode reaction intermediates, but are known for their reactivity with Li metal anodes. The ionic membrane design is able to regulate transport of matter and ions at the electrolyte/anode interface and thus provide address major barriers to practical Li- O_2 storage technology.

[0061] In an embodiment of the present disclosure, an ionic membrane is directly formed on a metallic anode such a metallic lithium anode for a rechargeable lithium-oxygen (Li- O_2) electrochemical cell. Figure 4 illustrates such an embodiment.

[0062] The rechargeable lithium-oxygen (Li- O_2) electrochemical cell is peerless among energy storage technologies for its high theoretical specific energy (3500 Wh/kg), which far exceeds that of current state-of-the-art Li-ion battery technology. Li- O_2 cells are under intense study for applications in electrified transportation because they are viewed as the gateway to Li-air storage technology that is capable of offering competitive specific storage capacities to fossil fuels. A Li- O_2 cell includes a Li metal anode, an electrolyte that conducts Li^+ ions, and uses O_2 gas hosted in a porous carbon or metal support as the active material in the positive electrode (cathode). The cell operates on the principle that Li_2O_2 is reversibly formed and decomposed in the cathode, with the net electrochemical reaction of $2(\text{Li}^+ + \text{e}^-) + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ at an equilibrium potential of 2.96 V versus Li/Li $^+$.

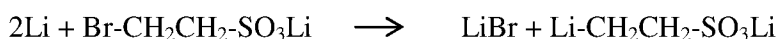
[0063] The ionic membrane can be directly formed on a metallic anode by including an ionomer such as a halogenated alkyl sulfonate salt together with a liquid electrolyte in the rechargeable battery. Such a halogenated alkyl sulfonate salt can adsorb directly onto the anode surface forming a tethered alkyl anion that supplies ions near the anode electrode and stabilize the anode metal electrode.

[0064] The additive and the in situ-formed SEI that it forms are deliberately designed to take advantage of three fundamentally based mechanisms for stabilizing electrochemical processes at the anode and cathode of the Li- O_2 cell. First, consistent with predictions from recent continuum and density functional analyses of lithium deposition, we report that ionomer electrolyte additives that can ensure low diffusion barriers and high cation fluxes in the SEI at the anode are highly effective in stabilizing deposition of Li. We demonstrate the success of these additives by means of electrochemical analysis and postmortem imaging. Second, we show that if the ionomer additives are designed to form thin conformal coatings at the Li surface, it is possible to passivate the anode surface against chemical attack by high-

DN (DN = 27.8) liquid electrolytes capable of stabilizing oxide intermediates on the cathode. Finally, we report that the same material that stabilizes Li deposition on the anode also functions as an effective redox mediator that lowers the overpotential for the OER reaction at the Li-O₂ cathode.

[0065] Understanding the anode protection mechanism

[0066] **Characterization of the anode.** The electrolyte ionomer salt additive (2-bromoethanesulfonate lithium salt) investigated for the present embodiment can react with lithium as provided in the scheme below.



Scheme 1. Shows the reaction of lithium 2-bromoethanesulfonate with lithium metal forming LiBr salt and lithium-based organometallic.

[0067] The particular ionomer was chosen for this embodiment because of its ability to react with lithium to simultaneously anchor lithium ethanesulfonate at the anode/electrolyte interface and to generate partially soluble LiBr in the electrolyte. The specific ionomer chemistry selected for the study is motivated by four fundamental considerations. First, recent continuum theoretical analysis and experiments indicate that tethering anions, such as sulfonates at the anode/electrolyte interface, lowers the potential at the interface during Li deposition and in so doing stabilizes the deposition. Second, joint density functional theoretical (JDFT) calculations show that the energy barrier E_a for Li⁺ diffusion at a Li anode coated with LiBr salt ($E_{a,\text{LiBr}} \approx 0.03$ eV) is much lower, by a factor of around 8, compared to Li₂CO₃ ($E_{a,\text{Li}_2\text{CO}_3} \approx 0.24$ eV), which forms naturally when aprotic solvents react with Li. This means that under isothermal conditions, stable deposition of Li in a given electrolyte can occur at deposition rates more than three orders of magnitude higher on a LiBr-coated Li anode than on an anode with a spontaneously formed Li₂CO₃-rich SEI. Third, the short hydrocarbon stem that connects the tethered sulfonate groups to Li should allow a dense hydrocarbon brush to form at the interface to protect the Li electrode from chemical attack by a high-DN electrolyte required for stability at the cathode. Finally, soluble LiBr undergoes electrochemical oxidation and reduction in an appropriate potential window to function as a soluble redox mediator.

[0068] Cryo-focused ion beam (cryo-FIB) was used to characterize the morphology and thickness of the ionomer-enriched electrode/electrolyte interface with the liquid electrolyte intact but cryo-immobilized. In this technique, a symmetric lithium cell (with an ionomer-based electrolyte) was opened manually, and the sample was snap-frozen by

immediately plunging it into slush nitrogen to preserve the electrolyte and to avoid air exposure. The sample was then transferred under vacuum into an FEI Strata 400 FIB fitted with a Quorum PP3010T Cryo-FIB/SEM Preparation System and maintained at -165°C for the duration of the experiment. To produce a cross section of the interface, we used the focused gallium ion beam to mill through the frozen electrolyte and into the electrode. This interface was then examined by scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX) spectroscopy directly in the cryo-FIB. SEM images revealed an interfacial layer up to approximately 25 nm thick in most areas. EDX analysis shows that the chemical composition of the layer is similar to that in the bulk electrolyte and that bromine species are distributed more or less uniformly throughout.

[0069] Additional insight into the nature of the interfacial region can be obtained by washing away the electrolyte and analyzing the ionomer layer that remains immobilized on the Li metal. For this purpose, we used EDX and high-resolution x-ray photoelectron spectroscopy (XPS) analytical measurements. The XPS measurements used monochromatic Al K- α x-rays (1489.6 eV) with a beam diameter of 1 mm to probe a surface layer on the electrodes approximately 15 to 25 nm thick, that is, comparable to the thickness of the interface revealed by cryo-FIB. Sulfur and bromine signals are evident everywhere on the surface of the material. XPS analysis was also performed using postmortem measurements on lithium anodes harvested from Li-O₂ cells subjected to different running conditions. High-resolution scans for anodes retrieved after cycling or after a single discharge with the ionomer additive in the 1 M LiNO₃- *N,N*-dimethylacetamide (DMA) electrolyte were reviewed and compared to a corresponding Li anode without the ionomer. From this comparison, it is apparent that after the first discharge, a Li 1s peak at 55.2 eV is observed on anodes with or without the ionomer present in the electrolyte. The peak may be attributed to the presence of LiOH, Li₂O₂, and Li₂CO₃. A more prominent Li 1s peak is observed at 53.8 eV, accounting for about 85% of lithium, only in spectra of anodes cycled in the presence of the ionomer additive. This peak is indicative of the formation of a different SEI in electrolytes containing the ionomer; Li 1s peaks with comparable binding energy are reported for organometallics containing Li-C bonds (54.2 eV). This observation is consistent with the ionomer reacting at the Li anode surface to form a lithium ethanesulfonate-rich SEI at the interface. Also, the fact that this binding energy is observed in the cycled anodes confirms that the SEI layer is stable and present even after repeated insertion and extraction of lithium ions into the underlying electrode.

