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Novel transmetalation reaction for electrolyte synthesis for rechargeable magnesium batteries

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A simple strategy for the synthesis of the electrolyte solutions comprised of binuclear magnesium aluminate complexes without the need for organomagnesium compounds is established. The as-prepared phenolate based electrolyte exhibits an anodic stability of up to 3.4 V, good ionic conductivity and air-stability.

The long term success of electric vehicles requires the development of safe, low-cost rechargeable batteries with long cycle lives. Limitations in available lithium resources and unresolved safety issues are important incentives for the development of so-called post-lithium-ion batteries. Because magnesium is an abundant element in the earth's crust, whose metallic form can be safely used as an anode, it has emerged as an attractive alternative. Particularly promising is magnesium's theoretical volumetric capacity of up to 3832 mA h cm^{-3}, which due to the divalent nature of Mg^{2+} is significantly higher than that of either lithium (2062 mAh cm^{-3}) or sodium (1136 mAh cm^{-3}).[1,2] In contrast to the cases of lithium and sodium, conventional Mg salts such as magnesium perchlorate or magnesium bis(trifluoromethane sulfonyl)-imide are not able to reversibly conduct magnesium ions in aprotic solvents.[3,4] Thus, a major challenge in the commercialization of Mg batteries is the development of an electrolyte which is stable in contact with the electrode materials, does not form a blocking layer and has a wide electrochemical window.

Gregory *et al.* initially demonstrated the magnesium ion conductivity of solutions containing Mg organo-borates or organo-aluminates.[1] Aurbach *et al.* then improved the oxidative stability of this new class of electrolytes by reacting $AlCl_{3-x}R_x$ Lewis acids with R_2Mg Lewis bases in ethers at various ratios, and demonstrated the first prototype of a rechargeable Mg battery.[2] Since then the properties of these electrolytes have been further optimized by combining different organomagnesium compounds with Lewis acids using the same concept.[5,6] The comprehensive analysis of solutions obtained by reacting an organomagnesium R_xMgCl_{2-x} (x = 1, 2) with a Lewis acid of the form R'_yAlCl_{3-y} (y = 0, 1, 2) reveals a complex mixture of various moieties,[7] originating from several transmetalation reactions that occur during the preparation. Interestingly, crystallographic studies of electrolytes generated from various combinations of organomagnesium compounds and Lewis acids reveal very similar structures. In all cases a cation, consisting of two magnesium atoms bridged by three chlorines, was paired with a counter anion such as an organo-aluminate or borate.[7-10] Similar complexes have also been obtained by reacting Bu_2Mg with $EtAlCl_2$,[8] in what was initially supposed to be a metathesis reaction resulting in $Mg(AlCl_2BuEt)_2$.[2] These results imply that such binuclear magnesium compounds are the thermodynamically favored product in reactions between organomagnesiums and Lewis acids. Moreover, the resulting binuclear magnesium complexes have been found to be capable of facilitating reversible Mg deposition while showing enhanced oxidative stability in comparison with the as-prepared solutions. For example, the non-nucleophilic THF solution of the recrystallized $[Mg_2(\mu\text{-}Cl)_3(THF)_6][HMDSAlCl_3]$ (HMDS = hexamethyldisilazide) showed a higher voltage stability than that of the reaction mixture.[8] We recently synthesized such electrolytes by reacting bis-hexamethyldisilazide magnesium $[(HMDS)_2Mg]$ with 2 equivalents of $AlCl_3$ in various ethers and obtained a binuclear magnesium complex, which proved to be the same as the electrochemically active species in our solutions.[10]

To avoid the negative influences of some of by-products produced during the previously utilized synthesis with organomagnesiums, a straightforward synthesis with minimal side products would be beneficial. Here we present a novel transmetalation reaction between $MgCl_2$ and organoaluminum compounds, which leads exclusively to the electrochemically active aluminate complex, as expressed in the general chemical equation 1 (x = 1, 2, 3; neglecting the solvent ligands).

