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(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventors; and
(71) Applicants : **LAMANNA, William M.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **TRAN, Tuan T.** [VN/CA]; 1459 Oxford Street, Halifax, Nova Scotia B3H 4R2 (CA). **OBROVAC, Mark N.** [CA/CA]; 1459 Oxford Street, Halifax, Nova Scotia B3H 4R2 (CA).

(74) Agents: **BRAMWELL, Adam M.,** et al.; 3M Center Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

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(54) Title: ELECTROCHEMICAL MAGNESIUM CELL AND METHOD OF MAKING SAME

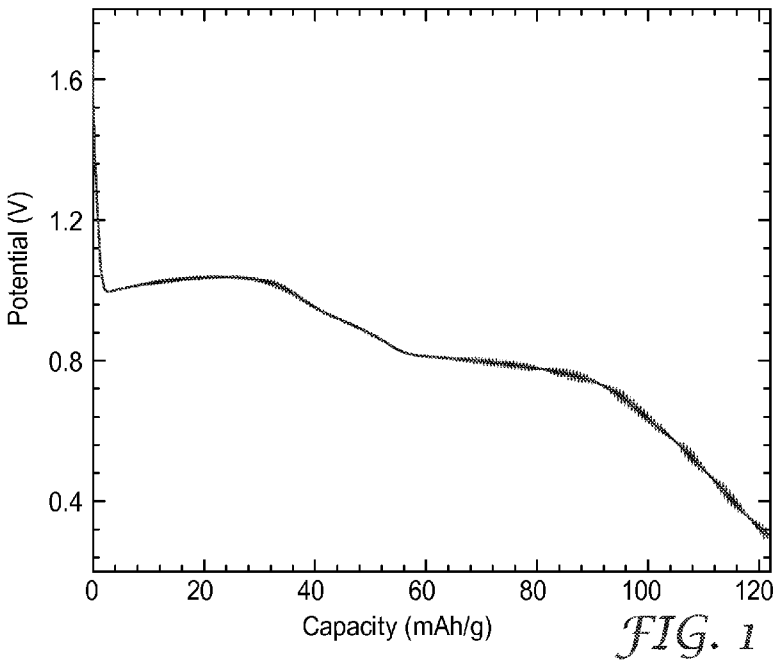

FIG. 1

(57) Abstract: An electrochemical cell is provided that includes at least one electrode that includes a magnesium intercalation compound. The provided electrochemical cell also includes an electrolyte that includes a fluorinated imide salt or a fluorinated methide salt substantially dissolved in an oxidatively stable solvent. The oxidatively stable solvent comprises a nitrile group and in some embodiments can include acetonitrile or adiponitrile.

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ELECTROCHEMICAL MAGNESIUM CELL AND METHOD OF MAKING SAME

Field

The present disclosure relates to primary and secondary electrochemical cells that include magnesium electrode materials and electrolytes for the same.

Background

There has been a lot of interest in rechargeable electrochemical cells as a way of storing energy for use in portable or mobile devices such as, for example, cell phones, personal digital assistants, plug-in hybrid vehicles, or electric vehicles. Much of the recent work has been to develop lithium-ion electrochemical cells that have high storage capacities and that can be operated safely. Magnesium has been suggested as a potential anode material for rechargeable nonaqueous electrochemical cells due to its abundance, its high charge density, and its ability to transfer two electrons upon ionization.

Hideyuku et al. (JP 2004-265765) have designed a secondary battery that has a sulfur positive electrode and a negative electrode that contains at least one of magnesium metal, magnesium alloy, magnesium oxide, silicon, carbon, and transition metal sulfide as an active material. The battery has a non-aqueous electrolyte containing a magnesium salt such as magnesium [bis(trifluoromethanesulfonyl)imide]$_2$.

NuLi et al. (*Electrochemical and Solid-state Letters,* **8,** (11) C166-C169 (2005)) and Shimamura et al. (*Journal of Power Sources,* **196**, 1586-1588 (2011)) have both reported the deposition and dissolution of magnesium from an ionic liquid. NuLi has reported electrochemical magnesium deposition and dissolution on a silver substrate in the ionic liquid N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonylimide) containing 1M Mg[$(CF_3SO_2)_2N]_2$. Shimamura has reported electrochemical reduction and oxidation of magnesium cation in ionic liquids containing simple magnesium salts. The ionic liquid that they used was N,N-diethyl-N-methyl-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide.

Summary

One of the challenges for the development of magnesium electrochemical cells and batteries is that of finding useful electrolytes. Magnesium analogues of common electrolyte salts (e.g. $Mg(PF_6)_2$, $Mg(ClO_4)_2$, $Mg(SO_3CF_3)_2$) generally have low solubility in electrolyte solvents. Furthermore, common electrolyte solvents are generally believed to form a blocking solid electrolyte interface (SEI) layer at low voltages that can increase internal impedance, reduce the charge rates, and impede electrochemical reactions essential to the efficient operation of magnesium electrochemical cells.

Nonaqueous magnesium electrolytes in which magnesium electrochemistry can be conducted at low overpotentials are typically solutions that contain Grignard reagents. Such solutions typically

are composed of a solution of magnesium alkyl halide in tetrahydrofuran. Such solutions are toxic and react spontaneously with oxygen in the air, making them not compatible with dry room environments. They also are oxidatively unstable, limiting the voltage of magnesium batteries to below about 2.5 V.

Provided are concentrated magnesium electrolyte solutions that can be made with magnesium [bis(trifluoromethanesulfonyl)imide]$_2$, or $Mg(TFSI)_2$ salts in common oxidatively stable organic solvents (acetonitrile, carbonates, pyridine). In such solutions magnesium metal can be stripped at low overpotentials. Efficient magnesium intercalation at voltages of 0.5 V or greater can be achieved only when acetonitrile or adiponitrile is used as the solvent. Since acetonitrile and adiponitrile are much more oxidatively stable than THF or the Grignard reagents currently used, electrolytes made from $Mg(TFSI)_2$ and acetonitrile or adiponitrile may be highly useful as electrolytes for high voltage magnesium batteries. The utility of this electrolyte in primary cells has been demonstrated using a Mg metal anode and a Mo_6S_8 cathode. Electrochemical reversibility of $Mg(TFSI)_2$ electrolytes has also been observed, demonstrating usefulness in high voltage magnesium secondary cells.

In one aspect, an electrochemical cell is provided that includes at least one electrode comprising a magnesium intercalation compound, and an electrolyte. The electrolyte includes a fluorinated imide salt or a fluorinated methide salt substantially dissolved in an oxidatively stable solvent. The at least one electrode can include a magnesium intercalation compound selected from transition metal sulfides, transition metal oxides, magnesium transition metal sulfides, magnesium transition metal oxides, and carbon fluorides. The provided electrochemical cell can include a negative electrode comprising magnesium. The provided electrochemical cell can be a primary (or non-rechargeable) electrochemical cell or a secondary (or rechargeable) electrochemical cell. In some embodiments, the provided electrochemical cell can be operated at temperatures greater than about 40°C and/or at voltages at or above 3.0V vs. Li/Li^+.

