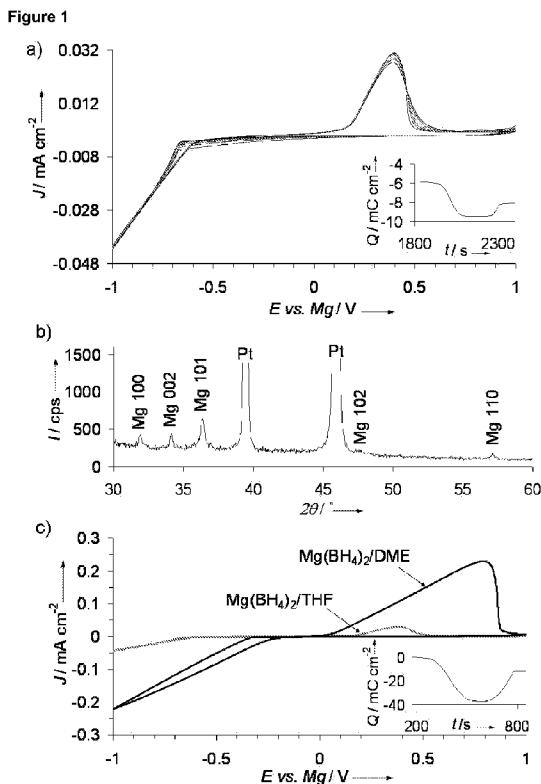


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(54) Title: MAGNESIUM BOROHYDRIDE AND ITS DERIVATIVES AS MAGNESIUM ION TRANSFER MEDIA

(57) **Abstract:** An electrolyte for a magnesium battery includes a magnesium salt having the formula MgB_aH_bX_y where a=2-12, b=0-12 y=0-8 wherein when b=0 X is O-alkyl and when b=1-1 X is O-alkyl or F. The electrolyte also includes a solvent, the magnesium salt being dissolved in the solvent. Various solvents including aprotic solvents and molten salts such as ionic liquids may be utilized.



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MAGNESIUM BOROHYDRIDE AND ITS DERIVATIVES AS MAGNESIUM ION TRANSFER MEDIA

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application claims priority to U.S. Patent Application Serial Number 13/956,933 filed on August 1, 2013, and U.S. Patent Application Serial Number 13/839,003 filed March 15, 2013, and U.S. Patent Application Serial Number 13/720,522, filed December 19, 2012, and U.S. Provisional Patent Application Serial Number 61/678,672, filed August 2, 2012, the entire contents of which are incorporated herein by reference.

10 FIELD OF THE INVENTION

[0002] The invention relates to electrolytes and more particularly to electrolytes for magnesium batteries.

BACKGROUND OF THE INVENTION

15 [0003] Rechargeable batteries, such as lithium-ion batteries, have numerous commercial applications. Capacity density is an important characteristic, and higher capacity densities are desirable for a variety of applications.

[0004] A magnesium ion in a magnesium or magnesium-ion battery carries two electrical charges, in contrast to the single charge of a lithium ion. Improved electrolyte materials would be very useful in order to develop high capacity density batteries.

20 [0005] Current state of the art electrolytes for magnesium batteries may use organomagnesium salts and complexes as they are the only ones known to be compatible with an Mg anode allowing for reversible electrochemical Mg deposition and stripping. However, such materials may be corrosive and may be difficult to utilize in a battery. Conventional inorganic and ionic salts such as Mg(ClO₄)₂ may be incompatible with the Mg

anode due to the formation of an ion-blocking layer formed by their electrochemical reduction.

[0006] There is therefore a need in the art for an improved electrolyte that solves the problems of the prior art and provides a stable rechargeable Mg battery system. There is a 5 further need in the art for an electrolyte that allows reversible Mg deposition and stripping in a chloride-free inorganic salt. There is also a need in the art for an improved battery having increased current densities and high coulombic efficiencies.

SUMMARY OF THE INVENTION

[0007] In one aspect, there is disclosed an electrolyte for a magnesium battery. The 10 electrolyte includes a magnesium salt having the formula $MgB_aH_bX_y$ where $a=2-12$, $b=0-12$ $y=0-8$ wherein when $b=0$ X is O-alkyl and when $b=1-11$ X is O-alkyl or F. Additionally, when $X=F$ $y=0-6$ and when $X=$ O-alkyl $y=0-8$. The electrolyte also includes a solvent, the magnesium salt being dissolved in the solvent. Various solvents including aprotic solvents and molten salts such as ionic liquids may be utilized.

[0008] In another aspect, there is disclosed an electrolyte for a magnesium battery. The 15 electrolyte includes a magnesium salt having the formula $MgB_2H_bX_y$ where $b=0-8$, $y=0-8$, $b+y=8$ wherein when $b=0$ X is O-alkyl and when $b=1-7$ X is O-alkyl or F. The electrolyte also includes a solvent, the magnesium salt being dissolved in the solvent. Various solvents including aprotic solvents and molten salts such as ionic liquids may be utilized.

[0009] In a further aspect, there is disclosed an electrolyte for a magnesium battery. The 20 electrolyte includes a magnesium salt having the formula MgB_aH_b where $a=2-12$, and $b=8-12$. The electrolyte also includes a solvent, the magnesium salt being dissolved in the solvent. Various solvents including aprotic solvents and molten salts such as ionic liquids may be utilized.

[0010] In a further aspect, there is disclosed a magnesium battery that includes a magnesium metal containing anode. The battery also includes an electrolyte including a magnesium salt having the formula $MgB_aH_bX_y$ where $a=2-12$, $b=0-12$ $y=0-8$ wherein when $b=0$ X is O-alkyl and when $b=1-11$ X is O-alkyl or F. Additionally, when $X=F$ $y=0-6$ and 5 when $X=$ O-alkyl $y=0-8$. The electrolyte also includes a solvent. The magnesium salt being dissolved in the solvent. The battery also includes a cathode separated from the anode. Magnesium cations are reversibly stripped and deposited between the anode and cathode.

[0011] In another aspect, there is disclosed a magnesium battery that includes a magnesium metal containing anode. The battery also includes an electrolyte including a 10 magnesium salt having the formula $MgB_2H_bX_y$ where $b=0-8$, $y=0-8$, $b+y=8$ wherein when $b=0$ X is O-alkyl and when $b=1-7$ X is O-alkyl or F. The electrolyte also includes a solvent. The magnesium salt being dissolved in the solvent. The battery also includes a cathode separated from the anode. Magnesium cations are reversibly stripped and deposited between the anode and cathode.

15 **[0012]** In yet another aspect, there is disclosed a magnesium battery that includes a magnesium metal containing anode. The battery also includes an electrolyte including a magnesium salt having the formula MgB_aH_b where $a=2-12$, and $b=8-12$. The electrolyte also includes a solvent. The magnesium salt being dissolved in the solvent. The battery also includes a cathode separated from the anode. Magnesium cations are reversibly stripped and 20 deposited between the anode and cathode.

[0013] In another aspect, there is disclosed an electrolyte for a magnesium battery. The electrolyte includes a magnesium salt having the formula MgB_aH_b where $a=11-12$ and $b=11-12$. The electrolyte also includes a solvent, the magnesium salt being dissolved in the solvent. Various solvents including aprotic solvents and molten salts such as ionic liquids 25 may be utilized.

