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COMMUNICATION

Lewis Acid-free and Phenolate-based Magnesium Electrolyte for Rechargeable Magnesium Batteries †

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A novel Lewis acid-free and phenolate-based magnesium electrolyte has been established. The excellent reversibility and stability of this electrolyte in battery cycling render this novel Lewis acid-free synthetic approach as highly promising alternative for the development of highly anodically stable magnesium electrolytes for rechargeable magnesium batteries.

Last two decades witnessed the extraordinary development of rechargeable lithium-ion batteries (LIBs), especially their great success for portable electronic applications and electric vehicles. However, the rapid growth of world energy consumption and environment crisis necessitate more efficient and safer stationary Electrical Energy Storage (EES) devises. In contrast to lithium, which possesses a volumetric capacity of 2062 mAh cm^{-3} and is prone to dangerous dendrite formation, magnesium has a higher volumetric capacity (3832 mAh cm^{-3}) and much better air stability, rendering rechargeable magnesium-ion batteries as promising candidates for the next generation of secondary batteries.[1] Currently, two technological obstacles are limiting the commercialization of rechargeable magnesium battery system: 1) high energy density cathodes which are able to intercalate Mg^{2+} ions; 2) highly ionic conductive electrolytes with a wide electrochemical window in which magnesium could be deposited reversibly.[2] Although effective magnesium deposition in ethereal Grignard reagent solutions can date back to early 20th century, the low anodic stability (less than 1.8 V vs Mg/Mg^{2+}) limited their potential applications in high voltage rechargeable magnesium batteries.[3] Thus, not much attention had been placed on magnesium for rechargeable batteries, until early this century. The breakthrough was made by Aurbach $et\ al$ with the development of a strong Lewis acid $EtAlCl_2$ induced Grignard derivative ($^nBu_2Mg\text{-}2EtAlCl_2$) which possesses a reversible magnesium deposition with an improved anodic stability at 2.4 V vs Mg/Mg^{2+}, and successful magnesium ion intercalation was achieved with the Chevrel phase Mo_6S_8 as the cathode material.[4] Since then, much more efforts have been dedicated to the design of high anodically stable magnesium electrolytes, most of which apply strong Lewis acids ($R_mAlCl_{3\text{-}m}$, R = alkyl; R'$_3$B, R' = aryl) to Grignard reagents or their derivatives (R''MgCl, R'' = chloride, aryl, alkyl, amide, or alkoxide).[5-12] This strategy has achieved a success with developments of electrolytes with more than 3 V (vs Mg/Mg^{2+}) anodic stability. However, the use of those very corrosive and combustible strong Lewis acids brings up the safety concern both for the preparation and storage of the electrolytes. Herein, we present the preparation of an all-magnesium phenolate-based electrolyte, which is strong Lewis acid-free, easy to prepare and possesses comparable stability and reversibility to its strong Lewis acid counterpart. The mechanism for its wide electrochemical window and excellent battery cycling reversibility will also be discussed.

Phenolate-based electrolytes for rechargeable magnesium batteries were initially reported by Yang $et\ al$ in 2012, and the work was further investigated by Bartlett $et\ al$.[11,13] Upon the addition of a strong Lewis acid $AlCl_3$, a series of ArOMgCl (Ar = aryl) electrolytes have shown good electrochemical performance with the anodic stability ranging from 2.1 V to 2.6 V. A great advantage of these phenolate-based electrolytes over their Grignard counterparts is the improved air stability. Inspired by this pioneer work and our recent contribution about enhanced electrochemical behavior of Hauser base ($Mg(HMDS)_2$, HMDS = hexamethyldisilazide) upon simply mixing with $MgCl_2$,[14] we decided to look into this phenolate-based strong Lewis acid-free all magnesium electrolyte system $(DTBP)MgCl\text{-}MgCl_2$ (DTBP = 2, 6-di-$tert$-butylphenolate). $(DTBP)MgCl$ could be generated $in\ situ$ via the reaction of 2, 6-di-$tert$-butylphenol and EtMgCl in THF. As presented in Figure 1(a), typical cyclic voltammogram shows that 0.5 M $(DTBP)MgCl$ in THF solution possesses reversible magnesium deposition-dissolution process with a 70% coulombic efficiency, while the anodic stability is only around 1.5 V. In addition, its low current density (0.40 mA cm^{-2}), ionic conductivity (0.13 mS cm^{-1}) and diffusion coefficient (2.1*10^{-10} cm^2 s^{-1}) all suggest that $(DTBP)MgCl$ itself is not a suitable candidate for rechargeable magnesium batteries. Strong Lewis acid $AlCl_3$ has already been proven a good additive to increase $(DTBP)MgCl$ anodic stability to around 2.2 V.[11] Herein, we