In another aspect, a method of making an electrochemical cell is provided that includes dissolving a fluorinated imide or fluorinated methide salt in an oxidatively stable solvent to form an electrolyte, immersing at least one electrode that includes a magnesium intercalation compound into the electrolyte, and immersing a second electrode comprising magnesium into the electrolyte. The at least one electrode can be selected from transition metal sulfides, transition metal oxides, magnesium transition metal sulfides, magnesium transition metal oxides, and carbon fluorides.

In yet another aspect a magnesium electrochemical cell is provided that includes a liquid organic electrolyte, wherein the electrochemical cell is operated at a temperature greater than 40°C.

In this disclosure:

"active" or "electrochemically active" refers to a material that can undergo magnesiation and demagnesiation by reaction with magnesium;

"chevrel" refers to chalcogenides that include molybdenum sulfides, selenides and tellurides that have structures that can intercalate magnesium;

"inactive" or "electrochemical inactive" refers to a material that does not react with magnesium and does not undergo magnesiation or demagnesiation;

"magnesiation" or "demagnesiation" refer to the processes of reactively inserting magnesium into an active material such as a magnesium intercalation compound or removing magnesium from an active material such as a magnesium intercalation material respectively;

"intercalation" refers to a processes in which magnesium can be reversibly inserted into and removed from a magnesium intercalation compound without substantially changing the crystal structure of the magnesium intercalation host compound;

"negative electrode" refers to an electrode (often called an anode) where electrochemical oxidation and demagnesiation occurs during a discharging process; and

"positive electrode" refers to an electrode (often called a cathode) where electrochemical reduction and magnesiation occurs during a discharging process.

The provided electrochemical cells and methods of making the same provide an electrolyte salt that has high solubility in nitrile-containing solvents. Furthermore, the provided electrochemical cells and methods resist the formation of a blocking solid electrolyte interphase layer that can impede electrochemical reactions essential to the efficient operation of magnesium electrochemical cells.

The above summary is not intended to describe each disclosed embodiment of every implementation of the present invention. The brief description of the drawings and the detailed description which follows more particularly exemplify illustrative embodiments.

Brief Description of the Drawings

Fig. 1 shows the voltage curve of the Mo_6S_8 vs. Mg coin cell of Example 1.

Fig. 2 shows the x-ray diffraction pattern of the discharged Mo_6S_8 electrode of Example 1.

Fig. 3 shows the voltage curve of the Mo_6S_8 vs. Mg coin cell of Example 2.

Fig. 4 shows the x-ray diffraction pattern of the discharged Mo_6S_8 electrode of Example 1.

Fig. 5 shows the voltage curve of the Mo_6S_8 vs. Mg coin cell with Mg wire reference electrode of Example 4.

Fig. 6 shows the voltage curve of the Mo_6S_8 vs. discharged Mo_6S_8 coin cell of Example 5.

Fig. 7 shows the voltage curve of the Mo_6S_8 vs. Mg coin cell of Example 6.

Fig. 8 shows the cyclic voltammagram of the cell described in Example 7.

Detailed Description

In the following description, reference is made to the accompanying set of drawings that form a part of the description hereof and in which are shown by way of illustration several specific embodiments. It is to be understood that other embodiments are contemplated and may be made without departing from the scope or spirit of the present invention. The following detailed description, therefore, is not to be taken in a limiting sense.

Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings disclosed herein. The use of numerical ranges by endpoints includes all numbers within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5) and any range within that range.

Electrochemical cells are provided that include at least one electrode that includes a magnesium intercalation compound and an electrolyte that includes a fluorinated imide salt or a fluorinated methide salt that is substantially dissolved in an oxidatively stable solvent. A number of materials are known to intercalate magnesium. Exemplary materials include TiS_2, V_6O_{13}, V_2O_5, WO_3, MoO_3, MnO_2, InSe, and some sulfides of molybdenum. These materials are discussed, for example, in P. G. Bruce et al., "Chemical Intercalation of Magnesium into Solid Hosts", *J. Mater. Chem.,* 1(4), 705-706 (1991) and Z. D. Kovalyuk et al, "Electrical Properties of Magnesium-Intercalated InSe", *Inorganic Materials,* 45(8), 846-850 (2009). Another set of materials that can intercalate magnesium are the chevrel phase materials of molybdenum sulfide, selenide, and telluride. For example, $Mg_xMo_3S_4$ intercalation cathodes have been disclosed in an article by D. Aurbach et al., *Nature,* 407, 724 (2000) and in U. S. Pat. Appl. Publ. No. 2004/0137324 (Itaya et al.). Magnesium chevrel phases can have various stoichiometries such as $MgMo_3S_4$ or $Mg_2Mo_6S_8$. Since magnesium intercalates into the chevrel materials, the amount of magnesium can vary depending upon the amount of intercalation. Other intercalation electrode materials that may be useful are described in International PCT Pat. App. Publ. No. WO2011/150093 (Doe et al.).

The provided electrochemical cells may include a current collector comprising one or more elements selected from the group consisting of carbon, Al, Cu, Ti, Ni, stainless steel, and alloys thereof, as described in U. S. Pat. App. Publ. No. 2011/0159381 (Doe et al.).

The provided electrochemical cells include an electrolyte that includes a fluorinated imide salt or a fluorinated methide salt substantially dissolved in an oxidatively stable solvent. The fluorinated imide or fluorinated methide salts include a bis(trifluoromethylsulfonyl)imide anion or a bis(trifluoromethylsulfonyl)methide anion having the formulae:



or ,

wherein each R_f group is, independently, F or a fluoroalkyl group having 1-4 carbon atoms, which may optionally contain catenary oxygen or nitrogen atoms within the carbon chain, and wherein any two adjacent R_f groups may optionally be liked to form a 5-7 membered ring. The salts can have cations selected from ammonium, imidazolium, pyrazolium, triazolium, thiazolium, oxazolium, pyridinium, pyridazinium, pyrimidonium, and pyrazinium. In some embodiments, the cations can be

metals such as sodium, lithium, potassium, or magnesium. Generally, at least some of the cations are magnesium cations. Typically, magnesium [bis(trifluoromethanesulfonyl)imide]$_2$ or magnesium [tris(trifluoromethanesulfonyl)methide]$_2$ are employed in the provided electrolytes. Magnesium [bis(trifluoromethanesulfonyl)imide]$_2$ can be produced by reacting magnesium carbonate or magnesium hydroxide or magnesium metal with bis-(trifluoromethanesulfonyl)imide acid. Magnesium [tris(trifluoromethanesulfonyl)methide]$_2$ can be produced in an analogous manner from tris-(trifluoromethanesulfonyl)methide acid.