$$2MgCl_2 + R_xAlCl_{3-x} \rightarrow [Mg_2Cl_3]^+[R_xAlCl_{4-x}]^- \qquad 1$$

By means of this reaction, we are able to obtain a chemical bond between aluminum and the ligand in the complexes which is more stable than the Al-C bonds and are thus able to optimize the properties of the electrolyte. Since it is possible to estimate the relative oxidative stability of molecules or ions by calculating the energy of their highest occupied molecular orbitals (HOMOs) energy,[7] we use density functional (DFT) calculations to predict the proper aluminum Lewis acid for the reaction, on the assumption that ions with lower HOMO energy levels exhibit greater stability toward oxidation. (ESI†) It should be mentioned that a similar reaction of $MgCl_2$ and $AlCl_3$ for an inorganic Mg ion electrolyte was reported by Aurbach *et al.* while we were independently carrying out this work.[11]

To validate the supposed reaction 1, we first chose a series of commercially available organoaluminums such as Et_2AlCl, $EtAlCl_2$ and Et_3Al to react with $MgCl_2$ in three ethereal solvents (THF, diglyme and tetraglyme). The detailed synthesis is described in ESI†. $MgCl_2$ has a very low solubility in ethereal solvents. However, as organoalumium was added to a suspension of $MgCl_2$, it gradually reacted upon stirring, giving a clear colorless solution. The amount of organoaluminum added was determined by watching for the solid $MgCl_2$ to completely vanish. The concentration of the electrolytes was based on the amount of $MgCl_2$.

This transmetalation reaction was confirmed by means of single crystal X-ray diffraction and NMR methods. Quantitative colorless crystals were prepared by slow diffusion of hexane after the reaction between $MgCl_2$ and Et_2AlCl at a ratio of 1.5:1 in THF. The crystal structure was determined by single-crystal X-ray diffraction as $[Mg_2(\mu\text{-}Cl)_3(THF)_6][Et_2AlCl_2]$ **1** (Fig. 1a‡), where the crystal unit consists of an ionic pair. The cation is a typical binuclear Mg bridged by three chlorine atoms, with each Mg ion being solvated by three THF molecules to complete the octahedral coordination. The counter anion is an aluminum atom tetrahedrally coordinated by two ethyl groups and two chlorine atoms.

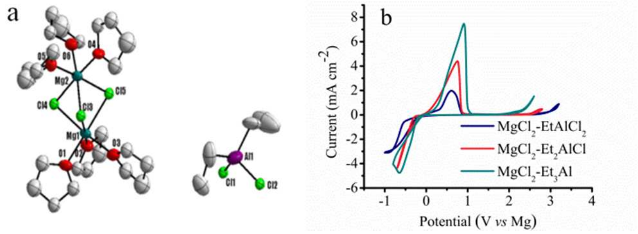

Fig. 1 a ORTEP plot (50% thermal probability ellipsoids) of $[Mg_2(\mu\text{-}Cl)_3(THF)_6][Et_2AlCl_2]$, Hydrogen atoms are omitted for clarity; b Cyclic voltammograms of the 1 M tetraglyme solutions using Pt as electrode at a scan rate of 25 mV s^{-1}.

The composition of the reaction products was further characterized by ^1H, ^{13}C and ^{27}Al NMR. The spectra of the reaction mixture in THF and that of the dissolved crystals are nearly identical, indicating that the transmetalation is completed under the reaction conditions. It has been proved that $[Mg_2(\mu\text{–}Cl)_3]^+$ exists in the equilibrium shown in chemical equation 2[7-9] (neglecting the solvent ligands).

$$[Mg_2Cl_3]^+ \leftrightarrow MgCl_2 + MgCl^+ \qquad 2$$

Therefore, we propose that the transmetalation reaction (1) is in dynamic equilibrium. The organoaluminum Lewis acid acts as a Cl^- acceptor and converts into a tetrakis-ligated aluminate by taking a chloride from $MgCl_2$. The experimental mole ratio of $MgCl_2$ to aluminum compounds is not the stoichiometrically anticipated 2:1, but about 1.5:1, and varies depending on which Lewis acid is used. The electrochemical properties of the solutions prepared by the reactions between $MgCl_2$ and Et_3Al, Et_2AlCl or $EtAlCl_2$ in various ethereal solvents were investigated. The cyclic voltammograms reveal that all solutions are capable of reversible Mg deposition. Fig. 1a illustrates representative cyclic voltammograms of the tetraglyme solutions, in which the electrolyte obtained from the combination of $MgCl_2$ and $EtAlCl_2$ shows the highest oxidative stability, *i.e.* up to 2.9 V.