[0070] Further evidence that the ionomer additive forms a stable SEI on Li can be deduced from the O 1s and Br 3d high-resolution scans. The O 1s peak at 532.2 eV comprises approximately 18% of the oxygen signal in cells without the ionomer additive, whether the anodes originate from cells that were subjected to a single discharge or were cycled. The 532.2-eV peak has been previously reported to originate from sulfonates, which accounts for 27 and 38%, respectively, of the oxygen signal when the anode is discharged once or cycled in the presence of the ionomer additive. The corresponding sulfur atomic contribution for the same materials can be computed from the wide survey scans to be about 2% for the once discharged anode and about twice as high for the cycled anodes. The high-resolution scans of Br 3d reveal the formation of a single bond (a $3d_{5/2}$ and $3d_{3/2}$ doublet) with a Br $3d_{5/2}$ peak at 68.5 eV when the anode is discharged once in the presence of the ionomer. We attribute this peak to the formation of the Br–Li bond, which has been previously reported to occur at binding energies between 68.8 and 69.5. The same peak persists when the anode is cycled in the presence of the ionomer, but with a contribution of only around 15%. The reduced Li-Br species in the anodes of cycled cells is an indication of LiBr being solvated by the DMA electrolyte that can further participate in the redox mediation of oxygen cathode recharging. A more prominent Br 3d peak at 67.0 eV is observed only for the cycled anodes, likely originating from Br–C bonds [binding energies between 66.7 and 71.0 eV] in the SEI originating from an untethered ionomer. The untethered ionomer in the electrolyte can help in the regeneration of the SEI layer in repeated cycling. Our results based on XPS analysis thus show that the ionomer-added electrolyte forms a SEI layer of lithium ethanesulfonate and LiBr, in accordance with the proposed reaction mechanism.

[0071] The effectiveness of ionomer-based SEI on Li was analyzed using impedance spectroscopy measurements on symmetric lithium cells. The results were compared with Nyquist-type plots at progressive time periods for control cells and those that contain 10% or 5% (by weight) ionomer additive. The experimental data points are fitted with the circuit model to deduce the bulk and interfacial resistances (Figure 5) as a function of time for the control electrolyte as well as with 10 and 5% (by weight) ionomer additive. It is seen that the bulk resistance for all cells remain essentially constant for approximately 20 hours, beyond which the bulk resistance of the control diverges (the increase is much larger for the results for the control cells after 48 and 56 hours). The time-dependent interfacial impedance provides an even more sensitive indicator of the stability of the anode-electrolyte interphase in a high-DN solvent. It is seen that the initial interfacial resistances for control and ionomer

SEI-stabilized Li electrodes are approximately equal (~50 ohms). However, there is an exponential rise in the interfacial resistance of the control cell over time consistent with rapid reaction between Li and DMA. It is important to note that this reaction is observed although LiNO_3 is present at large concentrations in the electrolyte. These results therefore challenge the view that LiNO_3 provides an effective means of passivating Li metal anodes against reactive liquid electrolytes. In contrast, the results in Figure 5 show that the interfacial resistance remains constant when the ionomer-based SEI is present. It is seen that the stabilization with 10% ionomer additive is marginally better than the 5% case. Together, these findings demonstrate that a SEI based on bromide ionomers has a large stabilizing effect on Li anodes in DMA-based electrolyte solvents.

[0072] **Lithium-electrolyte stability.** The quality of lithium ion deposition on stainless steel substrates mediated by control and ionomer-containing 1 M LiNO_3 -DMA electrolytes were compared. For these experiments, cells were assembled with lithium as an anode and stainless steel as a virtual cathode. Lithium with a capacity of 10 mAh/cm^2 was deposited at a rate of 1 mA/cm^2 onto stainless steel, after which the cell was rested for a period of 10 hours and the voltage was monitored over time. For the cell including an ionic membrane, 10 wt% of 2-bromoethanesulfonate lithium salt was added to the electrolyte to form the membrane. Figure 6 shows that in case of a control electrolyte, Li deposition takes place at a higher voltage compared to the ionomer-containing electrolyte. Also, it can be observed that after the rest period, the voltage measured in the control cells immediately rises to approximately 0.5 V. This high open-circuit potential after Li deposition is a reflection of the complete decomposition of Li deposits on stainless steel due to corrosion by the electrolyte. It is again worth noting that despite using the Li-passivating salt LiNO_3 at high concentrations in the electrolyte, the freshly deposited lithium reacts completely with the electrolyte solvent. Figure 6 also reports the corresponding voltage profiles observed in rested cells containing the ionomer as an electrolyte additive. It is seen that the cell voltage remains close to 0 V (versus Li/Li^+), that is, near the open-circuit potential of a symmetric lithium cell, which means that the Li electrode is chemically stable in the reactive DMA electrolyte solvent.

[0073] To further examine the morphology of Li deposits, we performed postmortem analysis, wherein the surface features of the electrodes were visualized under a SEM. For the control, there are few patches of Li observed, and large sections of bare stainless steel are clearly visible. In contrast, in electrolytes containing the ionomer, the stainless steel surface is

covered with a thick layer of lithium. It is also seen that Li electrodeposits formed in the latter electrolytes are evenly sized and spherical, even at a relatively high current density of 1 mA/cm². This observation is consistent with previous reports of more compact electrodeposition of Li in electrolytes with halide salt-enriched SEIs and single-ion-conducting features.

[0074] To fundamentally understand the basis of these observations, we characterized the electrochemical stability of the electrolytes by means of linear scan voltammetry in the range of -0.2 to 5 V versus Li/Li⁺, at a fixed scan rate of 1 mV/s. We plotted current as a function of voltage in a two-electrode setup of Lillstainless steel. It is seen that for the control, the current diverges at a value around 4 V versus Li/Li⁺, whereas for electrolytes containing ionomer additives, the current diverges at a higher voltage, around 4.3 V versus Li/Li⁺. This improved stability is consistent with previous reports of electrolyte composites with tethered anions, wherein anions fixed at or near the electrode surface limit access to and chemical reaction of anions in an electrolyte with the negative electrode. Another important feature of the results can be seen at a potential close to 0 V versus Li/Li⁺. The significant current peak apparent at approximately -0.2 V versus Li/Li⁺ for both control and ionomer-containing electrolytes is a characteristic of lithium plating onto stainless steel. However, as the voltage is progressively increased, the corresponding Li stripping peak is not seen in the control cell but is readily apparent in cells with the ionomer-containing electrolyte. This behavior is indicative of the complete consumption of lithium deposits on stainless steel in the control cells and is consistent with previous results of SEM.

[0075] Results from so-called galvanostatic “plating-stripping” experiment are used to evaluate the stability of Li electrodeposition and to assess the propensity of the material to electrodeposit as rough, dendritic structures. In contrast to previous studies, where thick (~0.75 mm) Li foil is used on both electrodes in plate-strip protocols, we performed these experiments using asymmetric Li/Li cells composed of one thick Li and one Li-lean (10 mAh/cm² of Li deposited on stainless steel at 1 mA/cm²) electrode. The stability of the Li deposition reaction is normally assessed using three criteria: (i) magnitude of overpotential of lithium deposition, (ii) steep decrease of the cell voltage to zero with continuous charge-discharge, and (iii) a steady increase of the voltage over extended cycles of charge and discharge. In the first criterion, higher overpotential is indicative of formation of insulating products on the surface of the Li electrodes. At a fixed current density (0.05 mA/cm²), the voltage response for cells with ionomer-based SEI is low (approximately 6 mV), whereas the

corresponding value for the control is much higher (approximately 150 mV). The second criterion is related to the short-circuiting of the cell when dendritic lithium that formed at one or both electrodes bridges the two electrodes. It is apparent that this phenomenon is not observed either in the control or for the ionomer SEI-stabilized electrodes. Thirdly, a rise in voltage over cycles represents an unstable SEI that grows continuously, eventually consuming the Li deposited on the stainless steel substrate. It was observed, after only two cycles at both current densities studied, the control cell fails after a steep rise in voltage. This is quite different from what is observed for cells in which Li is stabilized by an ionomer SEI, which is stable for over 150 cycles. Figure 7 reports the number of cycles at which the cell voltage diverges as a function of current density (J). The ionomer-based SEI is seen to improve cell lifetime at a fixed current density by nearly two orders of magnitude. These results underscore the effectiveness of the ionomer-based SEI in stabilizing electrodeposition of Li in amide-based electrolytes, which were previously thought to be unfeasible for lithium metal batteries because of their high reactivity with and ready decomposition by Li.