[0014] In another aspect, there is disclosed a magnesium battery that includes a magnesium metal containing anode. The battery also includes an electrolyte including a magnesium salt having the formula MgB_aH_b where $a=11-12$ and $b=11-12$. The electrolyte also includes a solvent. The magnesium salt being dissolved in the solvent. The battery also 5 includes a cathode separated from the anode. Magnesium cations are reversibly stripped and deposited between the anode and cathode.

[0015] In yet another aspect, there is disclosed a method of forming an electrolyte material for a magnesium battery that includes the steps of: providing a borane material; providing a magnesium borohydride material; combining the borane and magnesium 10 borohydride material forming a combined mixture; adding an aprotic solvent to the combined mixture forming a combined solvent mixture; heating the combined solvent mixture under reflux; and removing the aprotic solvent forming an electrolyte material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Figure 1 is a diagram of 0.5 M $Mg(BH_4)_2$ /THF showing (a) Cyclic voltammetry 15 (8 cycles) with the inset showing deposition/stripping charge balance (3rd cycle) (b) XRD results following galvanostatic deposition of Mg on a Pt working electrode, (c) Cyclic voltammetry for 0.1 M $Mg(BH_4)_2$ /DME compared to 0.5 M $Mg(BH_4)_2$ /THF with the inset showing deposition/stripping charge balance for $Mg(BH_4)_2$ /DME;

[0017] Figure 2 is a diagram of $Mg(BH_4)_2$ in THF and DME: (a) IR Spectra, (b) ^{11}B 20 NMR, and (c) 1H NMR;

[0018] Figure 3 is a diagram of $LiBH_4$ (.6 M)/ $Mg(BH_4)_2$ (.18 M) in DME: (a) cyclic voltammetry with the inset showing deposition/stripping charge balance, (b) XRD results following galvanostatic deposition of Mg on a Pt disk and (c) IR spectra (|) indicates band maxima for $Mg(BH_4)_2$ /DME);

[0019] Figure 4 is a diagram of Charge/discharge profiles with Mg anode/Chevrel phase cathode for 3.3:1 molar LiBH₄ / Mg(BH₄)₂ in DME;

[0020] Figure 5A-B is a NMR scan of a compound of the formula MgB_aH_b, where a=11-12 and b=11-12;

5 **[0021]** Figure 6 is a plot of the Current density as a function of Potential for a compound of the formula MgB_aH_b, where a=11-12 and b=11-12.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0022] There is disclosed a novel electrolyte for an Mg battery. The novel electrolyte allows electrochemical reversible Mg deposition and stripping in a halide-free inorganic salt.

10 **[0023]** In one aspect, there is disclosed an electrolyte for a magnesium battery. The electrolyte includes a magnesium salt having the formula MgB_aH_bX_y where a=2-12, b=0-12 y=0-8 wherein when b=0 X is O-alkyl and when b=1-11 X is O-alkyl or F. Additionally, when X=F y=0-6 and when X= O-alkyl y=0-8. Examples of electrolytes may include magnesium salts such MgBH₄, MgB₁₁H₁₁, MgB₁₂H₁₂, MgB₂H₈, MgB₂H₂F₆, MgB₂H₄F₄,
15 MgB₂H₆F₂ MgB₂O-alkyl₈, MgB₂H₂O-alkyl₆, MgB₂H₄O-alkyl₄, MgB₂H₆O-alkyl₂, MgBF₃, MgBH₂F₂, MgBH₃F and MgBO-alkyl. The electrolyte also includes a solvent, the magnesium salt being dissolved in the solvent. Various solvents including aprotic solvents and molten salts such as ionic liquids may be utilized. Aprotic solvents may include, for example solvents such as tetrahydrofuran (THF) and dimethoxyethane (DME). Other examples of aprotic solvents include: dioxane, triethyl amine, diisopropyl ether, diethyl ether, t-butyl methyl ether (MTBE), 1,2-dimethoxyethane (glyme), 2-methoxyethyl ether (diglyme), tetraglyme, and polyethylene glycol dimethyl ether. In one aspect, the magnesium salt may have a molarity of from .01 to 4 molar.

[0024] The electrolyte may further include a chelating agent. Various chelating agents including glymes and crown ethers may be utilized. The chelating agent may be included to increase the current and lower the over-potential of a battery that includes the electrolyte.

[0025] The electrolyte may further include acidic cation additives increasing the current density and providing a high coulombic efficiency. Examples of acidic cation additives include lithium borohydride, sodium borohydride and potassium borohydride. The acidic cation additives may be present in an amount of up to five times the amount in relation to $MgB_aH_bX_y$.

[0026] In another aspect the novel electrolyte may include a magnesium salt having the formula $MgB_2H_bX_y$ where $b=0-8$, $y=0-8$, $b+y=8$ wherein when $b=0$ X is O-alkyl and when $b=1-7$ X is O-alkyl or F. The magnesium salt is dissolved in the solvent. Various solvents including aprotic solvents and molten salts such as ionic liquids may be utilized. Aprotic solvents may include, for example solvents such as tetrahydrofuran (THF) and dimethoxyethane (DME). Other examples of aprotic solvents include: dioxane, triethyl amine, diisopropyl ether, diethyl ether, t-butyl methyl ether (MTBE), 1,2-dimethoxyethane (glyme), 2-methoxyethyl ether (diglyme), tetraglyme, and polyethylene glycol dimethyl ether.

[0027] In one aspect, the magnesium salt may have a molarity of from .01 to 4 molar.

[0028] The electrolyte may further include a chelating agent. Various chelating agents including glymes and crown ethers may be utilized. The chelating agent may be included to increase the current and lower the over-potential of a battery that includes the electrolyte.

[0029] The electrolyte may further include acidic cation additives increasing the current density and providing a high coulombic efficiency. Examples of acidic cation additives include lithium borohydride, sodium borohydride and potassium borohydride. The acidic

cation additives may be present in an amount of up to five times the amount in relation to $MgB_2H_bX_y$.

[0030] In another aspect the novel electrolyte may include a magnesium salt having the MgB_aH_b where $a=2-12$, and $b=8-12$. The magnesium salt is dissolved in the solvent. Various 5 solvents including aprotic solvents and molten salts such as ionic liquids may be utilized. Aprotic solvents may include, for example solvents such as tetrahydrofuran (THF) and dimethoxyethane (DME) as well as the above described solvents. In one aspect, the magnesium salt may have a molarity of from .01 to 4 molar.

[0031] The electrolyte may further include a chelating agent. Various chelating agents 10 including monoglyme may be utilized. The chelating agent may be included to increase the current and lower the over-potential of a battery that includes the electrolyte.

[0032] The electrolyte may further include acidic cation additives increasing the current density and providing a high coulombic efficiency. Examples of acidic cation additives include lithium borohydride, sodium borohydride and potassium borohydride. The acidic 15 cation additives may be present in an amount of up to five times the amount in relation to MgB_aH_b .

