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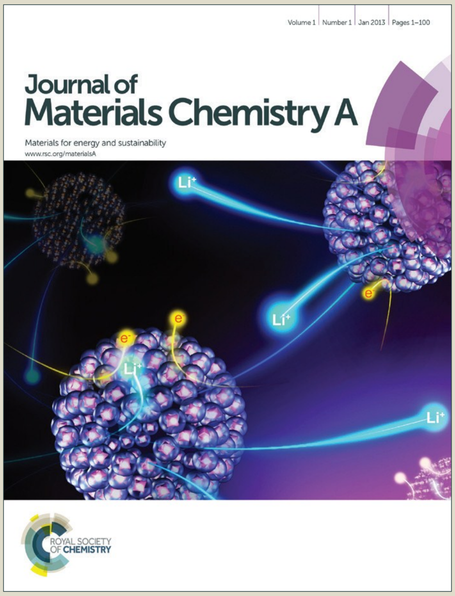

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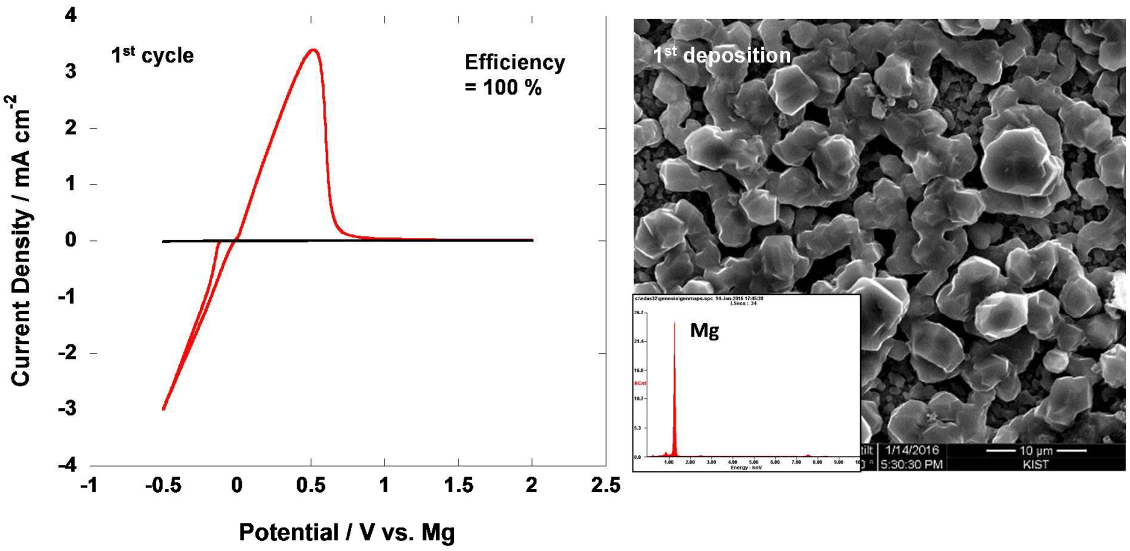
TOC abstract: The catalytic dissolution of Mg metal in THF leads to a highly stable electrolyte for rechargeable magnesium batteries which share many common features with MACC, but does not requre an onerous conditioning process. This crucial advantages originates from the very high Mg to Al ratio in the electrolyte, which promotes 100 % coulombic efficiency for Mg on the first cycle



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COMMUNICATION

Conditioning-Free Magnesium Chloride Complex Electrolyte for Rechargeable Magnesium Batteries

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The dissolution of Mg metal in $AlCl_3$/THF using $CrCl_3$ as a "promoter" yields a magnesium aluminum chloride complex electrolyte which shares many common features with MACC, but does not require an onerous conditioning process. This crucial advantage originates from the very high Mg to Al ratio in the new electrolyte, "MaCC", which promotes 100% coulombic efficiency for Mg on the first cycle.