[0076] **Anode protection mechanism.** We hypothesize that the stability of the Li anode in DMA originates from two fundamental sources: (i) accumulation of LiBr salt at the Li/electrolyte interface, which facilitates Li-ion transport to the Li electrode during charging; and (ii) the existence of tethered sulfonate anions at the interface, which lowers the electric field at the electrode. Previous JDFT analysis revealed that the presence of lithium halides in the SEI of Li metal anode lowers the activation energy barrier by an order of magnitude or more for lateral Li diffusion at a Li/electrolyte interface, thereby increasing the tendency of Li to form smooth deposits. Comparing the surface diffusion barriers for various constituents of a typical SEI layer, it was reported that Li_2CO_3 , a common SEI constituent in carbonate electrolytes, has an energy barrier of 0.23 eV, whereas the barrier for a SEI composed of LiF is 0.17 eV. This difference has been argued previously to explain the much greater tendency of Li to form flat, compact deposits during battery recharge, as revealed by experiments in which weakly soluble LiF salts are enriched in the SEI by precipitating out of liquid electrolytes. The JDFT analysis shows that the activation energy barrier for Li-ion diffusion at a LiBr/Li interface is much lower (0.062 eV) and comparable to that of magnesium, which is known in the literature to electrodeposit without formation of dendrites. Thus, the LiBr created during the formation of the SEI should provide an even more powerful (than LiF) stabilizing effect on Li deposition.

[0077] In addition to the presence of LiBr, the SEI created by the ionomer contains bound anionic groups in the form of lithium ethanesulfonate ($\text{Li-CH}_2\text{CH}_2\text{-SO}_3^-$). Thus, the electrolyte includes a combination of free and tethered anions. In the past, researchers have realized the importance of single-ion-conducting electrolytes, because these electrolytes prevent the formation of ion concentration regions within a cell, leading to stable ion transport even at a high charge rate. Recent linear stability analysis of electrodeposition showed that the stability of an electrolyte can be significantly enhanced by immobilizing only a small fraction (10%) of the anions. The design of an electrolyte for this embodiment, which is composed of a fraction of anions near the anodic surface, with LiNO_3 as the free salt, is to capture this theoretical framework. Thus, a modified SEI based on bromide ionomers tethered to the Li anode provides a powerful combination of processes that stabilize the anode against unstable electrodeposition.

[0078] **Characterizing cathode products.** A representative voltage profile for the galvanostatic discharge and charge for a Li-O₂ cell with 1 M LiNO_3 in an ionomer-enriched DMA electrolyte was prepared. Cutoff voltages of 2.2 and 4.3 V were used for the discharge and charge cycles, respectively, and both processes were performed at a fixed current density of $31.25 \mu\text{A}/\text{cm}^2$. Postmortem SEM analysis was used to study the evolution of discharge products on the cathode at three stages of discharge (D1, D2, and D3) and two stages of charge (C1 and C2). The SEM images show the reversible formation and decomposition of an insoluble solid product on the cathode. Complementary x-ray diffraction (XRD) analysis shows that the cathode product is exclusively Li_2O_2 (no other products, such as LiOH, are observed). The SEM analysis shows that Li_2O_2 particles grow increasingly larger as the discharge progresses and nucleation sites for growth are filled, and the full discharge capacity of the cell is reached. Analysis of the particle sizes on discharge reveals that, at low current densities (for example, $15 \mu\text{A}/\text{cm}^2$), large Li_2O_2 particles (1 μm and higher) are formed. Comparing these results to those reported by Lau and Archer (Nano Lett. 15, 5995-6002 (2015)) for Li-O₂ cells discharged in a 1 M LiTF in tetraethylene glycol dimethyl ether (TEGDME) (a low-donor number solvent), the Li_2O_2 particles formed in DMA are at least four times larger. These findings are consistent with expectations for the high DN of DMA, which solvates Li^+ cations and enables a solution-mediated mechanism, circumventing capacity limitations from the passivation layer formed at the cathode, which enables deep discharge. At higher current densities, the particle size at the voltage cutoff decreases drastically, consistent with the idea that kinetic diffusion limitations set the maximum particle

size. Upon charge, the SEM images show a cathode that closely resembles that of the pristine electrode before discharge. Redox mediation from lithium 2-bromoethanesulfonate is thought to aid in the electrochemical decomposition of the large, insulating Li_2O_2 particles formed on the cathode. Support for this belief comes from the effectiveness of the recharge process as well as from the flat charge profile observed until the full capacity of the discharge is reached; the voltage ultimately begins to rise because of the set voltage limit of 4.3 V. Thus, it was shown that a Li- O_2 cell with 1 M LiNO_3 -DMA in an ionomer-based SEI on Li can reach a high capacity through LiO_2 disproportionation, fully use the formed Li_2O_2 during the recharge, and cycles with features indicative of the presence of a redox mediator.

[0079] **Cycling performance.** To evaluate whether a high-DN electrolyte solvent and a redox mediator provide significant synergistic benefits for Li- O_2 cells, we compare the voltage profiles for fully discharged cells without and with these attributes. It is seen that the discharge capacity of Li- O_2 cells with a 1 M LiNO_3 -DMA with an electrolyte containing ionomer is noticeably higher (~6.5 mAh) than the discharge capacity of Li- O_2 cells with a conventional 1 M lithium bis(trifluoromethane)sulfonimide (LiTFSI)-diglyme (~5.1 mAh) with the same cathode loading. This finding is consistent with the observation of large-sized lithium peroxide structures owing to the solution-mediated nucleation of peroxides. Comparison of the charge cycle shows that with the diglyme electrolyte, the voltage diverges to >4.2 V in ~3.5-mAh capacity, which is believed to be an indication of Li_2CO_3 formation and its effect on the charging process, whereas with the ionomer-based electrolyte, the voltage diverges at ~6.5 mAh (same as discharge). Cyclic voltammetry experiment for a Li- O_2 cell in a two-electrode setup with lithium as both reference and counter electrode were performed between 1.9 and 4.5 V (versus Li/Li^+) at a scan rate of 1 mV/s, and the normalized current is plotted against voltage. The current peaks for the ionomer-based electrolyte are an order of magnitude higher than those for the control electrolyte. Thus, it can be inferred that there is higher electrochemical activity owing to the higher stability of the electrolyte and redox mediation due to the presence of LiBr. The peak seen at ~3.5 V can be attributed to a $\text{Br}_3^-/\text{Br}^-$ redox couple.