Fluorinated imide or methide salts such as, for example, magnesium [bis(trifluoromethylsulfonyl)imide]$_2$ ($Mg(TFSI)_2$) or magnesium [tris(trifluoromethylsulfonyl)methide]$_2$ ($Mg(TFSM)_2$), can be dissolved in oxidatively stable solvents such as organic carbonates, nitriles, and pyridine solvent systems. The disclosed $Mg(TFSI)_2$ or $Mg(TFSM)_2$ electrolyte salts can provide a number of surprising benefits when used in primary or secondary Mg cells. These salts can be both highly soluble and highly dissociated in oxidatively and reductively stable, nonaqueous organic solvents, including but not limited to, organic carbonates, nitriles, and pyridines. In some embodiments, the oxidatively stable organic solvents can include aliphatic nitriles such as acetonitrile, propionitrile, valeronitrile, isobutylnitrile, isopentylnitrile, t-butylnitrile, and dinitriles such as succinonitrile, malononitrile, or adiponitrile.

High concentrations of electrolyte salt possessing high dissociation constants in organic solvents can be highly desirable for achieving high ionic conductivity in the electrolyte and to support high rate charge and discharge performance in Mg cells. With $Mg(TFSI)_2$, electrolyte salt, concentrations up to 1.0 M (molar) or higher are possible, depending on the choice of solvents. For example, $Mg(TFSI)_2$ can be dissolved in acetonitrile to form solutions having a concentration of at least 0.1M, at least 0.5M, or even at least 1.0 M at room temperature. The solubility of $Mg(TFSI)_2$ can be even greater at elevated temperatures such as at temperatures greater than about 40°C. Solvents such as organic carbonates, nitriles, and pyridines provide a wide electrochemical stability window and thus enable production of high voltage Mg batteries. Acetonitrile has been found to be a particularly useful solvent because it is capable of supporting reversible Mg electrochemistry at relatively low overpotentials. Another advantage of $Mg(TFSI)_2$ is that it is chemically stable to air and moisture, unlike certain background art electrolytes, like Grignard reagents, which are extremely difficult to handle due to their air and moisture sensitivity and their pyrophoric nature. Furthermore, whereas Grignard reagents are oxidatively unstable and therefore limit overall cell potentials for Mg batteries, $Mg(TFSI)_2$ is much more stable to oxidation and thereby enables production of high voltage Mg batteries.

The thermally stable nature of electrolytes that include $Mg(TFSI)_2$ or $Mg(TFSM)_2$ and solvents such as organic carbonates, nitriles, and pyridine enables batteries comprising these electrolytes to be operated a elevated temperature. For example, batteries comprising these electrolytes can be operated at temperatures above 30°C, or above 40°C, or above 50°C or above 60°C,

or even higher. The limiting temperature factor can be the boiling point of the most volatile solvent in the electrolyte solution.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

Examples

Preparation of magnesium [bis-(trifluoromethanesulfonyl)imide]$_2$ ($Mg(TFSI)_2$)

High purity Mg chips (99.98% from Aesar, 9.350g) and 150 g of deionized water (18 MOhm) were charged to a 1.0 L flask equipped with a condenser, nitrogen line, Claisen adapter and an addition funnel. A 55.5 weight percent (wt%) solution of $H\text{-}N(SO_2CF_3)_2$ in water (360.36 g, prepared according to PCT Pat. Appl. Publ. No. WO 97/23448, Example #12) was added dropwise with magnetic stirring at room temperature causing a mild exotherm and moderate gas evolution. After all of the imide acid solution was added, the reactor was equipped with a thermocouple probe and a heating mantle and the reaction solution was heated to 90°C with stirring for two hours. After 2 hours, the pH of the reaction solution was 8.0 (according to pH stick) indicating that the reaction of the imide acid with excess Mg was complete. After the reaction solution was cooled to room temperature, it was filtered by suction through a 0.2 micron filter membrane to remove insoluble magnesium fines to yield 530.2 g of clear colorless aqueous filtrate (pH = 8.0). The recovered filtrate was concentrated by short path distillation at atmospheric pressure to a final weight of 321.57 g and the concentrate was filtered again by suction through a 0.2 micron filter membrane to remove a small amount of insoluble solids. The filtered concentrate was transferred to a Pyrex crystallizing dish and evaporated to near dryness at 145°C in a convection oven and then dried more completely in a vacuum oven at the same temperature. Once dry, the fused white solid was chipped out of the crystallizing dish and transferred to a mortar and pestle where it was ground to a fine powder and immediately transferred to a glass canning jar for further vacuum drying overnight at 145°C to a final pressure of 45 mTorr. The product was allowed to cool to room temperature in vacuo and then vented with dry nitrogen, immediately capped and transferred to a nitrogen-filled drybox for storage. The isolated yield of anhydrous $Mg(TFSI)_2$ product was 165.2g (79.5% of theory). Analysis of the product by quantitative ^1H and ^{19}F NMR spectroscopy indicated that it was of high purity, containing 99.902% by wt. $Mg[(N(SO_2CF_3)_2]_2$. Water levels measured by Karl-Fischer analysis were 34 ppm and chloride ion levels measured by ion chromatography were < 3ppm. Levels of common metal ion impurities (24 element scan) were determined by ICP-MS and all metallic impurities were found to be present at less than 3 ppm in the product.

Mo_6S_8 Electrode Preparation

Chevrel phase Mo_6S_8 was prepared by chemical extraction of Cu from $Cu_2Mo_6S_8$. 5.0839 g of Cu powder (Alfa Aesar, -325 mesh, 10% max +325 mesh, 99% metals basis), 7.7136 g Mo powder (Sigma Aldrich, 1-2 μm, ≥99.9%, trace metals basis) and 25.6209 g of MoS_2 powder (Alfa Aesar, -325 mesh, 99% metals basis) were blended together by hand and placed in an alumina boat. The powder mixture was then heated under vacuum at 150°C for 12 hours, ramped to 985°C at a rate of 500°C/hr and held at 985°C for 150 hours. The sample was then cooled to room temperature over 12 hours under vacuum. X-ray diffraction measurement showed that the product was $Cu_2Mo_6S_8$.

About 10 g of $Cu_2Mo_6S_8$ were placed in a 100 ml round bottom flask. A 6M HCl was prepared by diluting concentrated HCl (ACP, A.C.S Reagent). About 80 ml of the 6M HCl solution were added to the round bottom flask. The powder / HCl slurry was stirred for 18 hours while oxygen was bubbled through the slurry. The slurry was then filtered through a Buchner funnel and washed with 6M HCl until the filtrate became colorless. The washed powder was dried 120°C in air for two hours. X-ray diffraction measurements of this powder showed that it was the Chevrel phase of Mo_6S_8.