Following the report of the prototype cell for magnesium rechargeable batteries consisting of a Chevrel phase[1] cathode (Mo_6S_8) and a magnesium-organohaloaluminate electrolyte by Aurbach *et al.* in 2000[2], the Mg battery system has gained world-wide attention as a potential medium/large-scale energy storage system.[3-9] Magnesium is attractive as a negative electrode material because it has high gravimetric (2,205 Ah kg^{-1}) and volumetric (3,822 Ah L^{-1}) capacities with a low standard electrode potential ($Mg^{2+} + 2e^- \rightarrow Mg$) of -2.372 V relative to the standard hydrogen electrode (SHE). It is found in large natural mineral deposits and is the 8th most abundant element in the earth's crust. More importantly, magnesium electrodeposition does not involve the formation of either dendrites or a thick, complex solid-electrolyte interphase; both of which underlie the most critical safety concerns for rechargeable batteries employing metallic negative electrodes.[3-7,10,11] A rechargeable magnesium battery with a high energy density could thus be realized by the combination of a magnesium metal anode and a cathode material with a high electrode potential. However, this possibility is hampered by the difficulty in developing new electrolyte systems which have a sufficiently wide electrochemical window to utilize such materials.

One approach towards new electrolyte systems is focused on the generation of charge-transporting ionic species by the combination of a Lewis acid (such as $AlCl_3$) and a Lewis base containing Mg^{2+} ions followed by trans-metallization reactions.[3-7,12] This leads to the formation of groups of cations and anions whose existence is based on complex chemical equilibria. This strategy originated from earlier work that utilized various magnesium organoborates, $Mg(BR^1_nR^2_{4-n})_2$ in ethereal solvents.[13] The approach was refined by Aurbach *et al.* in a series of new electrolytes based on the combination of R_2Mg as a Lewis base and $AlCl_{3-n}R_n$ as a Lewis acid.[2,14,15] This greatly increased the ionic conductivity and expanded the anodic stability, although the latter was initially limited to around 2.0 V which is not suitable for 3V-class cathodes.

A few different approaches have been used to push back this barrier. Magnesium organohaloaluminate or "all phenyl complex, APC" solutions generated via reaction of $AlCl_3$: 2 PhMgCl, are stabilized by the lack of β-H elimination from the alkyl group in the anion $[AlCl_{4-n}R_n]^-$.[16] Muldoon *et al.* cleverly employed hexamethyldisilazide magnesium chloride (HMDS MgCl) as a non-nucleophilic Lewis base to result in an electrolyte with anodic stability up to 3.0 V vs. Mg/Mg^{2+}.[17-20] A major breakthrough showed that oxidation of the weak Al-R bond can be prevented with an all-inorganic-salt, stable up to 3.0 V vs. Mg/Mg^{2+}.[21] A few very recent reports have sparked some understanding of this complex system.[22-26] In "MACC", the primary cations responsible for charge transport are thought to be $[Mg_2Cl_3\cdot 6THF]^+$ [25] (or $[MgCl\cdot 5THF]^+$),[26] and the $[AlCl_4]^-$ anion, formed by transmetallization of the Lewis acid and base species. However, the electrolyte requires up to 100 cycles for "conditioning", in order to achieve close to 100% coulombic efficiency.[22]

Here, we report a new stable "MaCC" electrolyte consisting of all inorganic species formed by the catalysed dissolution of Mg into THF, which needs no conditioning. This leads to electrolyte solutions with a very high Mg/Al ratio that exhibit reversible magnesium deposition/stripping with essentially 100 % coulombic efficiency starting from the 1st cycle, and a high anodic stability of 3.1 V vs. Mg/Mg^{2+}. Practical application of this electrolyte solution is demonstrated by 250 cycles of a prototype cell consisting of Mo_6S_8 Chevrel as the cathode and Mg as the anode.

The one-pot synthesis of electrolyte **A** involves the dissolution of finely divided Mg metal powder into tetrahydrofuran (THF) containing a small amount of dissolved $CrCl_3$ and 0.2 M $AlCl_3$ (see ESI† for details). Both Cr^{3+} and Al^{3+} will be reduced by Mg to their metallic state based on the corresponding half-cell potentials; however, the reduction of $AlCl_3$ by Mg is known to be very sluggish.[25] When $CrCl_3$ is present in solution, a black precipitate, whose composition can be expressed as Cr_pAl_q based on EDS mapping (**Fig. S1** and **S2**, ESI†), was deposited onto the surface of the Mg powder. The black precipitate was identified as $Al_{0.983}Cr_{0.017}$ (ICSD file: 107761) based on the XRD pattern of the material deposited onto a Mg plate (**Fig 1**). EDS mapping also showed its surface is decorated with Cl. Electrolyte **A′** was prepared similarly but without the addition of $CrCl_3$, resulting in no observable reaction with Mg (**Fig. 1,** insert).