[0080] Discharge and charge profiles for cells having the electrolyte 1 M LiNO_3 -DMA with and without ionomers with a capacity cutoff of 3000 mAh/g and a current density of $0.04 \text{ mA}/\text{cm}^2$ were prepared. It was seen that both discharge and charge voltage curves tend to diverge to lower and higher values, respectively. Further, it was seen that the voltage profile becomes extremely noisy in the fifth cycle of the control electrolyte, whereas that with

the ionomer additive is stable. This instability without ionomers can be attributed to the degradation of the electrolyte by reaction with the unprotected lithium metal. One major benefit of cells cycled with ionomers is reduced overpotential during charge relative to that of the control cell, thus increasing cycling efficiency. This is studied in a Li-O₂ battery with a lower capacity cutoff of 800 mAh/g at a current density of 0.08 mA/cm² for the control electrolyte and the ionomer-added electrolyte. The highest voltage on charge for cells with ionomers is approximately 3.7 V, close to the Br⁻/Br₃⁻ redox reaction at 3.48 V. Control cells with solely 1 M LiNO₃-DMA reach voltages of around 4.45 V. This suggests a similar action to a redox mediator, in which Li₂O₂ is oxidized by Br₃⁻ to reform Br⁻ in a cycle that lowers charge overpotential. The discharge and charge profiles remain similar over 30 cycles for cells with additive, whereas the charge profile in untreated cells increases more drastically. The distinct gentle slope of the initial portion of the discharge profile in cells with ionomers can be attributed to the presence of bromine species in the system. Figure 8 compares the end voltage of recharge with and without the ionomer additive. The ~1-V improvement in the round-trip efficiency not only saves loss of input energy but also ensures long-life cycling by preventing electrolyte decomposition.

[0081] **Cathode stabilization mechanism.** At the cathode surface, LiBr is thought to participate in the redox mediation that promotes the OER reaction. In this process, the Li₂O₂ can be co-reduced with Br⁻ to form O₂ and Br₃⁻. The potential for Br⁻→Br₃⁻ is 3.48 V; thus, the charging of a Li-O₂ cell can be limited to this voltage. DMA's ability to dissolve peroxides also aids in the effective electrolyte-side redox mediation. Support for the uniqueness of these ideas comes from recent experiments that demonstrate the efficacy of LiI and LiBr as redox mediators in Li-O₂ cells based on glymes. In the absence of water in the electrolyte, LiI was reported to produce a gradual rise in the discharge voltage due to formation of iodine and similar products. LiBr was found to be ineffective in maintaining a steady charge voltage. In electrolytes with high water content and LiI, LiOH has been shown to be the primary discharge product, which has been reported to be thermodynamically impossible to undergo OER. Our results therefore clearly show that protecting the Li anode in a 1 M LiNO₃-DMA electrolyte with a SEI based on bromide ionomer overcomes fundamental limitations of the anode, cathode, and electrolyte in previously studied systems and enables stable cycling of these cells.

[0082] In summary, the present disclosure demonstrates that the addition of an ionomer to an electrolyte, viz lithium 2-bromoethanesulfonate (ionomer) to 1 M LiNO₃-DMA

electrolytes, produces an ionic membrane that act like a SEI at the lithium surface that stabilizes the anode in Li-O₂ cells by at least two powerful processes. Compared to control cells with the ionomer SEI, Li-O₂ cells based on lithium 2-bromoethanesulfonate exhibit flatter, more stable charge profiles and can withstand deeper cycling. Furthermore, we show that electrochemical charge-discharge processes in the cells coincide with the formation and decomposition of large Li₂O₂ particles as the principal OER product in the cathode. Analysis by linear scan voltammetry and “plate-strip” cycling analysis of the Li anode show that a SEI based on a lithium 2-bromoethanesulfonate ionomer on the anode provides chemical stability to Li against attack by DMA, as well as physical stability against rough, dendritic electrodeposition.

EXAMPLES

[0083] The following examples are intended to further illustrate certain preferred embodiments of the invention and are not limiting in nature. Those skilled in the art will recognize, or be able to ascertain, using no more than routine experimentation, numerous equivalents to the specific substances and procedures described herein.

[0084] **Materials Synthesis:** Functional IL monomers AMIM, DAIM and AVIM bearing perchlorate anion were synthesized according to the previous methods with modifications [7a]. In this work, NaClO₄ was used as the anion exchange source. The Na₃V₂(PO₄)₃ [23a] and SPAN [25b] cathode was synthesized based on the previous studies. The synthesized Na₃V₂(PO₄)₃ contains no graphene additive.

[0085] **Material Characterization:** The morphology of the sodium metals was studied by A LEO 1550 high resolution scanning electron microscopy (SEM), Olympus light microscope and Asylum MFP-3D atomic force microscopy (AFM). Waters Ambient-Temperature GPC was applied to analyze the molecular weight of the polymers. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Surface Science SSX-100 spectrometer using a monochromatic Al K α source (1486.6 eV). Non-linear least squares curve fitting was applied to the high-resolution spectra, using CasaXPS software.

[0086] **Electrochemical Characterization:** Protected sodium metal anode was created by charging Na/Na symmetric cell at constant current of 1mA/cm² for 10 hours in a carbonate electrolyte containing 20 wt% IL monomers. 2032 coin-type cells were assembled using sodium metal (Sigma Aldrich) as the anode electrode, a microporous material, Celgard 3401, membranes as separator, a cathode with 80% active material, 10% Super-P Li carbon

black from TIMCAL, and 10% poly (vinylidene difluoride) (PVDF, Sigma Aldrich) as binder in an excess of N-methyl-2-pyrrolidone in NMP, and electrolyte of 50 μ L 1M sodium perchlorate (NaClO_4) in ethylene carbonate/propylene carbonate (EC/PC vol:vol=1:1) for each cell. Cell assembly was carried out in an argon-filled glove-box (MBraun Labmaster). The room-temperature cycling characteristics of the cells were evaluated under galvanostatic conditions using Neware CT- 3008 battery testers and electrochemical processes in the cells were studied by cyclic voltammetry using a CHI600D potentiostat. Electrochemical impedance and floating tests were conducted by using a Solartron Cell Test System model 1470E potentiostat/galvanostat. For post-mortem studies, cells were disassembled in an argon-filled glove-box and the electrodes were harvested and rinsed thoroughly with the electrolyte solvent before analysis.

[0087] Li-O₂ battery methods and materials

[0088] **Cathode preparation.** A cathode slurry was prepared by mixing 180 mg of Super P carbon (TIMCAL), 20 mg of polyvinylidene fluoride (Sigma-Aldrich), and 2000 mg of N-methyl-2-pyrrolidone (Sigma-Aldrich) in a ball mill at 50 Hz for 1 hour. Toray TGP-H-030 carbon paper was coated with an 80- μ m-thick layer of carbon slurry using a doctor blade. The resulting coated carbon paper was dried at 100°C overnight under vacuum and transferred into an argon-filled glove box [O_2 , <0.2 parts per million (ppm); H_2O , <1.0 ppm; Innovative Technology] without exposure to air. Disks (15.9 mm in diameter) were punched and weighed from the carbon paper to yield individual carbon cathodes. The weight of the active carbon layer (not including the carbon paper) averaged 1.0 ± 0.1 mg.

[0089] **Electrolyte preparation.** LiNO_3 and LiTFSI were heated under vacuum overnight at 100°C to remove all traces of water and transferred directly into the glove box. DMA (Sigma-Aldrich) and bis(2-methoxyethyl) ether (diglyme; Sigma-Aldrich) solvents were dried over 3 Å molecular sieves (Sigma-Aldrich). Lithium 2-bromoethanesulfonate was obtained through ion exchange with sodium 2-bromoethanesulfonate (Sigma-Aldrich).