3.2 g Mo_6S_8 powder, 0.4 g of Super P carbon black (MMM Carbon, Belgium), 0.4 g PVDF (Kynar, HSV900) and 10 g N-methylpyrrolidone (Sigma Aldrich, 99.5% anhydrous) were added to a 50 ml hardened steel grinding jar (Retsch) with two 1.25 mm tungsten carbide balls. The slurry was mixed at 120 rpm for one hour using a Retsch PM 200 planetary mill. The slurry was then coated onto aluminum foil using a doctor blade with a 0.008 inch (203.2 μm) gap. The coating was dried at 120°C for one hour in air prior to use. Electrode disks 12.95 mm in diameter were punched from the foil for use in coin cells. Each disk had approximately 5-6 mg of Mo_6S_8 active material.

Electrolyte and Coin Cell Preparation

All electrolyte and coin cell preparation was performed in an argon glovebox with less than 0.1 ppm moisture and oxygen. Coin cells were constructed from 2325 coin cell hardware. Mg electrodes were prepared by punching 15.60 mm disks from 250 μm Mg foil (99.95%, GalliumSource LLC). Each cell contained a Mg foil electrode, CELGARD 2320 separator, electrolyte, a Mo_6S_8 disk electrode and a stainless steel spacer.

All electrolyte solvents were dried with molecular sieves (Sigma Aldrich, Type 3Å, bead 4-8 mesh), unless otherwise stated. Electrolytes were prepared by dissolving $Mg(TFSI)_2$ salt in either acetonitrile (Sigma Aldrich, ≥99.9%, for HPLC), pyridine (Sigma Aldrich, 99.8% anhydrous) and a 1:2 w/w solution of ethylene carbonate (EC) / diethyl carbonate (DEC) (EC/DEC solvent mixture used as received from Novolyte). All coin cells were electrochemically cycled at a rate of C/100 or C/50, based on 122 mAh/g for Mo_6S_8 using a Maccor Series 4000 Battery Test System. Cycling tests were performed in a thermostatically controlled chamber (±0.5°C) at either 30°C or 60°C. Dimethyl carbonate (DMC) was used as received from Novolyte for rinsing electrodes.

Example 1

A Mo_6S_8 vs. Mg coin cell was constructed using an electrolyte consisting of a 0.5 M solution of $Mg(TFSI)_2$ in acetonitrile. The cell was discharged at a rate of C/100 for 100 hours at 60°C. The voltage curve of the cell is shown in Fig. 1. The cell was then disassembled in an argon filled glovebox and the discharged Mo_6S_8 electrode powder was scraped off the current collector, rinsed with DMC, dried under vacuum and placed in a gas-tight x-ray sample holder with an aluminized MYLAR window. The x-ray diffraction pattern of this sample was measured while helium gas was flowed through the sample holder. The diffraction pattern (Fig. 2) shows that the discharged Mo_6S_8 electrode was primarily composed of $Mg_2Mo_6S_8$ with some $MgMo_6S_8$ present as a minority phase.

Example 2

A Mo_6S_8 vs Mg coin cell was constructed using an electrolyte consisting of a 0.5 M solution of $Mg(TFSI)_2$ in pyridine. The cell was discharged and charged at a C/50 rate at 60°C between -0.6 V and 1.2 V and the voltage curve is shown in Figure 3. The negative voltage is likely due to polarization at the Mg metal electrode. A separate cell was fully discharged to -0.6 V, disassembled in an argon filled glovebox and the discharged Mo6S8 electrode powder was scraped off the current collector, rinsed with DMC, dried under vacuum and placed in a gas-tight x-ray sample holder with an aluminized mylar window. The x-ray diffraction pattern of this sample was measured while helium gas was flowed through the sample holder. The diffraction pattern (Figure 4) shows that the Mo_6S_8 electrode intercalated magnesium during the discharge to form $Mg_2Mo_6S_8$ and $MgMo_6S_8$.

Example 3

A Mo_6S_8 vs Mg coin cell was constructed as described in Example 1, except that a Mg wire reference electrode was placed between the Mo_6S_8 and Mg electrodes. The cell was cycled such that the voltage of the Mo_6S_8 vs Mg wire reference electrode was between 0.5 V and 1.5 V at 60°C and a C/50 rate. The voltage curve of this cell is shown in Figure 5, showing reversible cycling of the Mo_6S_8 electrode.

Example 4

A symmetric Mo_6S_8 coin cell was constructed as follows. First a Mo_6S_8 vs Mg coin cell was constructed and discharged as described in Example 1. The cell was then disassembled in an argon-filled glovebox and the discharged Mo_6S_8 electrode was removed. A new coin cell was then prepared with an electrolyte consisting of a 0.5 M solution of $Mg(TFSI)_2$ in acetonitrile and one electrode being the discharged Mo_6S_8 electrode and the other electrode being a newly prepared Mo_6S_8 electrode. The cell was then cycled at a C/40 rate between +/- 0.7 V. The voltage curve of this cell is shown in Figure 6.

Example 5

A Mo_6S_8 vs Mg coin cell was constructed as described in Example 1, except a solution of 0.5 M $Mg(TFSI)_2$ in adiponitrile was used as the electrolyte. The cell was discharged to -0.8 volts, after which the Mo_6S_8 electrode reached its full theoretical capacity. The voltage curve of this cell is shown in Figure 7. The negative voltage is likely due to polarization at the Mg metal electrode.

Example 6

A three electrode cell with Mg foil reference and counter electrodes and a 4 mm diameter glassy carbon rod working electrode was constructed in a 20 ml glass vial and covered with a rubber stopper with holes for electrical feedthroughs. Enough electrolyte comprising a 0.5 M solution of $Mg(TFSI)_2$ in acetonitrile was added to the vial to cover the electrode surfaces. Cyclic voltammetry was conducted with this cell at a scan rate of 20 mV/s between 0.5 V and 4 V vs Mg at 25°C. The cyclic voltammagrams obtained are shown in Figure 8. The electrolyte showed stability towards oxidative decomposition at voltages up to about 3.2 V vs Mg.

Comparative Example 1

A Mo_6S_8 vs. Mg coin cell was constructed using an electrolyte consisting of a 0.5 M solution of $Mg(TFSI)_2$ in 1:2 w/w EC:DEC. The cell was discharged at a C/100 rate at 60°C to zero volts and showed almost no capacity.

Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows. All references cited in this disclosure are herein incorporated by reference in their entirety.