[0033] In a further aspect, there is disclosed a magnesium battery that includes a cathode, a magnesium metal containing anode, an electrolyte of the formula: $MgB_aH_bX_y$ where $a=2-12$, $b=0-12$ $y=0-8$ wherein when $b=0$ X is O-alkyl and when $b=1-11$ X is O-alkyl 20 or F. The electrolyte may also include the chelating agents and acidic cation additives as described above.

[0034] In a further aspect, there is disclosed a magnesium battery that includes a cathode, a magnesium metal containing anode, an electrolyte of the formula: $MgB_2H_bX_y$ where $b=0-8$, $y=0-8$, $b+y=8$ wherein when $b=0$ X is O-alkyl and when $b=1-7$ X is O-alkyl or

F. Additionally, when X=F y=0-6 and when X= O-alkyl y=0-8. The electrolyte may also include the chelating agents and acidic cation additives as described above.

[0035] In a further aspect, there is disclosed a magnesium battery that includes a magnesium metal containing anode, an electrolyte of either the formula: MgB_aH_b where a=2-5 12, and b=8-12. and a cathode. The electrolyte may also include the chelating agents and acidic cation additives as described above.

[0036] The anode may include magnesium metal anodes. The cathode may include various materials that show an electrochemical reaction at a higher electrode potential than the anode. Examples of cathode materials include transition metal oxides, sulfides, fluorides, 10 chlorides or sulphur and Chevrel phase materials such as Mo_6S_8 . The battery includes magnesium cations that are reversibly stripped and deposited between the anode and cathode.

[0037] In one aspect, magnesium boron based compounds having the formula MgB_aH_b , where a=11-12 and b=11-12 may be utilized to provide an improved stability towards electrochemical oxidation so that electrolytes may be utilized with high voltage cathodes such 15 as MnO_2 . In another aspect, a mixture of compounds having the formula MgB_aH_b , where a=11-12 and b=11-12 may be utilized.

[0038] Prior art attempts to synthesize $MgB_{12}H_{12}$ were conducted in aqueous media and have resulted in the formation of $MgB_{12}H_{12}H_2O$ with water strongly coordinated to the compound. Attempts to remove H_2O have been problematic as outlined in the prior art. For 20 example, (Chen, X.; Lingam, H.K.; Huang, Z.; Yisgedu, T.; Zhao, J.-C.; Shore, S.G. Thermal Decomposition Behavior of Hydrated Magnesium Dodecahydroadodecaborates. *J. Phys. Chern. Lett.* 2010, 1, 201-204) documented the difficulty in removing H_2O from the compounds.

[0039] For use as an electrolyte in an Mg battery, compounds of the formula MgB_aH_y , 25 where a=11-12 and y=11-12 should be free of H_2O or water. In one aspect, $MgB_{12}H_{12}$, that is

water free may be synthesized in aprotic media that results in the formation of water free compounds of the formula MgB_aH_y , where $a=11-12$ and $y=11-12$.

[0040] Examples

[0041] Magnesium borohydride ($Mg(BH_4)_2$, 95%), lithium borohydride ($LiBH_4$, 90%), 5 anhydrous tetrahydrofuran (THF) and dimethoxyethane (DME) were purchased from Sigma-Aldrich. The various components were mixed to provide the specified molar electrolyte solutions. Cyclic voltammetry testing was conducted in a three-electrode cell with an Mg wire/ribbon as reference/counter electrodes. The electrochemical testing was conducted in an argon filled glove box with O_2 and H_2O amounts kept below 0.1 ppm.

10 [0042] $Mg(BH_4)_2$ in THF

[0043] Mg deposition and stripping was performed for $Mg(BH_4)_2$ in ether solvents. Figure 1a shows the cyclic voltammogram obtained for 0.5 M $Mg(BH_4)_2$ /THF where a reversible reduction/oxidation process took place with onsets at -0.6 V/0.2 V and a 40% coulombic efficiency, as shown in Figure 1a inset, indicating reversible Mg deposition and 15 stripping. X-ray diffraction (XRD) of the deposited product following galvanostatic reduction from the above solution as shown in Figure 1b denotes that the deposited product is hexagonal Mg. The deposition of the hexagonal magnesium demonstrates the compatibility of the electrolyte, $Mg(BH_4)_2$ with Mg metal. The electrochemical oxidative stabilities measured on platinum, stainless steel and glassy carbon electrodes were 1.7, 2.2 and 2.3 V, 20 respectively. These results denote that $Mg(BH_4)_2$ is electrochemically active in THF such that ionic conduction and reversible magnesium deposition and stripping utilizing the electrolyte occurs.

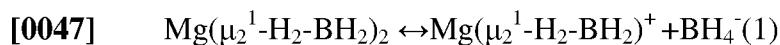
[0044] $Mg(BH_4)_2$ in DME

[0045] In addition to ether solvents, another solvent, dimethoxyethane (DME) having a 25 higher boiling temperature than THF was utilized. The cyclic voltammogram obtained for 0.1

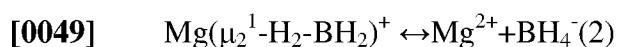
MgMg(BH₄)₂/DME is shown in Figure 1c. As can be seen in the Figure, there is an improvement in the electrochemical performance compared to Mg(BH₄)₂/THF. As seen in the Figure, there is a 10 fold increase in the current density and a reduction in the overpotential for deposition/stripping onsets at -0.34 V/0.03 V vs. -0.6 V/0.2 V in THF).

5 Additionally, the DME solvent based electrolyte demonstrated a higher coulombic efficiency at 67% in comparison to 40% in THF. These findings indicate the presence of Mg electroactive species in higher concentration and mobility in DME despite the lower solubility of Mg(BH₄)₂ in DME versus THF.

[0046] IR and NMR spectroscopic analyses as shown in Figure 2 were conducted for 0.5 M Mg(BH₄)₂/THF and 0.1 M Mg(BH₄)₂/DME to characterize the magnesium electroactive species. The IR B-H stretching region (2000-2500 cm⁻¹) reveals two strong widely separated vibrations (Mg(BH₄)₂/THF: 2379 cm⁻¹, 2176 cm⁻¹ and Mg(BH₄)₂/DME: 2372 cm⁻¹, 2175 cm⁻¹). The spectra for 0.1M DME and 0.5 M in THF are similar. The spectra are similar to covalent borohydrides and for Mg(BH₄)₂ solvates from THF and diethyl ether where 2 hydrogen atoms in BH₄⁻ are bridge bonded to 1 metal atom (μ_2^1 bonding). Therefore, we assigned the bands at the higher and lower B-H frequencies to terminal B-H_t and bridging B-H_b vibrations, respectively. The band and shoulder at 2304 and 2240 cm⁻¹ were assigned to asymmetric B-H_t and B-H_b vibrations, respectively. It is suggested that Mg(BH₄)₂ is present as the contact ion pair Mg(μ_2^1 -H₂-BH₂)₂ which partially dissociates into Mg(μ_2^1 -H₂-BH₂)⁺ and BH₄⁻ as in reaction (1). In one aspect, since the B-H peaks are likely overlapping, it is not possible to distinguish all the species.