Theoretical calculations imply that the electrochemical stability window of the solution containing an organohaloaluminate anion, represented as $[R_xAlCl_{3-x}]^-$, is correlated to the Cl:R-ligand ratio, such that a higher the Cl:R ratio leads to a higher oxidative potential.[12] The cyclic voltammograms of the as-prepared solutions from the three aforementioned combinations indicate that the experimental results follow the trend observed in the calculations.(ESI†) In addition, our measurements reveal a correlation between the current density of the deposition-dissolution and the Cl:R ratio, *i.e.* the higher the Cl:R ratio, the lower the exchange current density.

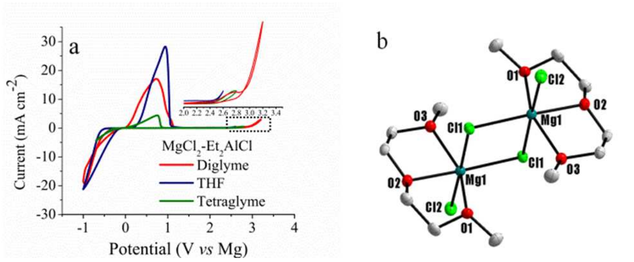

Fig. 2 a Cyclic voltammograms of the 1 M various ethereal solutions using Pt as electrode at a scan rate of 25 mV s^{-1}; b ORTEP plot (50% thermal probability ellipsoids) of $[Mg_2(\mu\text{-}Cl)_2(diglyme)_2]Cl_2$. Hydrogen atoms are omitted for clarity.

Glymes are suitable solvents for the electrolytes because of their thermal and chemical stabilities, high dielectric constants, and strong solvating power. Hence, we examined the electrochemical properties of the solutions prepared through the transmetalation between $MgCl_2$ and Et_2AlCl denoted as $MgCl_2$-Et_2AlCl in various ethereal solvents.(Fig.2a) The comparison of the oxidative stability and ionic conductivity of the as-prepared solutions with the same composition implies that diglyme has beneficial effects on the electrolyte properties *e.g.* a high cycling efficiency of 98% and an ionic conductivity of up to 3.0 mS cm^{-1} for a 1 M solution.(ESI†) An attempt to recrystallize the digylme adduct of the binuclear magnesium complex, however, resulted in dimers of the solvated $MgCl_2$, in which three oxygen atoms from diglyme and two bridging and one non-bridging chloride ions coordinate to the central Mg ion, which adopts a distorted octahedral coordination mode (Fig.2b‡). Based on our experimental observations and NMR studies, we believe that a binuclear complex similar to **1** should also be formed in the diglyme solution. This assumption is supported by the electrochemical studies discussed above. Considering the molecular tension caused by the chelating linear polyether ligand, we suppose that the $[Mg_2(\mu\text{–}Cl)_3]^+$ in diglyme is less stable than in THF and that the equilibrium shown as equation 2 thus shifts to the right until the stable $MgCl_2$ is finally isolated by means of recrystallization.

Previous investigations have indicated that the electrochemical stability window of the magnesium halo-alkyl aluminate complex solutions is dominated chiefly by the bonding between the ligand and the aluminum atom.[12] Owing to the higher electronegativity of nitrogen and oxygen, the polar Al-N or Al-O bond in the aluminate anion should benefit the oxidative stability of the electrolyte. The Al-N bond in the $[Mg_2(\mu\text{-}Cl)_3][HMDSAlCl_3]$ electrolyte has demonstrated an anodic stability in excess of 3.5 V.[10] Recently other non-Grignard electrolytes have been prepared by reacting phenolate magnesium chlorides with $AlCl_3$ in THF. There a similar binuclear Mg aluminate complex was revealed by single crystal X-ray diffraction.[13,14] However, despite the high stability of Al-O bonds, the voltage stability of such electrolytes is surprisingly found to be inferior to the best Grignard reagent based electrolytes.

We have developed a straightforward synthetic route for obtaining such electrolytes by employing the transmetalation reaction between $MgCl_2$ and dichloroaluminum phenolates and examined the electrochemical performance of the resulting electrolytes. The electrolyte solutions were prepared by adding $PhOAlCl_2$ to a suspension of $MgCl_2$ in diglyme at a ratio of 1:1 and stirred for 24 hours (ESI†). Based on the NMR spectra, the solution is similar to the above described equilibrium involving the binuclear magnesium aluminate expressed in the chemical formula: $[Mg_2Cl_3][PhOAlCl_3]$ (neglecting the solvent ligands).