Claims

1. An electrochemical cell comprising:

at least one electrode comprising a magnesium intercalation compound; and

an electrolyte comprising a fluorinated imide salt or fluorinated methide salt substantially dissolved in an oxidatively stable solvent,

wherein the oxidatively stable solvent comprises a nitrile group.

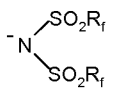
2. An electrochemical cell according to claim 1, wherein the at least one electrode is a positive electrode that comprises a magnesium intercalation compound selected from transition metal sulfides, transition metal oxides, magnesium transition metal sulfides, magnesium transition metal oxides, and carbon fluorides.

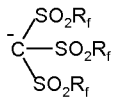
3. An electrochemical cell according to claim 2, wherein the magnesium intercalation compound comprises a magnesium molybdenum sulfide having a chevrel phase.

4. An electrochemical cell according to claim 1, further comprising a negative electrode comprising magnesium.

5. An electrochemical cell according to claim 4 wherein the negative electrode comprises magnesium metal.

6. An electrochemical cell according to claim 1, wherein the electrolyte comprises a salt having an anion with the formula:





or

wherein each R_f group is, independently, F or a fluoroalkyl group having 1-4 carbon atoms, which may optionally contain catenary oxygen or nitrogen atoms within the carbon chain, and wherein any two adjacent R_f groups may optionally be liked to form a 5-7 membered ring.

7. An electrochemical cell according to claim 6, wherein the electrolyte comprises magnesium [bis(trifluoromethanesulfonyl)imide]$_2$.

8. An electrochemical cell according to claim 1, wherein the oxidatively stable solvent comprises an alkyl nitrile, a dialkyl nitrile, or a combination thereof.

9. An electrochemical cell according to claim 8, wherein the oxidatively stable solvent comprises acetonitrile or adiponitrile.

10. An electrochemical cell according to claim 1, wherein the electrolyte comprises magnesium [bis(trifluoromethanesulfonyl)imide]$_2$ and at least one of acetonitrile or adiponitrile.

11. An electrochemical cell according to claim 1, wherein the cell is a primary electrochemical cell.

12. An electrochemical cell according to claim 1, wherein the cell is a secondary eletrochemical cell.

13. An electrochemical cell according to claim 1, wherein the cell comprises a liquid organic electrolyte and operates at a temperature greater than about 40°C.

14. An electrochemical cell according to claim 1, wherein the cell operations at voltages at or above 3.0 V vs. Li/Li^+.

15. A method of making an electrochemical cell comprising:

dissolving a fluorinated imide or fluorinated methide salt in an oxidatively stable solvent to form an electrolyte,

wherein the oxidatively stable solvent comprises a nitrile group;

immersing at least one electrode that comprises a magnesium intercalation compound into the electrolyte; and

immersing a second electrode comprising magnesium into the electrolyte.

16. A method of making an electrochemical cell according to claim 15, wherein the oxidatively stable solvent comprises acetonitrile or adiponitrile.

17. A magnesium electrochemical cell comprising:

a liquid organic electrolyte,

wherein the electrochemical cell is operated at a temperature greater than 40°C.