discovered that, instead of using corrosive $AlCl_3$, the addition of one equivalent $MgCl_2$ enhances the electrolyte's anodic stability to 2.3 V with 100% coulombic efficiency (as shown in Figure 1(b)), which is even better than its $AlCl_3$ counterpart. In addition to the + 0.8 V enhanced electrochemical window, adding $MgCl_2$ also improves the electrolyte's current density to 3.36 mA cm^{-2} (8 times higher), ionic conductivity to 0.66 mS cm^{-1} (5 times higher), and diffusion coefficient to 3.0*10^{-9} cm^2 s^{-1} (14 times higher). Differently from the $AlCl_3$-based systems, in which the Lewis acid-base ratio has an significant effect on the electrolytes' electrochemical window,[15] no such influence was observed for this all-magnesium electrolyte system. Upon varying (DTBP)MgCl to $MgCl_2$ ratio from 2:1 to 1:2, only the current density increases to some extent, and the anodic stability stays at about the same 2.3 V (Figure S1 in ESI).
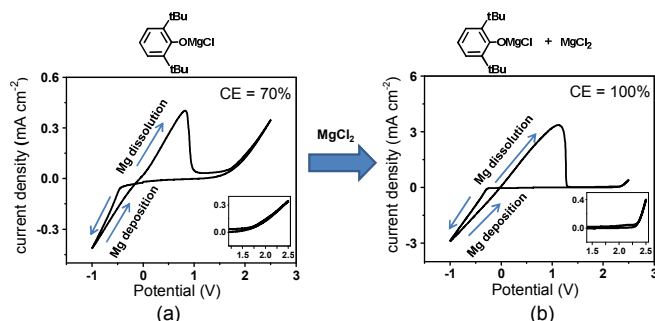

Figure 1. Typical steady-state cyclic voltammograms (0.1 V/s) with Pt as working electrode, Mg ribbons as counter and reference electrodes: (a) 0.5 M (DTBP)MgCl in THF (inset shows the enlargement region between 1.2 V and 2.5 V); (b) 0.5 M (DTBP)MgCl-MgCl$_2$ in THF (inset shows the enlargement region between 1.4 V and 2.5 V).

In order to obtain further insight into the mechanism behind the significantly enhanced electrochemical behavior for this all magnesium electrolyte, a single crystal X-ray diffraction analysis was carried out. As shown in Figure 2, in the solid state, the structure isolated from the THF solution of (DTBP)MgCl-MgCl$_2$ was confirmed as an ionic pair $[Mg_2Cl_3(THF)_6]^+[(DTBP)_3Mg]^-$. The cation contains the prototype three chloride bridged di-magnesium core structure coordinated by three THF donors for each metal center. The exact same cation has been reported to be present in most Grignard and Grignard derivative-based magnesium electrolytes, and this cation is also widely accepted as the active species for the reversible deposition of the electrolytes.[1] Interestingly, the anion is determined to be a C_3 symmetric tris-phenolate magnesium structure. The same magnesium centered anion was reported by Ruhlandt-Senge *et al* in an ionic lithium salt $[Li(THF)_3]^+[(DTBP)_3Mg]^-$, in which the anion's stability was attributed to the sterically hindered DTBP groups.[16] Consistent with this assumption, when sterically less bulky substituents were used, they observed the alkoxide bridged Li-Mg heterobimetallic molecules which are not ionized. Thus, in our all-magnesium electrolyte, it is highly possible that the sterically demanding DTBP substituents account for the stability of the $[Mg_2Cl_3(THF)_6]^+[(DTBP)_3Mg]^-$ ionic pair, which in turn results in good electrochemical properties for the electrolyte. To further assess the substituents' size effect on the anodic stability of the alkoxide-based magnesium electrolytes, a sterically less demanding derivative (2, 4-DTBP)MgCl (2, 4-DTBP = 2, 4-di-*tert*-butylphenolate) has been evaluated. The in *situ* generated (2, 4-DTBP)MgCl was mixed with one equivalent $MgCl_2$ in THF, and the resulting electrolyte shows an anodic stability at 1.5 V with a current density at around 0.8 mA cm^{-2} (see Figure S2 in ESI), suggesting the importance of