[0048] Where Mg(μ_2^1 -H₂-BH₂)⁺ may further dissociate:



[0050] For Mg(BH₄)₂/DME, while the main features present in THF were retained, vB-H_t broadening and shifting to lower values accompanied with relative weakening of vB-H_b intensity was observed. While vB-H_t broadening suggests a more pronounced presence of some species relative to that in THF, the band maximum shift indicates a more ionic B-H bond. The vB-H_t shift is similar to those resulting from an enhanced BH₄⁻ ionicity, such as in stabilized covalent borohydrides. In addition, the relative weakening in vB-H_b intensity suggests a more pronounced presence of free BH₄⁻ anion. The NMR results for BH₄⁻ in DME, as shown in Figure 2b and 2c, display an increased boron shielding by about 0.5 ppm as denoted by the center position of quintet in ¹¹B NMR and slightly reduced proton shielding by about 0.01 ppm, as denoted by the quartet in ¹H NMR consistent with a higher B-H bond ionicity compared to that in THF. These results are evidence of weaker interactions between Mg²⁺ and BH₄⁻ within the ion pair and an enhanced dissociation in DME per reactions (1) and (2). So despite the fact that DME has a slightly lower dielectric constant (7.2) compared to THF (7.4), its chelation properties due to the presence of two oxygen sites per molecule resulted in an enhanced dissociation and thus an improved electrochemical performance.

[0051] Mg(BH₄)₂ and LiBH₄ in DME

[0052] As recited above, the electrolyte may include an acidic cation additive. In one aspect, the acidic cation additive may include the following characteristics: (1) a reductive stability comparable to Mg(BH₄)₂, (2) non-reactive, (3) halide free and (4) soluble in DME. One such material that includes these properties is LiBH₄. Mg deposition and stripping was performed in DME using various molar ratios of LiBH₄ to Mg(BH₄)₂. As shown in Figure 3a cyclic voltammetry data was obtained for 3.3:1 molar LiBH₄ to Mg(BH₄)₂. Including the LiBH₄ material in the electrolyte increased by 2 orders of magnitude the current density as

denoted by the oxidation peak current $J_p = 26 \text{ mA cm}^{-2}$. Additionally, the electrolyte had a higher coulombic efficiency of up to 94%.

[0053] Referring to Figure 3b, the deposition and stripping currents are displayed for magnesium based on the absence of Li following galvanostatic deposition and also the lack of 5 electrochemical activity in LiBH₄/DME solution. Enhanced BH₄⁻ ionicity as shown in Figure 3c displayed as lower vB-H_t and higher vB-H_b values were obtained. The enhanced properties indicate that the acidic cation additive increases Mg(BH₄)₂ dissociation as indicated by the B-H bands for LiBH₄/DME which occur at lower values.

10 [0054] **Magnesium Battery with Mg anode, Chevrel phase cathode and Mg(BH₄)₂ and LiBH₄ in DME**

[0055] A magnesium battery was tested using an electrolyte for 3.3:1 molar LiBH₄ to Mg(BH₄)₂. The cathode of the test battery included a cathode active material having a Chevrel phase Mo₆S₈. The anode for the test battery included an Mg metal anode. Referring 15 to Figure 4, the test battery demonstrated reversible cycling capabilities at a 128.8 mA g⁻¹ rate. As can be seen in the Figure, the charge and discharge curves indicate reversible cycling of a magnesium ion.

[0056] **Synthesis of MgB_aH_y, where a=11-12 and y=11-12**

[0057] A mixture of 5.0 g (0.0409 mol) decaborane (B₁₀H₁₄) and 2.43 g (0.0450 mol, 1.1 20 eq.) magnesium borohydride (Mg(BH₄)₂) is prepared in a 100 ml Schlenk flask inside an argon filled glovebox. The flask is transferred from the glovebox to a nitrogen Schlenk-line and fitted with a reflux condenser. To this is added 50 ml Diglyme (C₆H₁₄O₃) via cannula transfer. Upon solvent addition, vigorous gas evolution begins, and a yellow homogeneous 25 solution is formed. When gas evolution has ceased, the mixture is slowly heated to reflux using a silicon oil bath. As the temperature of the mixture increases, vigorous gas evolution begins again, and is maintained for approximately one hour. The mixture is held at reflux for

5 days before being allowed to cool to room temperature. Following cooling, the solvent is removed under vacuum to give a pale yellow solid. The crude product obtained at this stage may be purified by dissolving in a minimal amount of hot (120 C) DMF. The resulting solution is allowed to cool to room temperature, and a colorless precipitate is observed which

5 is isolated by filtration.

[0058] The product obtained as outlined above was analyzed using an NMR scan. As can be seen in Figure 5, the NMR results confirm the successful synthesis of MgB₁₂H₁₂. As can be seen in the Figure, the product as synthesized shows the 11B Nuclear Magnetic Resonance of B₁₁H₁₁ and B₁₂H₁₂ in both the crude product and in the filtered product.

10 **[0059]** The product as synthesized was subjected to electrochemical testing. The electrochemical testing procedure included cyclic voltammetry collected using a 3-electrode cell in which the working electrode was platinum and both the counter and reference electrodes were magnesium. A plot of the electrochemical testing data is shown in Figure 6 as a plot of the current density as a function of the Potential. As can be seen in Figure 6, the

15 synthesized product is stable against both electrochemical reduction (> -2 V vs. Mg) and oxidation (> 3 V vs. Mg). The synthesized compound will allow a magnesium battery utilizing the synthesized compound as an electrolyte to operate at a high voltage necessary to achieve sufficient energy density for use in numerous applications such as in automotive applications.

20 **[0060]** The invention is not restricted to the illustrative examples described above. Examples described are not intended to limit the scope of the invention. Changes therein, other combinations of elements, and other uses will occur to those skilled in the art.

CLAIMS

1. An electrolyte for a magnesium battery comprising:
 - a magnesium salt having the formula $MgB_aH_bX_y$ where $a=2-12$, $b=0-12$ $y=0-8$ wherein when $b=0$ X is O-alkyl and when $b=1-11$ X is O-alkyl or F;
 - 5 a solvent, the magnesium salt being dissolved in said solvent.
2. The electrolyte of claim 1 wherein the magnesium salt has the formula $MgB_2H_bX_y$ where $b=0-8$, $y=0-8$, $b+y=8$ wherein when $b=0$ X is O-alkyl and when $b=1-7$ X is O-alkyl or F.
- 10 3. The electrolyte of claim 1 wherein the magnesium salt has the formula MgB_aH_b where $a=2-12$, and $b=8-12$.
4. The electrolyte of claim 1 wherein the magnesium salt has the formula MgB_aH_b , where $a=11-12$ and $b=11-12$.
- 15 5. The electrolyte of claim 1 wherein the solvent is an aprotic solvent.
6. The electrolyte of claim 5 wherein the aprotic solvent is selected from:
 - 20 tetrahydrofuran (THF) and dimethoxyethane (DME).
7. The electrolyte of claim 1 wherein the solvent is an ionic liquid.
8. The electrolyte of claim 1 wherein the magnesium salt has a molarity of from .01 to 4 molar.

9. The electrolyte of claim 1 further including a chelating agent.

10. The magnesium battery of claim 9 wherein the chelating agent includes
5 monoglyme.

11. The electrolyte of claim 1 further including an acidic cation additive.

12. The electrolyte of claim 11 wherein the acidic cation additive is selected from:
10 lithium borohydride, sodium borohydride and potassium borohydride.