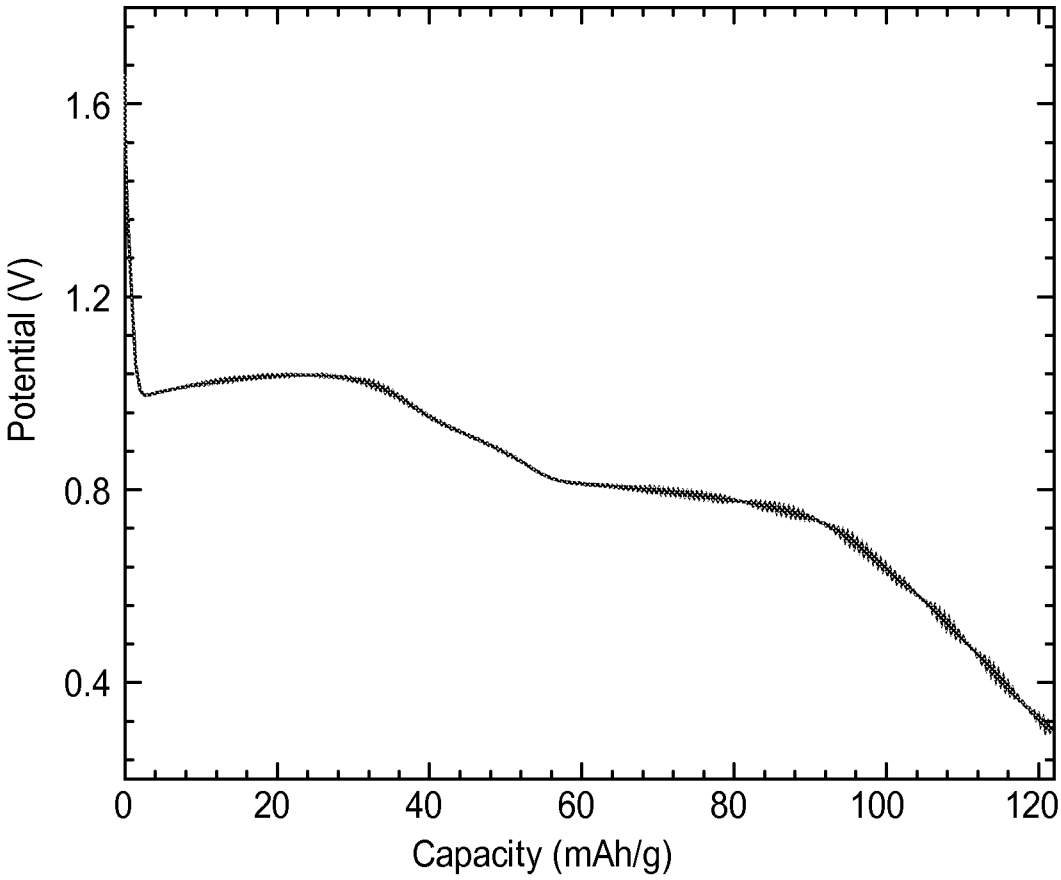


FIG. 1

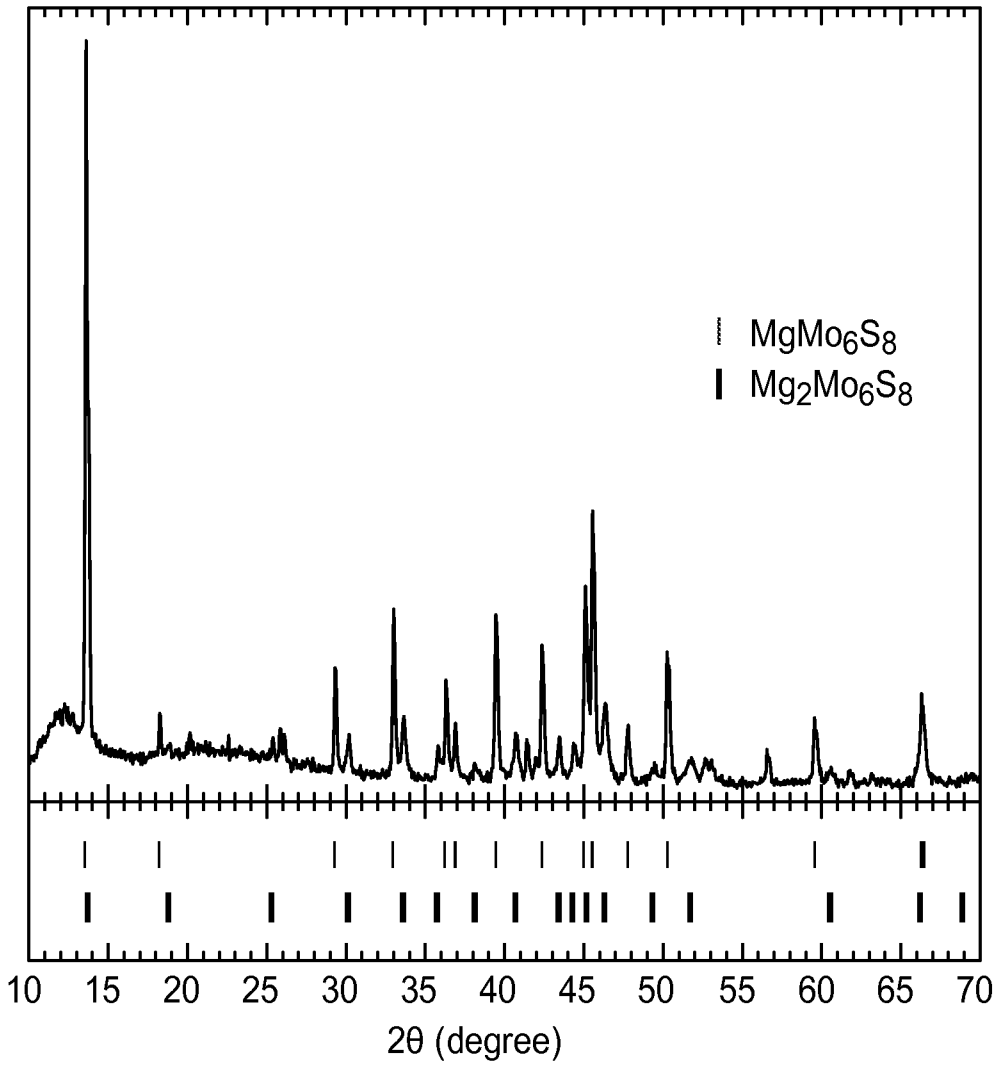


FIG. 2

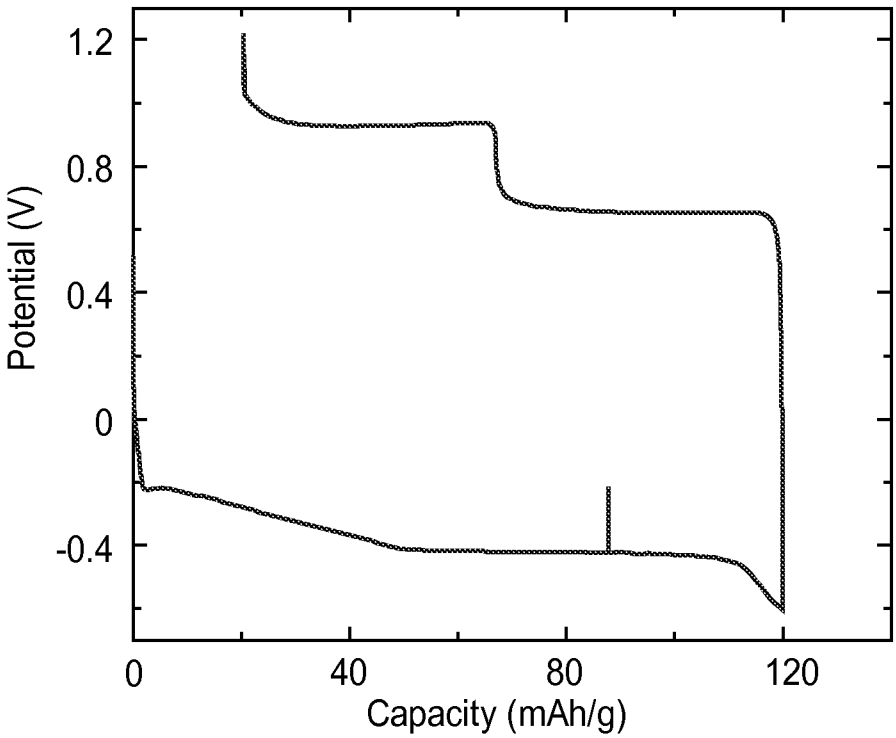

1.2
0.8
0.4
0
-0.4
Potential (V)
0
40
80
120
Capacity (mAh/g)