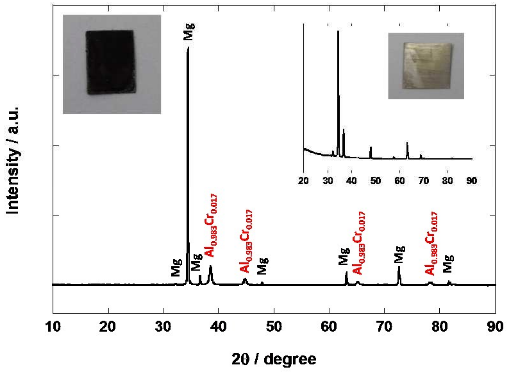

Figure 1. X-ray diffraction pattern of the Mg plate reacted in THF solution containing both $AlCl_3$ and $CrCl_3$ (electrolyte **A**) for 12 h; insert: Mg plate reacted for 12 h in THF solution containing only $AlCl_3$ (electrolyte **A'**).

Following a short reaction period, the solutions were extracted from the vessel and the Mg and Al content was analyzed by inductively coupled plasma (ICP). The results shown in **Table 1** are compared to those of standard 0.2M APC: here the Mg:Al ratio and concentrations are exactly as expected (**Table S1** in ESI†). This confirms the accuracy of the analysis. It is evident that electrolyte **A** is very rich in Mg, with a concentration of 0.28 M, and that only a trace of Cr is present. The aluminum concentration is also quite low (as discussed later). Magnesium dissolution is tremendously enhanced by the co-addition of $CrCl_3$ and $AlCl_3$, compared to the $AlCl_3$-only solution (electrolyte **A′**) which yields a negligible concentration of Mg (**Fig. S1** in ESI†).

Table 1 Mg and Al content in the electrolyte solution analysed by ICP. The value in 5 mL of electrolyte is given.

Solution (5 mL THF)	Mg [μg]	Al [μg]	Cr [μg]
$AlCl_3$ (0.1333g)	-	$2.35x10^4$	-
Electrolyte solution **A**	$3.39x10^4$	$2.60x10^3$	3.76
Electrolyte solution **A′**	834	$2.34x10^4$	-
0.2M APC solution	$4.89x10^4$	$2.47x10^4$	-

While the precise mechanism is not yet understood, it is clear that either $CrCl_3$ or the Cl-decorated $Al_{0.983}Cr_{0.017}$ alloy deposit greatly enhances the kinetics for magnesium dissolution by inducing the reduction of $AlCl_3$ and releasing magnesium chloride according to equation (1):

$$pCrCl_3 + qAlCl_3 + rMg^0 \rightarrow Cr_pAl_q + rMgCl_2 \qquad (1)$$

The high Mg content of electrolyte **A** results in extremely reversible Mg deposition and stripping, with a coulombic efficiency *for the first magnesium deposition and stripping cycle of 100 %*, and between 99.8% and 100% on subsequent cycles (**Table S2** in ESI†). Energy dispersive X-ray spectroscopy (EDS) results for the Mg deposited on a Ni plate from electrolyte **A** (**Fig. S3**, ESI†) shows that only pure magnesium is observed from the 1st cycle, which accounts for the 100 % efficiency. **Fig. 2a** shows the cyclic voltammograms for magnesium electrodeposition and stripping in as-prepared electrolyte **A** described above, compared to electrolyte **A′**. The latter is essentially inactive, because of the extremely low current density for magnesium deposition and stripping caused by its low ionic conductivity (0.064 mS cm^{-1}). This owes to the lack of Mg^{2+}-containing species in solution. In contrast, the ionic conductivity for electrolyte solution **A** is 0.23 mS cm^{-1}, which is comparable to that of MACC reported in the literature (σ_i = 0.26 mS cm^{-1}).[22] It is clear that the addition of $CrCl_3$ during the electrolyte preparation leads to the generation of stable ionic species for charge transport. However, in sharp contrast to a conventional MACC electrolyte, which requires lengthy voltammetric cycling up to a hundred cycles for good functioning[23-26] – a process deemed "electrolytic conditioning" - electrolyte **A** does not require any conditioning. This is highly beneficial in terms of practical cell assembly. Linear sweep voltammetry was also used to examine the anodic stability of each electrolyte solution with platinum as the working electrode and magnesium as counter and reference electrodes, respectively. Fig. 2b shows that electrolyte **A** is stable up to 3.1 V vs. Mg/Mg^{2+} (the potential was defined as where the current density reached 0.02 mA cm^{-2}, *see Note* in ESI†), similar to the MACC electrolyte.