[0090] **Coin cell assembly.** First, a 0.5-inch-diameter (12.7-mm-diameter) hole was punched in the top (cathode) side of each CR2032 case. Then, a stainless steel wire cloth disk [disk diameter, 0.75 inches (19 mm); wire diameter, 0.0055 inches (0.140 mm)] from McMaster-Carr was added, followed by a cathode disk, a 19-mm-diameter separator (either Whatman GF/D glass fiber or Celgard 3501), 100 μ L of desired electrolyte, 0.5-inch-diameter lithium metal, a 15.5-mm-diameter stainless steel spacer disk, a stainless steel wave spring

(MTI Corporation), and an anode cap of the CR2032 case. The assembly was crimped to a pressure of 14 MPa with a hydraulic coin cell crimp (BT Innovations).

[0091] **Testing environment.** Cells were tested at a regulated pure O₂ environment of 1.3 atm and allowed to equilibrate for 6 hours before electrochemical testing. Galvanostatic measurements were conducted using a Neware CT-3008 battery tester.

[0092] **Cyclic voltammetry.** The cyclic voltammetry test was performed in a two-electrode setup of Lillair cathode. The batteries were cycled between 1.9 and 4.5 V at a scan rate of 1 mV/s several times.

[0093] Evaluating anode stability

[0094] **Impedance spectroscopy.** Cells in the symmetric configuration were assembled in an Ar glove box. Measurements were carried out using a Solatron frequency analyzer at a frequency range of 10⁻³ to 10⁷ Hz. The data were fitted into Nyquist-type plots using the equivalent circuit shown in fig. S2 with the software ZSimpWin. Impedance was conducted at room temperature at various time intervals.

[0095] **Linear scan voltammetry.** Linear scan voltammetry was performed in a Lillstainless steel cell. The batteries were first swept to -0.2 V versus Li/Li⁺ and then they were swept in reverse direction until the voltage diverges.

[0096] **Lithium versus stainless steel cycling.** For cycling tests, lithium versus stainless steel cells were prepared and were cycled at 0.01 mA/cm² between 0 and 0.5 V 10 times to form a stable SEI layer. Then, different tests were carried out as previously described.

[0097] Characterization techniques

[0098] **SEM and energy-dispersive analysis of x-rays.** Discharged cells were disassembled inside the glove box, and the cathodes were removed and transported to the SEM (Zeiss, LEO 1550 Field Emission SEM) within an airtight container. The cathodes were loaded onto the stage in the presence of a nitrogen stream. Images were taken with a single pass after focusing on a nearby region. Energy-dispersive analysis of x-ray (EDAX) measurements were performed by taking multiple counts on a small section of the sample.

[0099] **X-ray diffraction.** Cathodes were mounted on a glass microscope slide inside an argon-filled glove box and coated with paraffin oil to protect them from air during the XRD measurements. Measurements were performed on a Scintag Theta-Theta x-ray diffractometer using Cu K- α radiation at $\lambda = 1.5406\text{\AA}$ and fitted with a two-dimensional

detector. Frames were captured with an exposure time of 10 min, after which they were integrated along χ (the polar angle orthogonal to 2θ to yield an intensity-versus- 2θ plot.

[00100] **X-ray photoelectron spectroscopy.** XPS was conducted using Surface Science Instruments SSX-100 with an operating pressure of $\sim 2 \times 10^{-9}$ torr. Monochromatic Al K- α x-rays (1486.6 eV) with a beam diameter of 1 mm were used. Photoelectrons were collected at an emission angle of 55° . A hemispherical analyzer determined electron kinetic energy using a pass energy of 150 V for wide survey scans and 50 V for high-resolution scans. Samples were ion-etched using 4-kV Ar ions, which were rastered over an area of 2.25 mm $\times$ 4 mm with a total ion beam current of 2 mA, to remove adventitious carbon. Spectra were referenced to adventitious C 1s at 284.5 eV. CasaXPS software was used for XPS data analysis with Shelby backgrounds. Li 1s and O 1s were assigned to single peaks for each bond, whereas Br 3d was assigned to double peaks ($3d_{5/2}$ and $3d_{3/2}$) for each bond with 1.05-eV separation. Residual SD was maintained close to 1.0 for the calculated fits. Samples were exposed to air only during the short transfer time to the XPS chamber (less than 5 s).

[00101] While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof. Thus, for example, those skilled in the art will recognize, or be able to ascertain, using no more than routine experimentation, numerous equivalents to the specific substances and procedures described herein. Such equivalents are considered to be within the scope of this invention, and are covered by the following claims.

WHAT IS CLAIMED IS:

1. A rechargeable battery comprising a metal anode, a cathode and an electrolyte, wherein the metal anode has an ionic membrane thereon which can continuously supply ions near the metal anode and protect the metal anode.
2. The rechargeable battery of claim 1, wherein the ionic membrane comprises an ionic polymer membrane.
3. The rechargeable battery of claim 2, wherein the ionic polymer membrane is formed from one or more polymerizable ionic liquids having more than one polymerizable groups and an anion.
4. The rechargeable battery of claim 3, wherein the metal anode comprises substantially metallic sodium.
5. The rechargeable battery of claim 1, wherein the ionic membrane comprises alkyl anions tethered to the metal anode.
6. The rechargeable battery of claim 5, wherein the alkyl anions tethered to the metal anode are formed from one or more halogenated alkyl anion salts.
7. The rechargeable battery of claim 5, wherein the alkyl anions tethered to the metal anode are formed from one or more halogenated alkyl sulfonate salts.
8. The rechargeable battery of claim 7, wherein the metal anode comprises substantially metallic lithium.
9. The rechargeable battery of any one of claims 1-8, wherein the electrolyte includes one or more ionomers that form the ionic membrane.
10. The rechargeable battery of any one of claims 1-9, wherein the rechargeable battery has a coulombic efficiency exceeding 90 %.

11. The rechargeable battery of any one of claims 1-10, wherein the rechargeable battery can stably cycle over 100 cycles.
12. The rechargeable battery of any one of claims 1-11, wherein the ionic membrane has a thickness in the range of about 5 nm to about 500 microns.
13. The rechargeable battery of any one of claims 1-3, 5-7, or 9-12 wherein the metal anode comprises substantially metallic lithium, metallic sodium, metallic aluminum, or metallic zinc.
14. A method of preparing a metal anode electrode for a rechargeable battery, the method comprising:

forming a conformal ionic membrane directly on a surface of the metal anode from one or more ionomers wherein the ionic membrane can continuously supply ions near the metal anode and protect the metal anode.
15. The method of claim 14, wherein forming the conformal ionic membrane includes electropolymerizing a polymerizable ionic liquid monomer as the ionomer onto the metal anode to form the ionic membrane.
16. The method of claim 14, comprising forming the conformal ionic membrane directly on the surface of a substantially metallic sodium anode by electropolymerizing a polymerizable ionic liquid monomer having more than one polymerizable groups onto the metal anode to form the ionic membrane.
17. The method of claim 14, wherein forming the ionic membrane includes adsorbing halogenated alkyl anion salts as the ionomer onto the metal anode to form the ionic membrane.
18. The method of claim 14, wherein forming the ionic membrane includes adsorbing halogenated alkyl sulfonate salt as the ionomer onto a substantially metallic lithium anode as the metal anode to form the ionic membrane.

19. The method of any one of claims 14-18, wherein the ionomer is added to an electrolyte of the rechargeable battery.
20. The method of claim 19, wherein the ionomer is added to the electrolyte in an amount of from about 1 to about 30 weight percent of the electrolyte.