13. The electrolyte of claim 4 wherein the magnesium salt includes $MgB_{12}H_{12}$.

14. The electrolyte of claim 4 wherein the magnesium salt includes $MgB_{11}H_{11}$.

15

15. The electrolyte of claim 4 wherein the magnesium salt includes a mixture of
 $MgB_{12}H_{12}$ and $MgB_{11}H_{11}$.

16. A magnesium battery comprising:

a magnesium metal containing anode;

20 an electrolyte including a magnesium salt having the formula $MgB_aH_bX_y$

where $a=2-12$, $b=0-12$ $y=0-8$ wherein when $b=0$ X is O-alkyl and when $b=1-11$ X is
O-alkyl or F, the magnesium salt being dissolved in said solvent;

a cathode;

wherein magnesium cations are reversibly stripped and deposited between the

25 anode and cathode.

17. The magnesium battery of claim 16 wherein the magnesium salt has the formula $MgB_2H_bX_y$ where $b=0-8$, $y=0-8$, $b+y=8$ wherein when $b=0$ X is O-alkyl and when $b=1-7$ X is O-alkyl or F.

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18. The magnesium battery of claim 16 wherein the magnesium salt has the formula MgB_aH_b where $a=2-12$, and $b=8-12$.

10 19. The magnesium battery of claim 16 wherein the magnesium salt has the formula MgB_aH_b , where $a=11-12$ and $b=11-12$.

20. The magnesium battery of claim 16 wherein the solvent is an aprotic solvent.

15 21. The magnesium battery of claim 20 wherein the aprotic solvent is selected from: tetrahydrofuran (THF) and dimethoxyethane (DME).

22. The magnesium battery of claim 16 wherein the solvent is an ionic liquid.

23. The magnesium battery of claim 16 wherein the magnesium salt has a molarity 20 of from .01 to 4 molar.

24. The magnesium battery of claim 16 further including a chelating agent.

25. The magnesium battery of claim 24 wherein the chelating agent includes monoglyme.

26. The magnesium battery of claim 16 further including an acidic cation additive.

27. The electrolyte of claim 26 wherein the acidic cation additive is selected from: lithium borohydride, sodium borohydride and potassium borohydride.

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28. A method of forming an electrolyte material for a magnesium battery comprising the steps of:

providing a borane material;

providing a magnesium borohydride material;

10 combining the borane and magnesium borohydride material forming a combined mixture;

adding an aprotic solvent to the combined mixture forming a combined solvent mixture;

heating the combined solvent mixture under reflux;

15 removing the aprotic solvent forming an electrolyte material.

29. The method of claim 28 including the step of filtering the electrolyte material including dissolving the electrolyte material in hot DMF followed by filtering.

20 30. The method of claim 28 where the borane material includes decaborane ($B_{10}H_{14}$).