substituents' steric bulkiness to this all-magnesium electrolytes' anodic stability. In addition to probing the steric effect on the stability of the electrolytes, a series of electron-withdrawing substituted derivatives (4-fluorophenolate, 3-trifluoromethylphenolate, pentafluorophenolate) have also been evaluated to assess the electronic effect on this all magnesium electrolyte system. As shown in Figure S5-S7 in ESI, all the electrolytes have anodic stability below 2.0 V *vs* Mg/Mg^{2+}, indicating that electron-withdrawing substituents are likely disfavoring the high anodic stability.
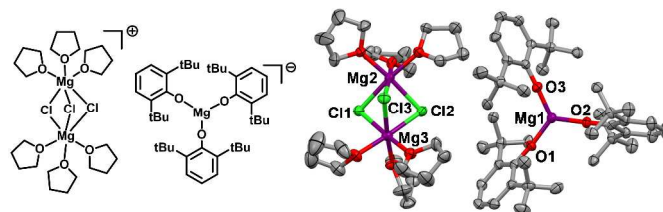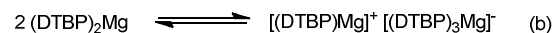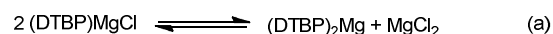

Figure 2. Displacement ellipsoid representation (50% probability level) of $[(DTBP)Mg]^+[(DTBP)_3Mg]^-$. For clarity, two solvated THF molecules and hydrogens are omitted. Selected bond length (Å) and angles (º): Mg1-O1, 1.851(3); Mg1-O2, 1.851(3); Mg1-O3, 1.947(3); Mg2-Cl1, 2.490(2); Mg2-Cl2, 2.521(2); Mg2-Cl3, 2.503(2); Mg3-Cl1, 2.490(2); Mg3-Cl2, 2.499(2); Mg3-Cl3, 2.531(2); O1-Mg1-O2, 119.5(2); O1-Mg1-O3, 120.6(2); O2-Mg1-O3, 119.8(2); Mg2-Cl1-Mg3, 78.4(1); Mg2-Cl2-Mg3, 77.6(1); Mg2-Cl3-Mg3, 77.4(1).

The discovery of the solid state structure enables us to propose the mechanism pathway to the electrochemically active ionic species of the electrolyte. Structures of DTBP containing magnesium compounds were initially reported by Ittel *et al* and the structures' variation was further investigated by Henderson *et al*.[17,18] As they reported, (DTBP)$_2$Mg exists as a dimer in non-coordinating solvents, while in THF the dimer is broken into monomer with coordinating solvent molecules. However, in solution they observed the formation of an ionic pair $[(DTBP)Mg]^+[(DTBP)_3Mg]^-$, which contains the same anion as isolated in our all-magnesium electrolyte. Due to its sensitivity and small amount, the solid state structure of their ionic pair was not isolated. Enlightened by this work and the solid state structure we successfully determined, we are able to propose the mechanism for the formation of the $[Mg_2Cl_3(THF)_6]^+$ cation in our electrolyte. As shown in Scheme 1, firstly, the Grignard-type Schlenk equilibrium takes place to generate (DTBP)$_2$Mg and MgCl$_2$ (step (a)). According to literature,[18] (DTBP)$_2$Mg then undergoes self-unsymmetric cleavage to form an ionic pair $[(DTBP)Mg]^+[(DTBP)_3Mg]^-$ (step (b)). The intermediate ionic pair $[(DTBP)Mg]^+[(DTBP)_3Mg]^-$ is not very stable in solution, and further reacts with MgCl$_2$ through the cation exchange, forming $[Mg_2Cl_3(THF)_6]^+[(DTBP)_3Mg]^-$ as the final stable species (step (c)). The mechanism suggests that, the addition of MgCl$_2$ does not introduce any new component to (DTBP)MgCl in solution, whereas, it helps to push the equilibriums to the electrochemically active ionic pair species. In contrast, for the strong Lewis acid induced magnesium electrolytes, addition of AlCl$_3$ or borane changes the components of the electrolytes drastically, generating aluminate or borate as the anions for the electrochemically active species.

$$2 \text{ (DTBP)MgCl} \rightleftharpoons \text{(DTBP)}_2\text{Mg} + \text{MgCl}_2 \qquad (a)$$

$$2 \text{ (DTBP)}_2\text{Mg} \rightleftharpoons [\text{(DTBP)Mg}]^+ [\text{(DTBP)}_3\text{Mg}]^- \qquad (b)$$

$$[\text{(DTBP)Mg}]^+ + 2\text{MgCl}_2 \rightleftharpoons [\text{Mg}_2\text{Cl}_3]^+ + \text{(DTBP)MgCl} \qquad (c)$$

Scheme 1. Proposed mechanism for the formation of ionic pair in THF, $[(DTBP)Mg]^+[(DTBP)_3Mg]^-$.