FIG. 3

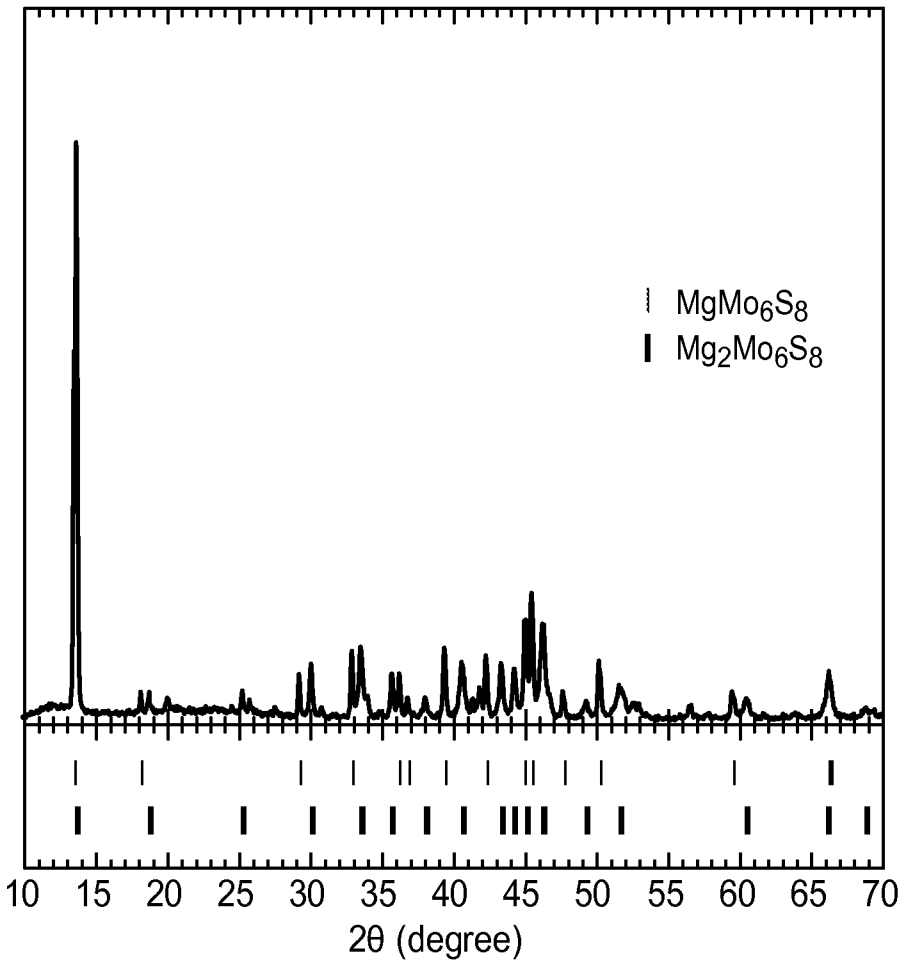

MgMo6S8
Mg2Mo6S8
10
15
20
25
30
35
40
45
50
55
60
65
70
2θ (degree)

FIG. 4

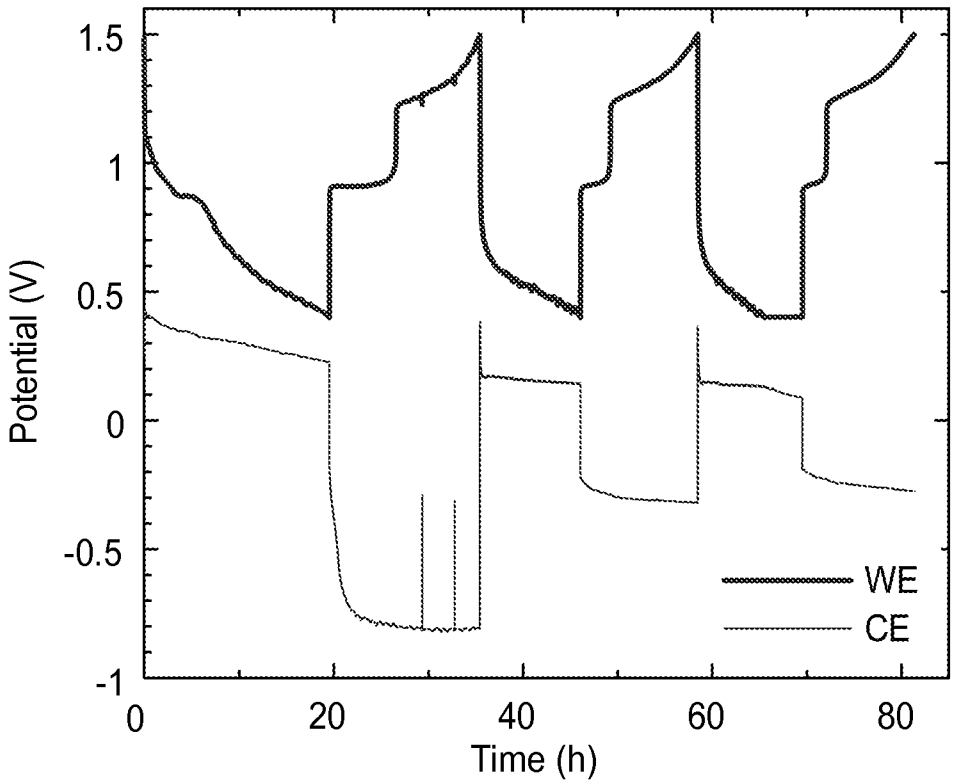

1.5
1
0.5
0
-0.5
-1
Potential (V)
0
20
40
60
80
Time (h)
WE
CE

FIG. 5

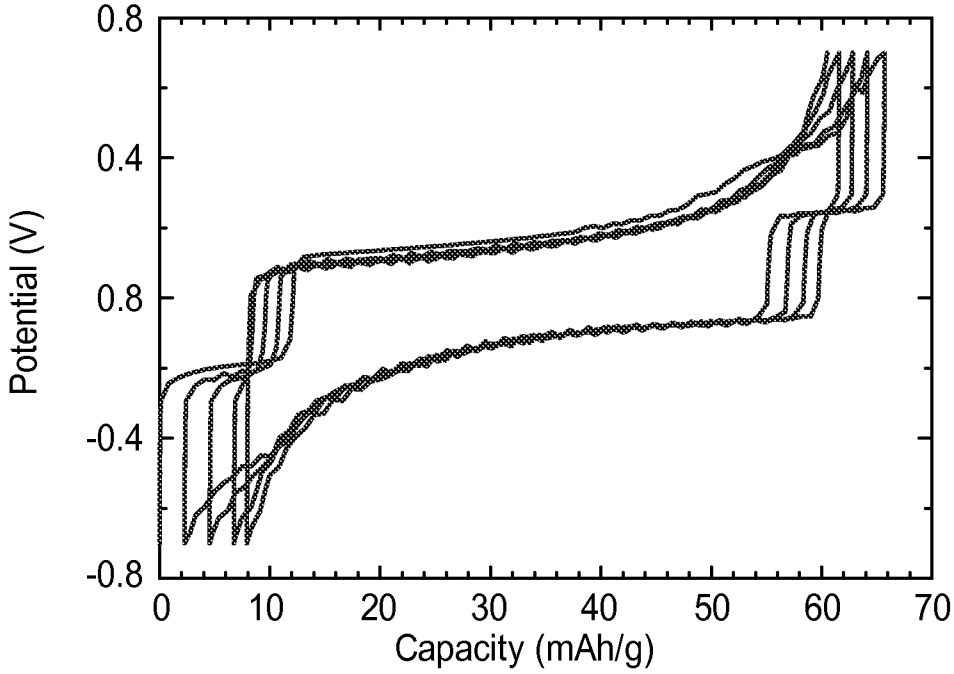

0.8
0.4
0.8
-0.4
-0.8
Potential (V)
0
10
20
30
40
50
60
70
Capacity (mAh/g)