31. The method of claim 28 where the magnesium borohydride material includes $Mg(BH_4)_2$.

25

32. The method of claim 28 where the aprotic solvent includes Diglyme ($C_6H_{14}O_3$).

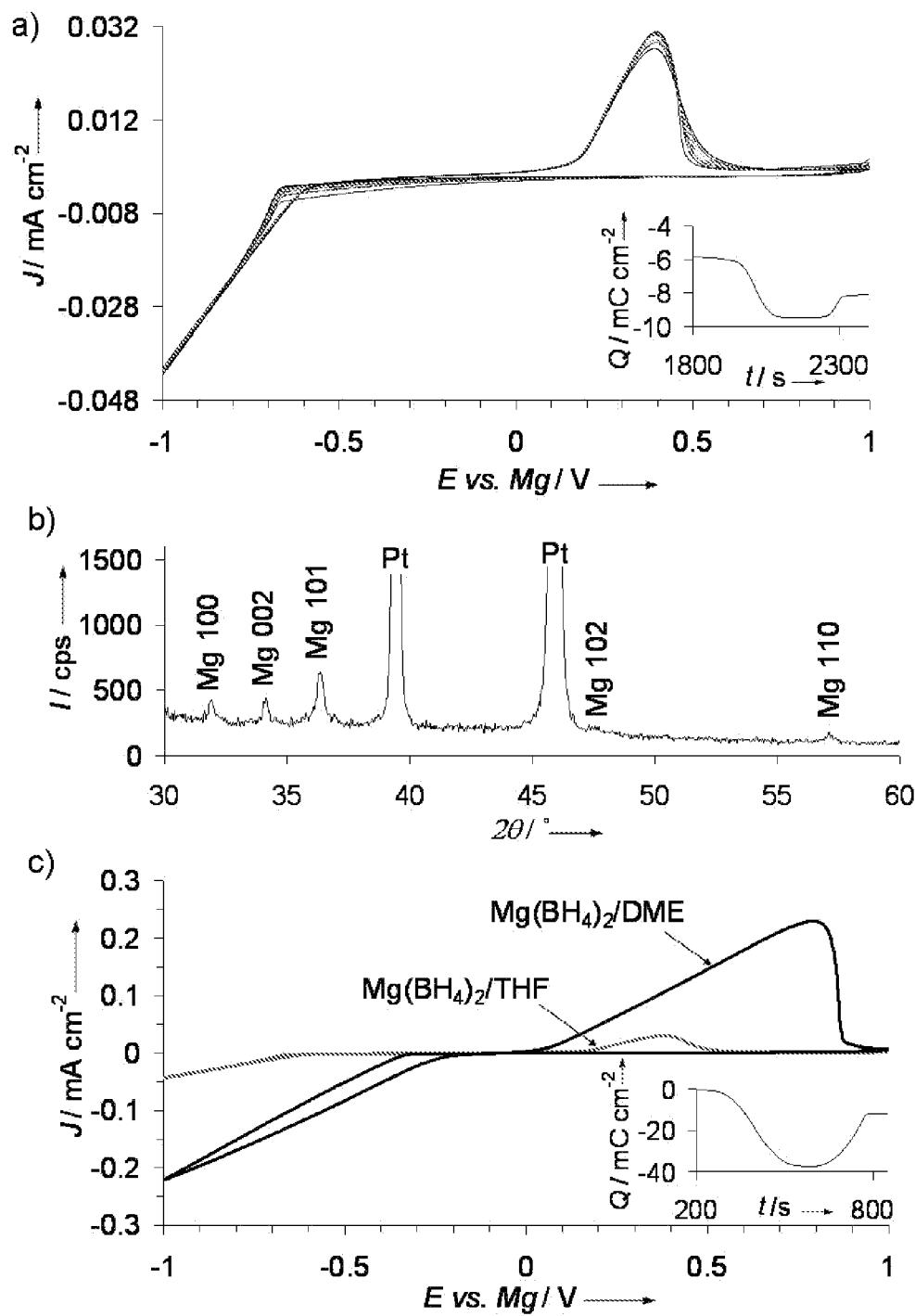
Figure 1

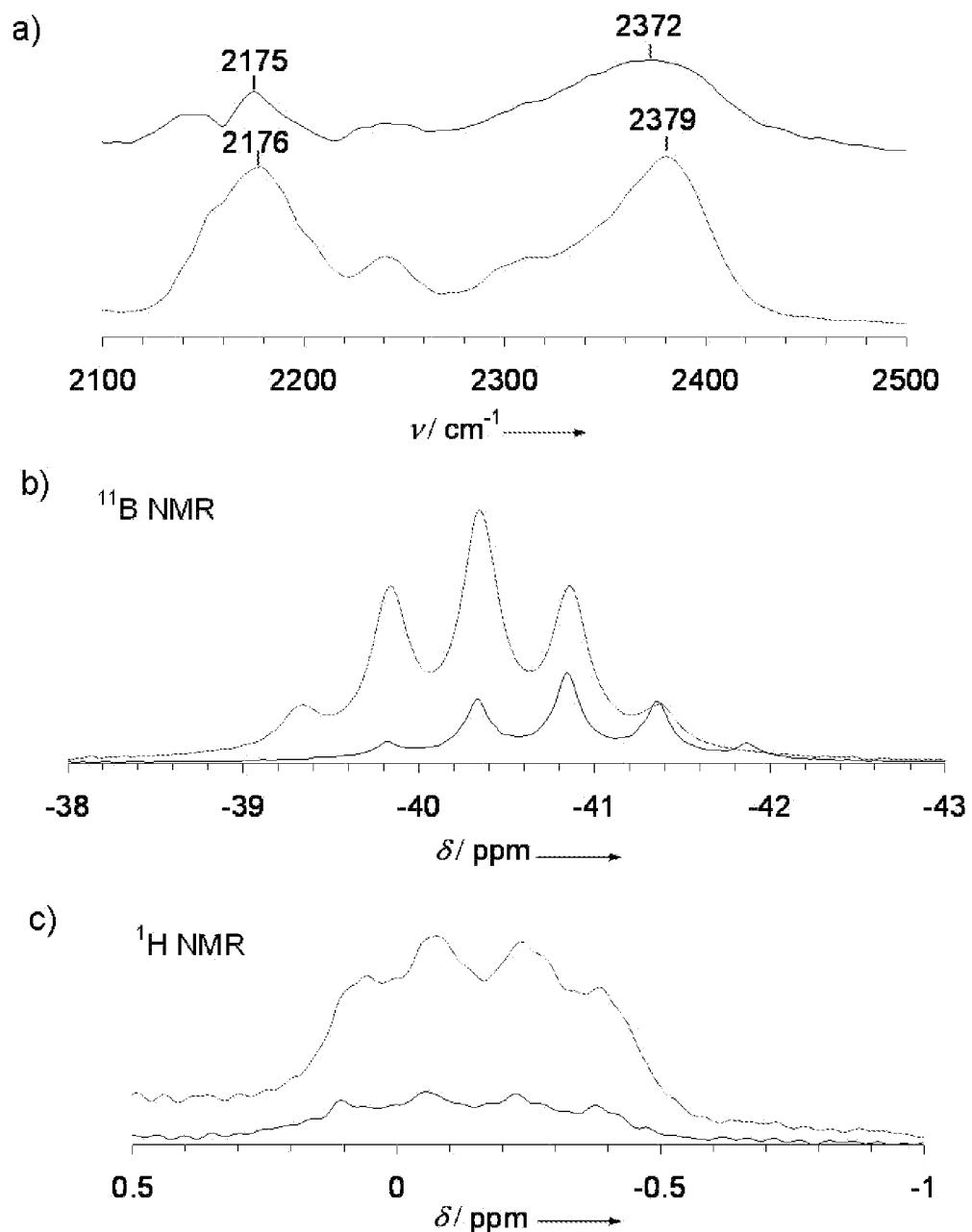
Figure 2

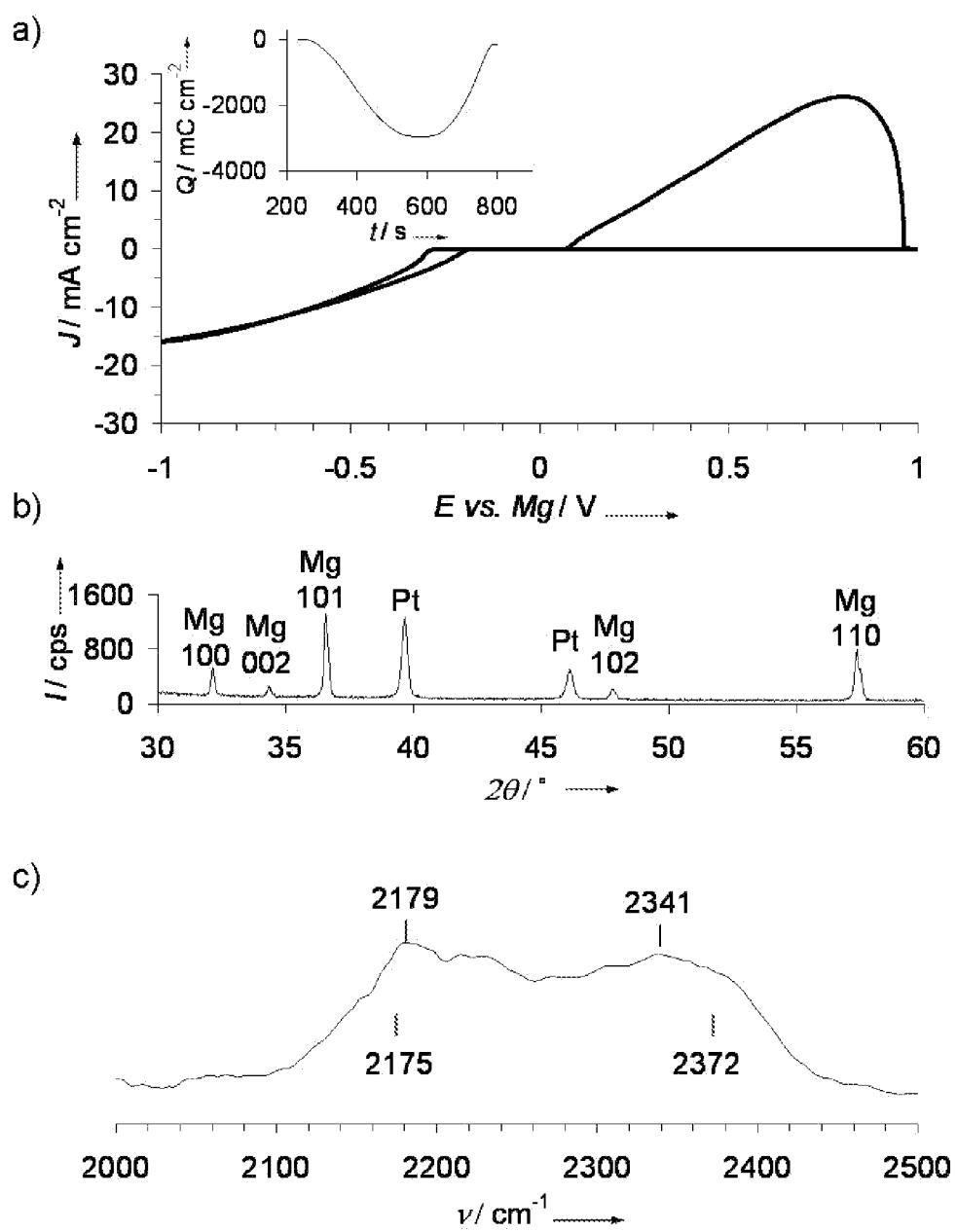
Figure 3

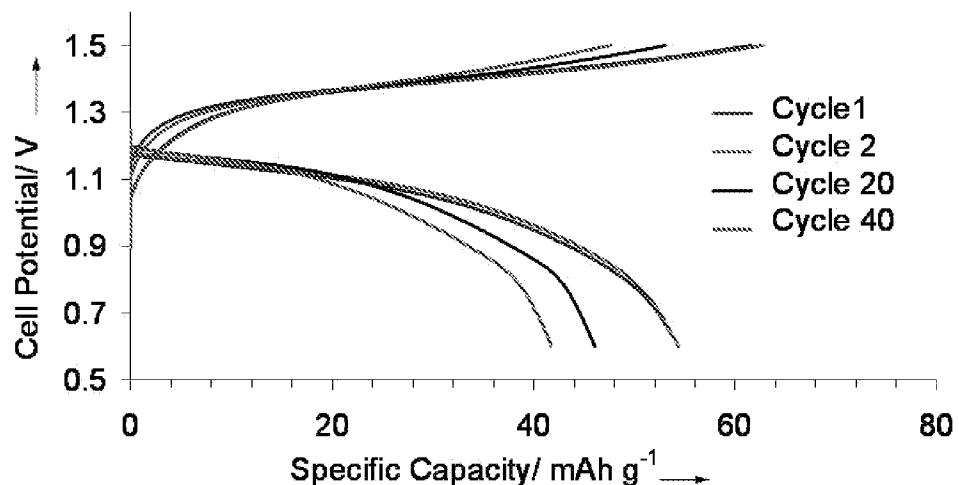
Figure 4

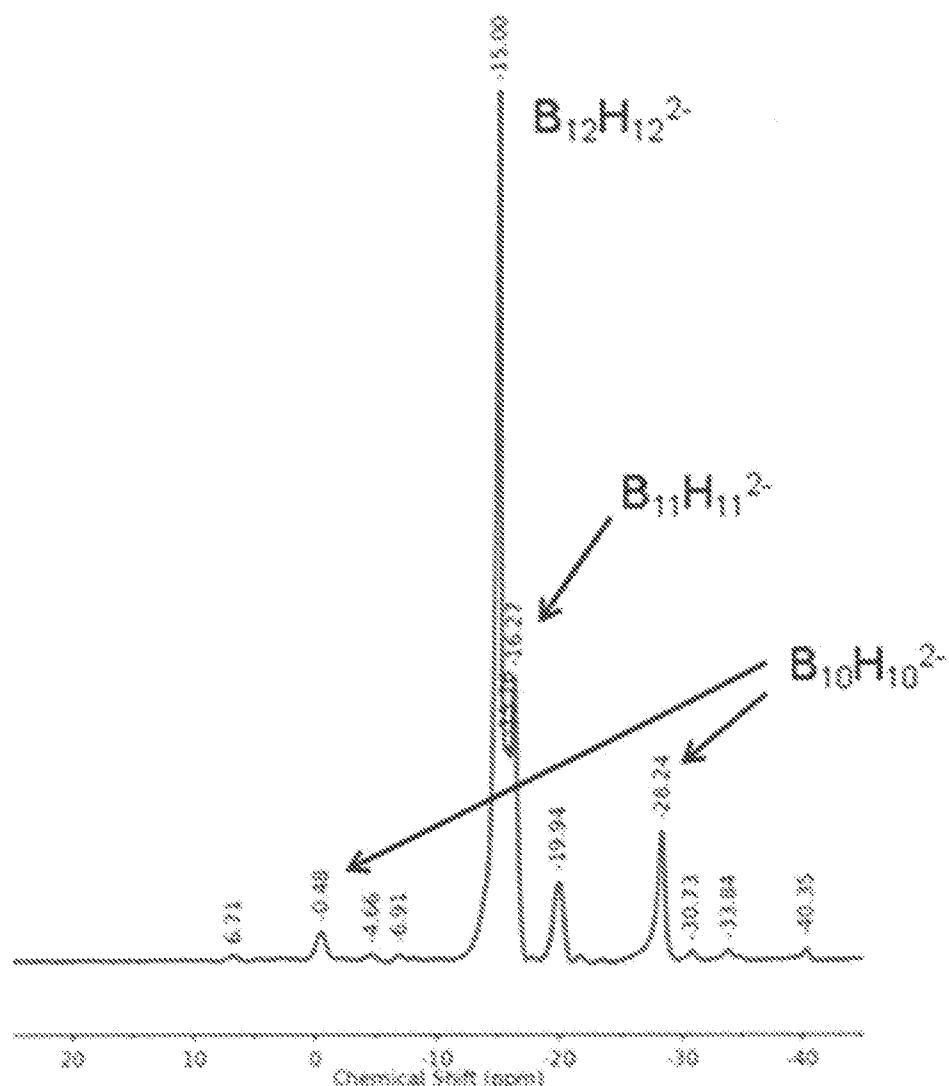
Figure 5A**Unpurified Product**

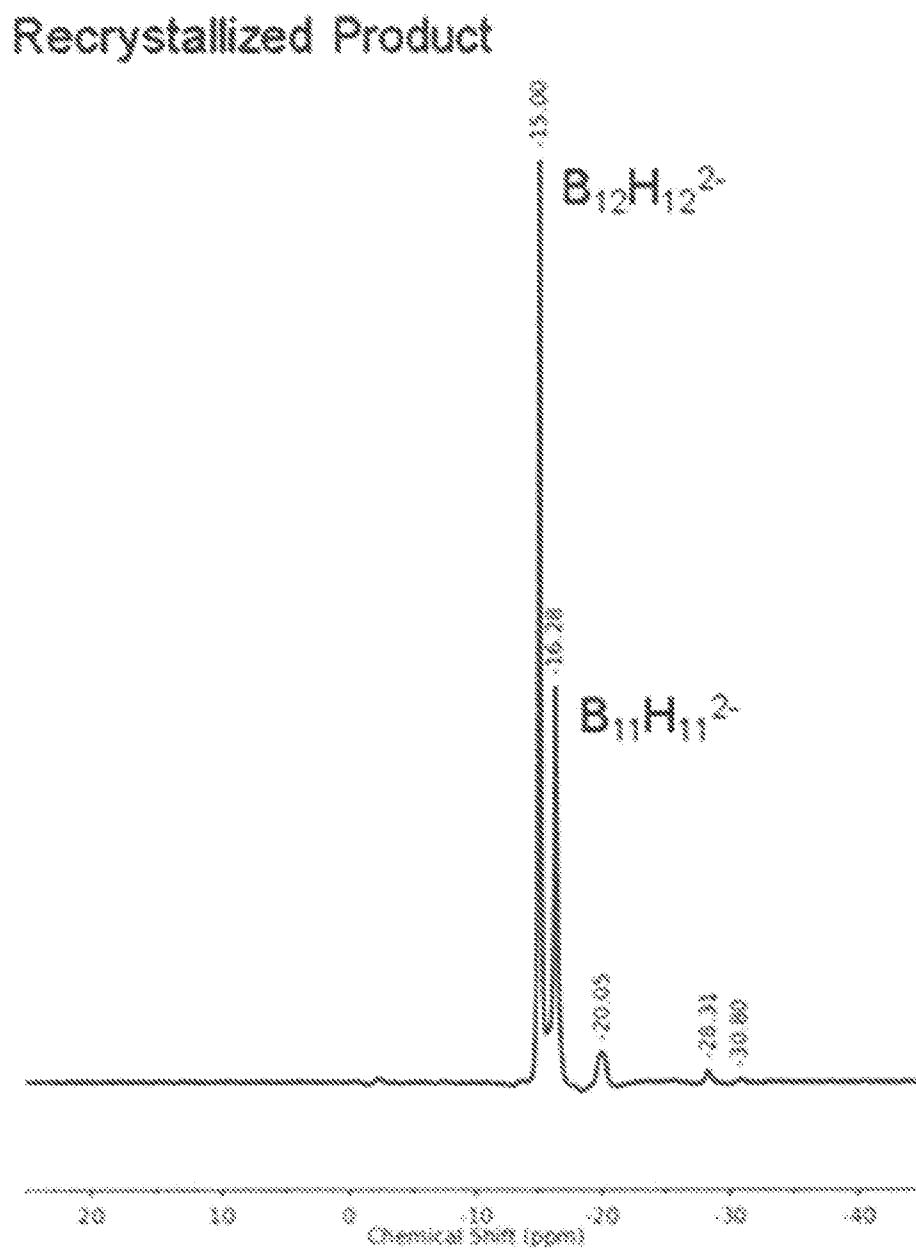
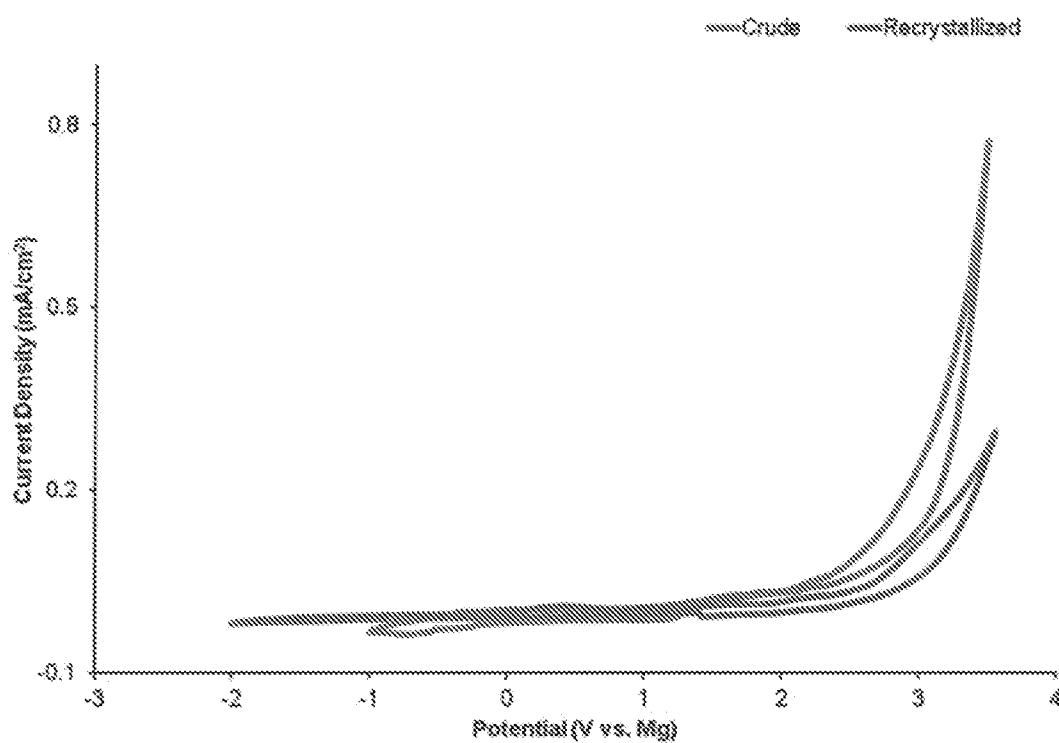
Figure 5B

Figure 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/053331**A. CLASSIFICATION OF SUBJECT MATTER****H01M 10/056(2010.01)i, H01M 10/054(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 10/056; C07F 5/02; H01M 10/40; H01M 6/04; H01M 10/0562; H01M 10/054

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 modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: magnesium, borohydride, electrolyte, battery**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0076572 A1 (AMINE, KHALIL et al.) 31 March 2011 See paragraphs [0006], [0016], [0064]–[0092]; and claims 1, 15–17.	1–32