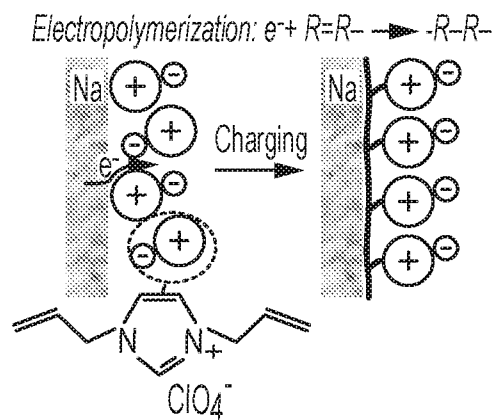


FIG. 1

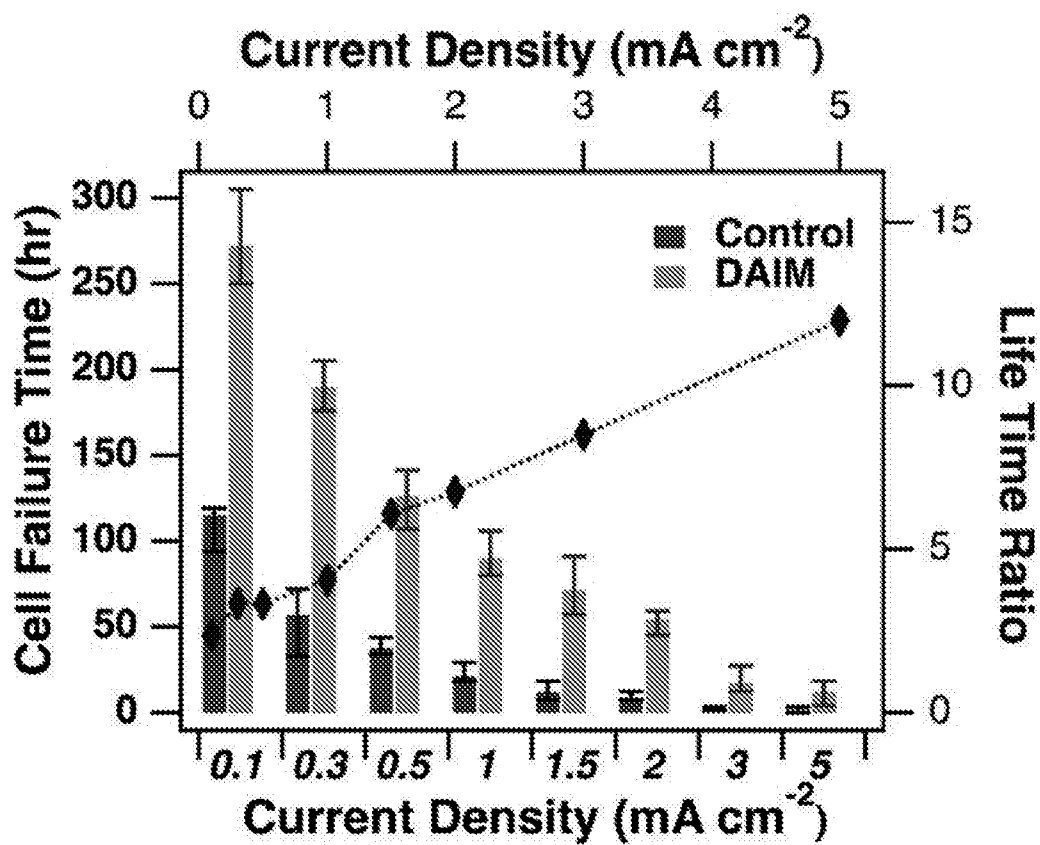


FIG. 2

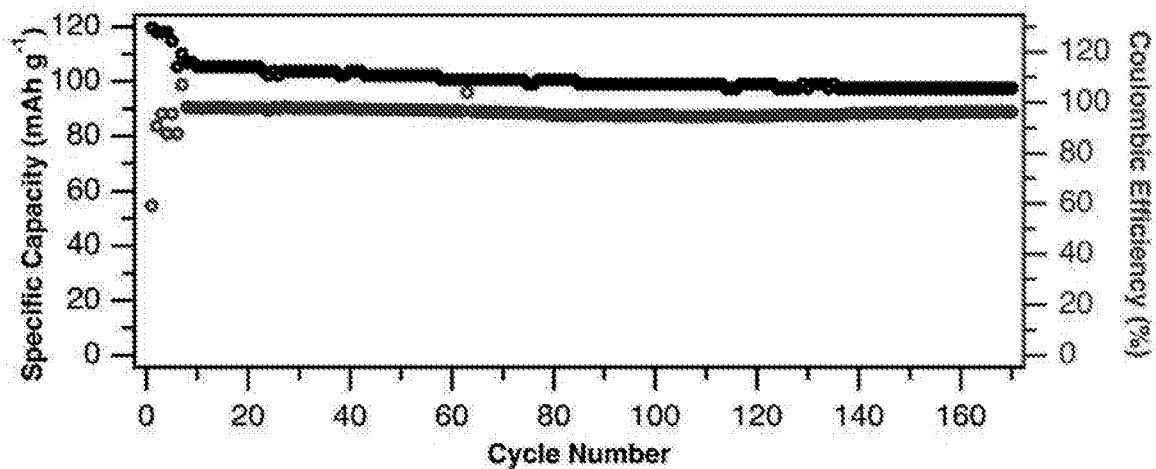


FIG. 3A

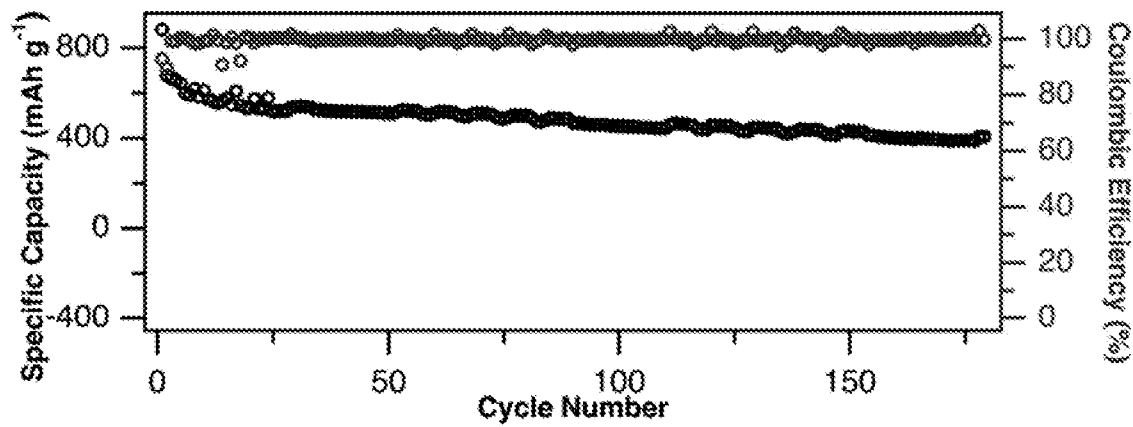


FIG. 3B

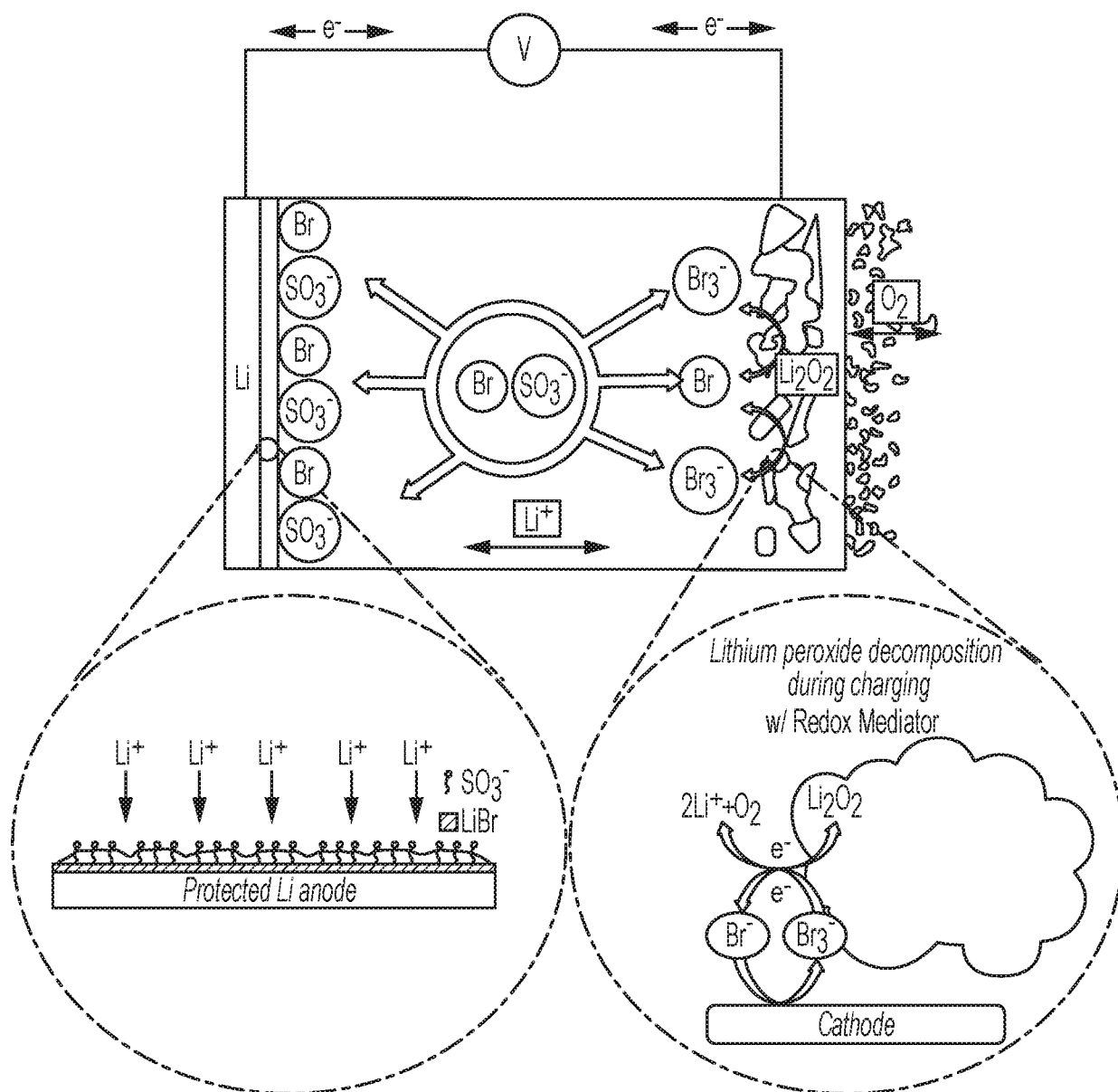


FIG. 4

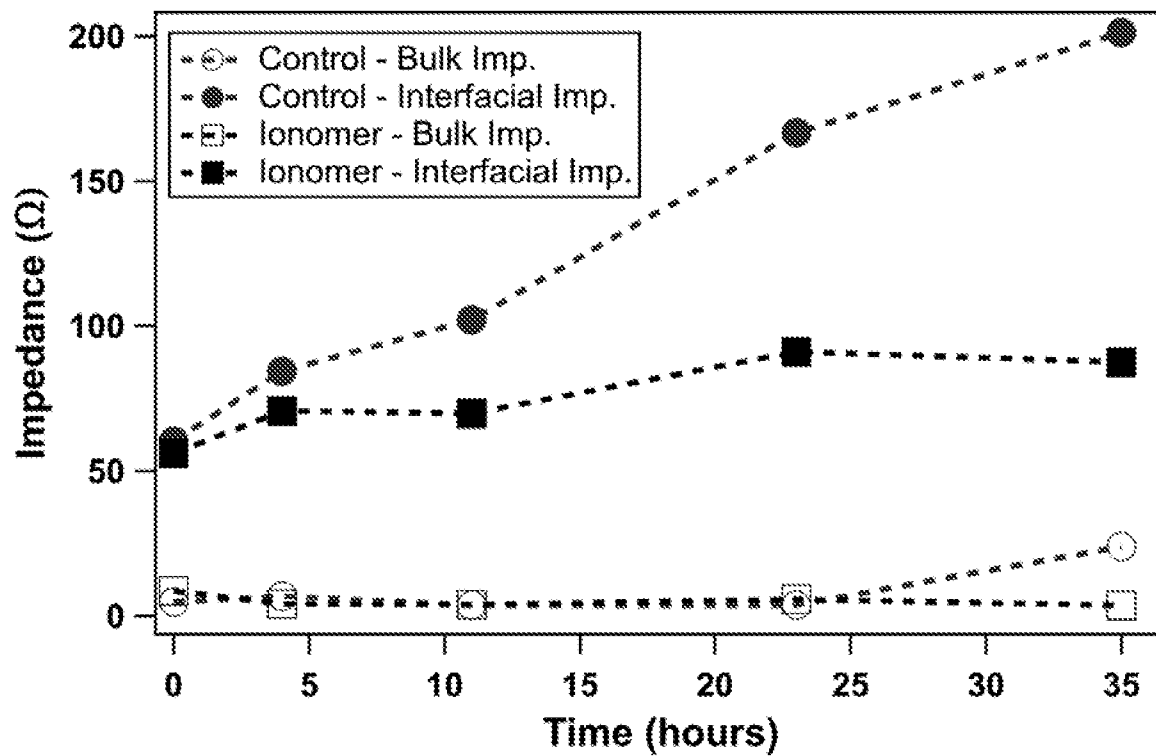


FIG. 5

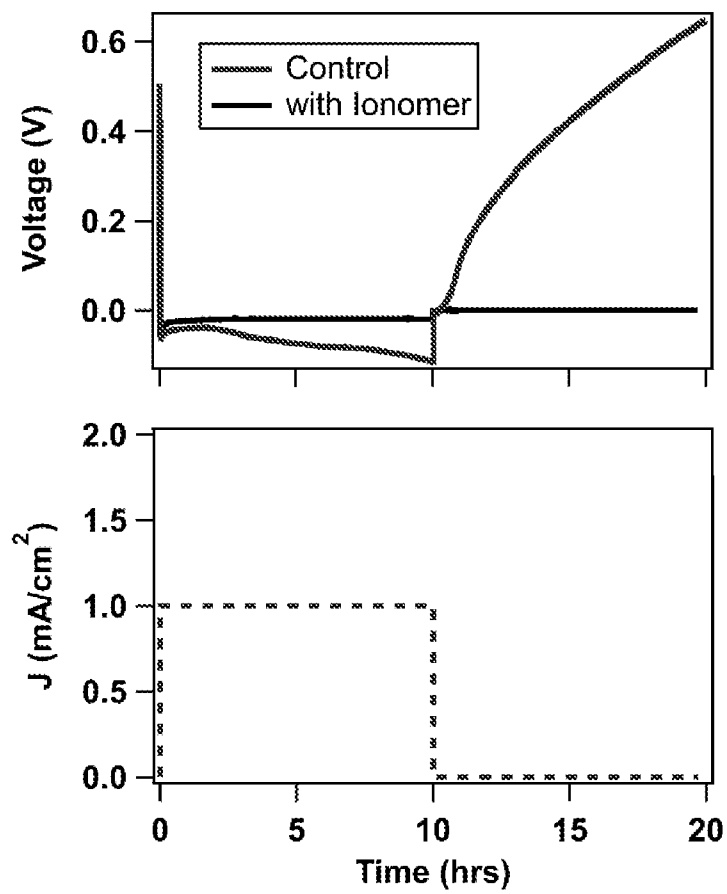


FIG. 6

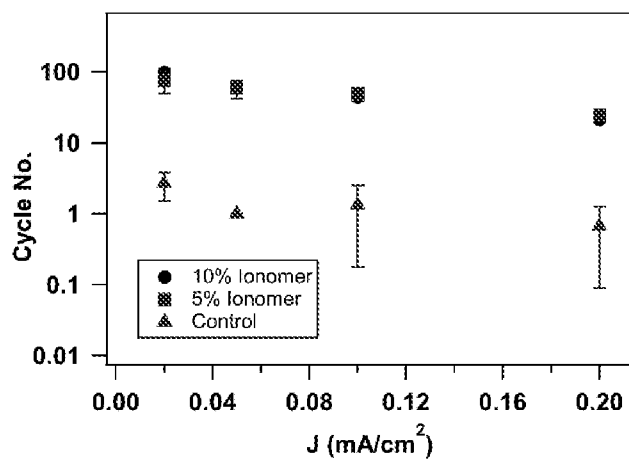


FIG. 7

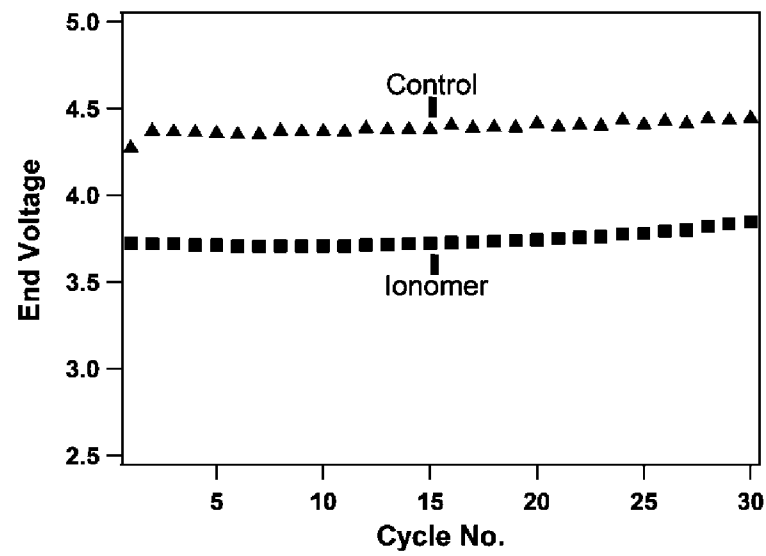


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/067357

A. CLASSIFICATION OF SUBJECT MATTER INV. H01M4/38 H01M10/052 H01M10/054 H01M10/0567 H01M4/04 H01M4/36 ADD. 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) H01M 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) EPO-Internal, CHEM ABS Data, WPI Data								
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category*</th> <th style="width: 70%; padding: 5px;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%; padding: 5px;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;"> M. D. TIKEKAR ET AL: "Stabilizing electrodeposition in elastic solid electrolytes containing immobilized anions", SCIENCE ADVANCES, vol. 2, no. 7, 15 July 2016 (2016-07-15), pages e1600320-e1600320, XP055457015, DOI: 10.1126/sciadv.1600320 abstract ----- -/-- </td> <td style="text-align: center; vertical-align: top; padding: 5px;"> 1,13,14, 19,20 </td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	M. D. TIKEKAR ET AL: "Stabilizing electrodeposition in elastic solid electrolytes containing immobilized anions", SCIENCE ADVANCES, vol. 2, no. 7, 15 July 2016 (2016-07-15), pages e1600320-e1600320, XP055457015, DOI: 10.1126/sciadv.1600320 abstract ----- -/--	1,13,14, 19,20