The as-prepared 0.6 M solution, denoted as Mg-TCP/DEG, demonstrates an anodic stability of up to 3.4 V (Fig 3a), which is 0.7 V higher than that reported for a THF solution prepared by the reaction between phenolate magnesium chloride and $AlCl_3$.[12] The Mg deposits, resulting from 3 hours of deposition at a current of 1 mA cm^{-2}, were probed using XRD (Fig.5b). After stirring under dry air overnight, the electrolyte Mg-TCP/DEG shows an outstanding air-insensitivity with a voltage stability of up to 3.2 V as depicted in Fig.3a. Furthermore, a reversible cycling efficiency of about 85 % was calculated by means of charge balance (Inset in Fig.3a) and an ionic conductivity of 2.6 mS cm^{-1} at 25 °C was determined for the Mg-TCP/DEG electrolyte. Fig.4a shows the reversible galvanostatic cycling of Mg deposition of Mg-TCP/DEG after being exposed to air overnight.

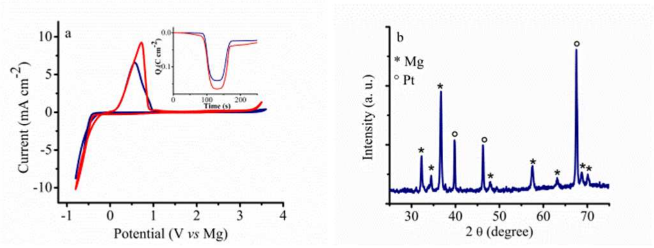

Fig.3 a Cyclic voltammograms of Mg-TCP/DEG (blue) and after being stirred in dry air overnight (red) using Pt as an electrode at a scan rate of 25 m V s^{-1}; Inset shows the charge balance of Mg deposition/dissolution; b XRD diffraction patterns of Mg deposited on Pt.

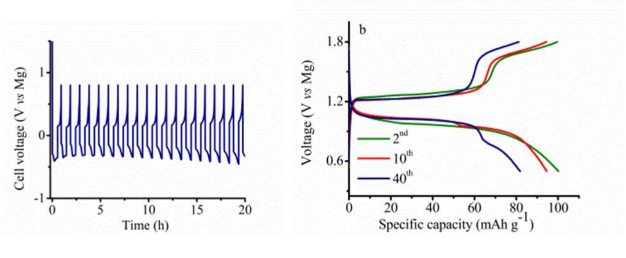

Fig. 4 a The chronopotentiograms of Mg deposition/dissolution on Pt in Mg-TCP/DEG at a current of 0.5 mA cm^{-2}; b Cycling behaviour of the Mg/Mo_6S_8 cell using 0.6 M of Mg-TCP/DEG at a current rate of 20 mA g^{-1} at 25 °C.

To confirm the compatibility of the Mg-TCP/DEG electrolyte with an intercalation cathode, the Mo_6S_8 Chevrel phase was synthesized.[15] Fig. 4a presents typical galvanostatic cycling curves with a specific discharge capacity of ca.100 mAh g^{-1}. The aforementioned electrolytes $MgCl_2$-Et_2AlCl in glymes have also demonstrated excellent rechargeable battery performance (ESI†). These results demonstrate that these transmetalation equilibrium based electrolytes can be incorporated into rechargeable Mg batteries.

In summary, we have established a new synthetic method using $MgCl_2$ and an aluminium Lewis acid to yield equilibrium solutions comprised of binuclear magnesium aluminate complexes, which are capable of reversible electrochemical Mg deposition and Mg ion conduction. The feasibility of this transmetalation reaction with various aluminium Lewis acids such as aluminium phenolates, which are more air insensitive than organomagnesium/aluminium compounds, opens the door for the further development of air-stable and non-nucleophilic electrolytes for the high energy magnesium batteries.

Notes and references

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† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

‡ Refinement details, atom coordinates, thermal parameters, and full tables of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, No. CCDC 993436, 993437, copies of this information can be obtained free of charge from CCDC via http://www.ccdc.cam.ac.uk or E-Mail: deposit@ccdc.cam.ac.uk

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A straightforward synthesis of the electrolyte solutions comprised of binuclear magnesium aluminate complexes without the need for organomagnesium compounds is established. The phenolate based electrolyte exhibits an anodic stability of up to 3.4 V, good ionic conductivity and air-stability.

$$\mathrm{MgCl_2 + PhOAlCl_2 \xrightarrow{solvent} Mg\ ion\ electrolyte}$$