FIG. 6

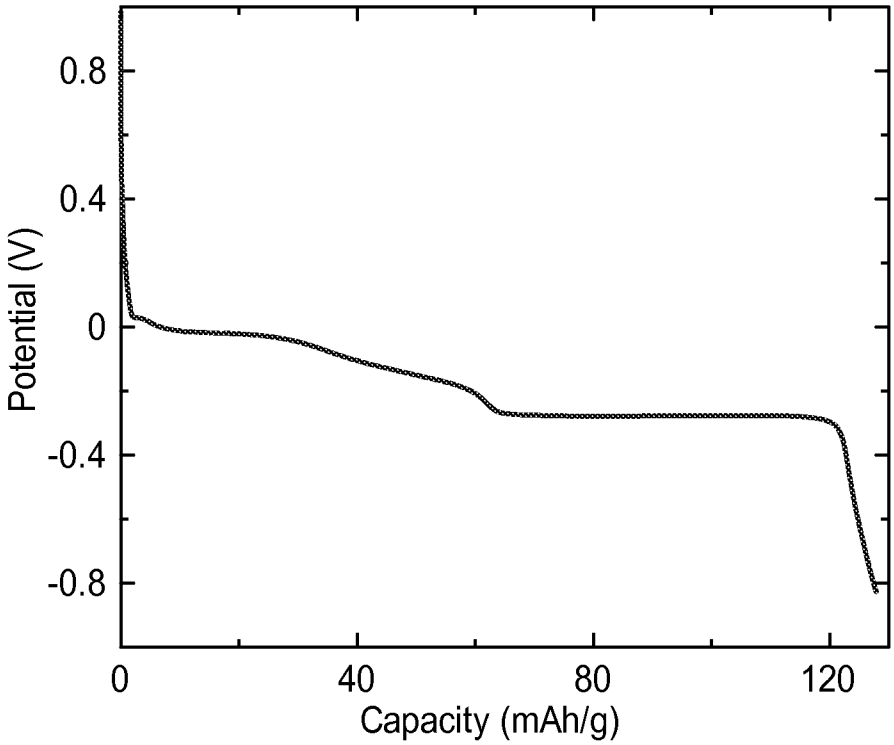

0.8
0.4
0
-0.4
-0.8
Potential (V)
0
40
80
120
Capacity (mAh/g)

FIG. 7

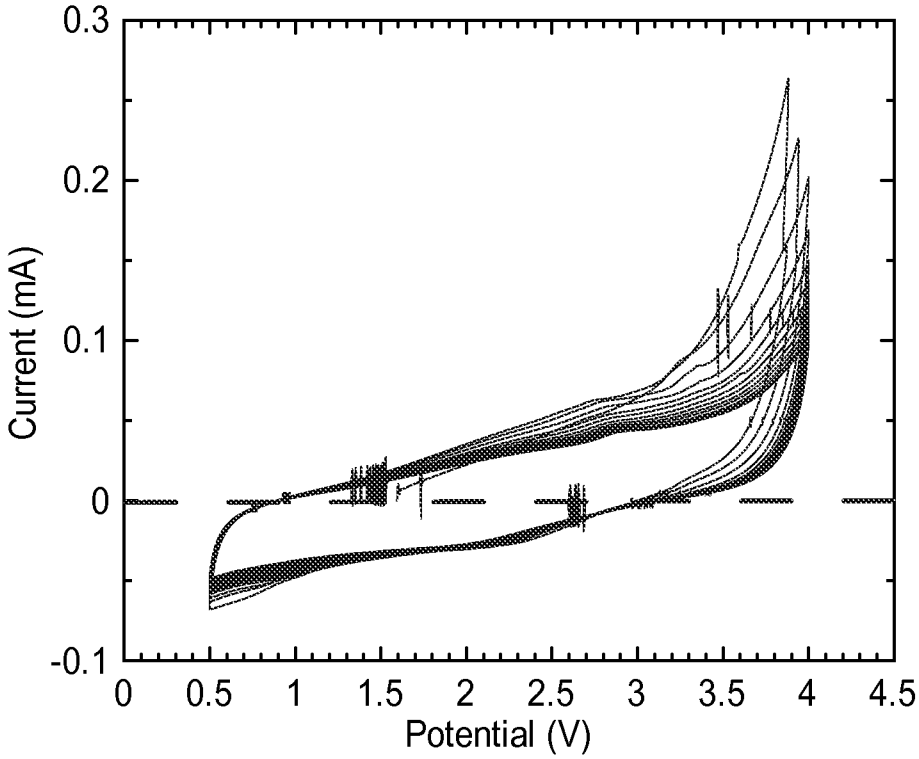

0.3
0.2
0.1
0
-0.1
Current (mA)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Potential (V)

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/024805

A. CLASSIFICATION OF SUBJECT MATTER

H01M 10/0566(2010.01)i, H01M 6/16(2006.01)i, H01M 10/05(2010.01)i

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 10/0566; H01M 10/40; H01M 4/48; C01B 19/00; H01M 4/46; H01M 6/16; H01M 4/02; H01M 6/04

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

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords:electrochemical cell,magnesium intercalation,electrolyte,fluorinated imide salt,fluorinated methide salt,oxidatively stable solvent,nitrile

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008-0182176 A1 (AURBACH, DORON et al.) 31 July 2008 See abstract; paragraphs [0024] - [0026], [0035], [0039], [0040]; and claims 1, 2.	1-17
Y	JP 2004-265675 A (SANYO ELECTRIC CO., LTD.) 24 September 2004 See paragraphs [0016], [0018], [0021]; and claims 1, 4.	1-17
A	US 2011-0244338 A1 (MULDOON, JOHN et al.) 06 October 2011 See abstract; paragraphs [0002], [0070] - [0073]; and claim 1.	1-17
A	US 6063522 A (HAMROCK, STEVEN J. et al.) 16 May 2000 See column 2, lines 4 - 9, column 3, lines 4 - 35, column 12, line 62 - column 13, line 25; and claim 20.	1-17
A	JP 2004-259650 A (KANEGAFUCHI CHEM IND. CO., LTD.) 16 September 2004 See abstract; paragraph [0035]; and claim 1.	1-17

☐ 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 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	Date of mailing of the international search report
14 May 2013 (14.05.2013)	**15 May 2013 (15.05.2013)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. 82-42-472-7140	LEE, Dong Wook Telephone No. 82-42-481-8163

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/024805

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008-0182176 A1	31.07.2008	None	
JP 2004-265675 A	24.09.2004	None	
US 2011-0244338 A1	06.10.2011	US 8354193 B2	15.01.2013
US 6063522 A	16.05.2000	AU 1998-86848 A1	18.10.1999
		CA 2325505 A1	30.09.1999
		CN 1160817 C0	04.08.2004
		CN 1290408 A0	04.04.2001
		EP 1066657 A1	10.01.2001
		JP 04503829 B2	30.04.2010
		JP 2002-508576 A	19.03.2002
		KR 10-0532180 B1	30.11.2005
		WO 99-49529 A1	30.09.1999
JP 2004-259650 A	16.09.2004	None	