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.						
X	M. D. TIKEKAR ET AL: "Stabilizing electrodeposition in elastic solid electrolytes containing immobilized anions", SCIENCE ADVANCES, vol. 2, no. 7, 15 July 2016 (2016-07-15), pages e1600320-e1600320, XP055457015, DOI: 10.1126/sciadv.1600320 abstract ----- -/--	1,13,14, 19,20						
☒ 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 "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family								
Date of the actual completion of the international search 8 March 2018	Date of mailing of the international search report 28/05/2018							
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Steinreiber, J							

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/067357

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHENGYUAN TU ET AL: "Nanostructured Electrolytes for Stable Lithium Electrodeposition in Secondary Batteries", ACCOUNTS OF CHEMICAL RESEARCH., vol. 48, no. 11, 23 October 2015 (2015-10-23), pages 2947-2956, XP055457028, US ISSN: 0001-4842, DOI: 10.1021/acs.accounts.5b00427 abstract	1,13,14, 19,20
X	KAI ZHANG ET AL: "Recent Developments of the Lithium Metal Anode for Rechargeable Non-Aqueous Batteries", ADVANCED ENERGY MATERIALS, vol. 6, no. 20, 27 June 2016 (2016-06-27), page 1600811, XP055457013, DE ISSN: 1614-6832, DOI: 10.1002/aenm.201600811 chapters 2.1.2; 2.2; 2.4.1	1,2,9, 13,14, 19,20
X	JUNHUI ZHOU ET AL: "N-Allyl-N-Methyl Piperidinium Bis (trifluoromethanesulfonyl) Imide as a Co-Solvent in Li-Ion Batteries", ADVANCED MATERIALS RESEARCH, vol. 750-752, 30 August 2013 (2013-08-30), pages 1194-1198, XP055457322, DOI: 10.4028/www.scientific.net/AMR.750-752.1194 abstract	1-3, 9-15,19, 20