The first step of our proposed mechanism suggests that the following equilibrium should also apply to this all-magnesium electrolyte system: $2(DTBP)MgCl + 2MgCl_2 \leftrightarrows (DTBP)_2Mg + 3MgCl_2$. Thus to further verify the mechanism and the above proposed equation, $(DTBP)_2Mg$ was synthesized according to the literature procedure.[18] No reversible magnesium deposition was detected for $(DTBP)_2Mg$ itself in THF solution. While mixed with three equivalent $MgCl_2$, the generated electrolyte $(DTBP)_2Mg$-$3MgCl_2$ (0.25 M in THF) shows quite comparable electrochemical behavior to 0.5 M $(DTBP)MgCl$-$MgCl_2$ in THF (Figure S3 in ESI). In addition, the exact same ionic pair featured solid state structure of $[Mg_2Cl_3(THF)_6]^+[(DTBP)_3Mg]^-$ was also isolated from $(DTBP)_2Mg$-$3MgCl_2$, suggesting the two electrolytes share the same components in solution. The results further support the mechanism we proposed in Scheme 1. Similarly, no anodic stability was affected when varying equivalence of $MgCl_2$ for electrolytes $(DTBP)_2Mg + xMgCl_2$ (x = 1, 2, 3 and 4, see Figure S4 in ESI).

Having established a good understanding about this all-magnesium electrolyte's electrochemical behavior, we would like to further demonstrate its compatibility with cathode intercalation. As the most widely understood and studied cathode for rechargeable magnesium batteries, Chevrel phase (Mo_6S_8) was synthesized and utilized to test our all magnesium electrolytes' reversibility. The reversibility and compatibility of our electrolytes with Mo_6S_8 were first confirmed in the three-electrode CV measurement in Swagelok cells using Mo_6S_8 as working, magnesium discs as counter and reference electrodes (Figure S11 in ESI). The 2032-type coin cell was assembled using 0.5 M $(DTBP)MgCl$-$MgCl_2$ THF solution as the electrolyte, Chevrel phase (Mo_6S_8) as the cathode material and freshly polished magnesium disc as the anode electrode. The cell was cycled at a current rate of 0.05 C at 55 ℃ with the discharge and charge potential cutoffs at 0.2 V and 1.6 V respectively. Figure 3(a) shows the typical charge-discharge profiles at several representing cycles (5th, 10th, 25th, and 50th, respectively). The discharge capacity remains at about 100 mAh g^{-1} with an almost 100% cycling efficiency (Figure 3(b)). Lower discharge capacity was observed when the battery cell was cycled at room temperature (around 65 mAh g^{-1}, see Figure S8 in ESI), which is due to the partial charge trapping in Mo_6S_8 host.[4] The quite comparable battery reversibility has also been observed when 0.25 M $(DTBP)_2Mg$-$3MgCl_2$ was used as the electrolyte (Figure S9 and S10 in ESI). The results suggest that our all-magnesium electrolytes have great potential for rechargeable magnesium batteries.

There is recently interest about current collector stability toward Grignard type electrolyte such as APC[19] and bisamide electrolyte.[20] One of the common features of APC and bisamide electrolyte is the high concentration of chloride anions, which is also a distinctive characteristic of our new Mg electrolyte. The stability of stainless steel was ~ 2.8 V vs Mg when it was used as a current collector for chloride-containing electrolytes, therefore it was selected as the current collector for the Mg-Mo_6S_8 batteries.
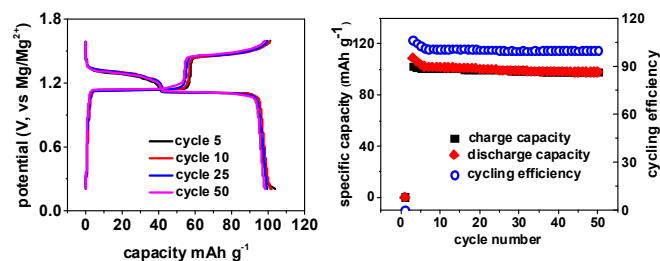

Figure 3. (a) charge-discharge profiles for cycle 5th (black), 10th (red), 25th (blue) and 50th (purple) at a current rate of 0.05 C at 55 ℃; (b) charge-discharge capacity performance and cycling efficiency.

In conclusion, a novel phenolate-based all-magnesium electrolyte $(DTBP)MgCl$-$MgCl_2$ has been established. This new strong Lewis acid-free electrolyte possesses comparable high oxidative stability to its strong Lewis acid counterpart. The excellent reversibility and compatibility with Chevrel phase Mo_6S_8 cathode suggest this electrolyte has great potential for rechargeable magnesium batteries. In addition, the synthetic concept herein also opens a new door for the development of more both strong Lewis acid-free and highly oxidative stable magnesium electrolytes for rechargeable magnesium batteries in the future.

Notes and references

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Table of content graphic

Strong Lewis acid-free and phenolate-based electrolyte development for rechargeable magnesium-ion batteries