A	US 6316141 B1 (AURBACH, DORON et al.) 13 November 2001 See column 4, line 63 – column 6, line 31; and claims 1–19.	1–32
A	US 2007-0048605 A1 (PEZ, GUIDO PETER et al.) 1 March 2007 See paragraphs [0065]–[0079]; and claims 1–2.	1–32
A	US 6383688 B1 (INAGAKI, HIROYUKI et al.) 7 May 2002 See column 3, line 24 – column 4, line 15; and claims 1–2.	1–32
A	US 2011-0117440 A1 (MAEKAWA, HIDEKI et al.) 19 May 2011 See paragraphs [0032]–[0041]; and claim 1.	1–32

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

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- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "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
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- "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 23 October 2013 (23.10.2013)	Date of mailing of the international search report 24 October 2013 (24.10.2013)
Name and mailing address of the ISA/KR  Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. +82-42-472-7140	Authorized officer LEE, Dong Wook Telephone No. +82-42-481-8163

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/053331

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0076572 A1	31/03/2011	None	
US 6316141 B1	13/11/2001	EP 1245053 A1 EP 1245053 A4 EP 1399999 A2 JP 2003-512704 A JP 2005-505099 A KR 10-2002-0060200 A KR 10-2004-0006005 A US 2001-0049060 A1 US 6713212 B2 WO 01-29919 A1 WO 02-097941 A2 WO 02-097941 A3	02/10/2002 10/08/2005 24/03/2004 02/04/2003 17/02/2005 16/07/2002 16/01/2004 06/12/2001 30/03/2004 26/04/2001 05/12/2002 27/02/2003
US 2007-0048605 A1	01/03/2007	CN 101132075 A CN 101132075 B EP 1763099 A2 EP 1763099 A3 JP 05013776 B2 JP 2007-087938 A KR 10-0815048 B1	27/02/2008 24/11/2010 14/03/2007 27/08/2008 29/08/2012 05/04/2007 18/03/2008
US 6383688 B1	07/05/2002	CN 1283315 A JP 04646399 B2 KR 10-2001-0033337 A WO 99-34471 A1	07/02/2001 09/03/2011 25/04/2001 08/07/1999
US 2011-0117440 A1	19/05/2011	JP 05187703 B2 KR 10-1182972 B1 KR 10-2010-0139116 A WO 2009-139382 A1	24/04/2013 18/09/2012 31/12/2010 19/11/2009