Y	abstract	3,12,15
Y	JAKUB REITER ET AL: "-Allyl--methylpiperidinium bis(trifluoromethanesulfonyl)imideA film forming ionic liquid for graphite anode of Li-ion batteries", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 71, 10 March 2012 (2012-03-10), pages 22-26, XP028421960, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2012.03.088 [retrieved on 2012-03-27] abstract	3,15
A	abstract	1
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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/067357

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JUNYOUNG MUN ET AL: "Allylic ionic liquid electrolyte-assisted electrochemical surface passivation of LiCoO ₂ for advanced, safe lithium-ion batteries", SCIENTIFIC REPORTS, vol. 4, no. 1, 29 August 2014 (2014-08-29), XP055457324, DOI: 10.1038/srep05802 abstract	3,12,15
X,P	----- SHUYA WEI ET AL: "Highly Stable Sodium Batteries Enabled by Functional Ionic Polymer Membranes", ADVANCED MATERIALS, vol. 29, no. 12, 23 January 2017 (2017-01-23), page 1605512, XP055456982, DE ISSN: 0935-9648, DOI: 10.1002/adma.201605512 the whole document -----	1-4, 9-16,19, 20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/067357

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

2-4, 15, 16(completely); 1, 9-14, 19, 20(partially)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 2-4, 15, 16(completely); 1, 9-14, 19, 20(partially)

metal anodes comprising an ionic polymer membrane

2. claims: 5-8, 17, 18(completely); 1, 9-14, 19, 20(partially)

metal anodes comprising alkyl anions tethered to the metal anode