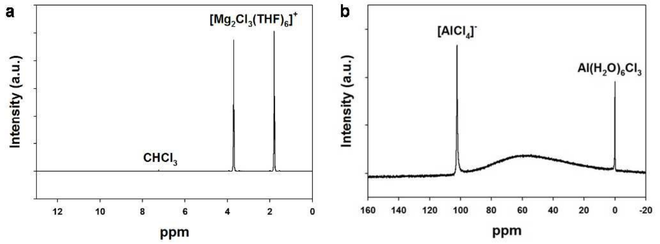

Fig. 3 NMR analysis of electrolyte solution **A**. (a) The ^{1}H-NMR spectrum of the dried salt re-dissolved in $CDCl_3$. The residual $CHCl_3$ solvent peak is at 7.26 ppm and the other two peaks arise from the coordinated THF molecules in the $[Mg_2Cl_3(THF)_6]^+$ cation (δ = 1.79, 3.68 ppm). (b) ^{27}Al-NMR spectrum for the neat electrolyte. A sealed capillary with 50 mM $AlCl_3$ in H_2O was added as an internal standard (δ = 0 ppm), and the broad resonance at about 60 ppm is from the probe. The peak at δ = 102.4 ppm is from the $AlCl_4^-$ anion.

To attempt to determine the nature of electrolyte **A**, we carried out nuclear magnetic resonance (NMR) spectroscopy and single crystal X-ray diffraction (XRD) measurements. For the former, the electrolyte solution was dried at room temperature under vacuum to remove all excess THF and to precipitate the electrolyte salt. ^{1}H-NMR (**Fig. 3a**) was performed on this salt after re-dissolving it in $CDCl_3$. The proton signals correspond to the CH_2 (δ = 1.79 ppm) and CH_2O (δ = 3.68 ppm) moieties of coordinated THF in MACC,[22] which are slightly shifted from THF itself (δ = 1.85 ppm; 3.76 ppm). The fact that the protons are easily detected under typical NMR acquisition conditions indicates that they have a low spin-spin constant (T_2) and therefore the complex they are associated with is not of high molecular weight. In contrast, in previously reported MACC electrolyte systems, it has been suggested that polymeric THF-containing complexes are initially formed, which are degraded upon conditioning.[23] Their absence using the synthesis protocol described here may partly explain the reason for why electrolyte **A** needs no conditioning, a topic that future studies will explore in detail but which is beyond the scope of this study. The ^{27}Al-NMR spectrum of electrolyte **A** (in THF, without drying) exhibited a single peak at 102.4 ppm (**Fig. 3b**)[22] that has been previously assigned to $[AlCl_4]^-$. Based on these results, the active electrolyte contains protons from coordinated THF molecules, and the anion $[AlCl_4]^-$ is present in solution albeit in a very low concentration (0.02M based on chemical analysis (**Table 1**)). Our single crystal XRD studies showed that the only material that can be readily crystallized from solution is comprised of $[Mg_2Cl_3(THF)_6]^+/[AlCl_4]^-$ in accord with the work of Liu *et al.*,[22] albeit with some disorder in the THF molecules (**Fig S4**, **Table S3** in ESI†). The cation-anion pair is formed *via* the reaction of $MgCl_2$ generated in equation (1) with excess $AlCl_3$ present in the initial one-pot synthesis, following the reported reaction:

$$rMgCl_2 + r/2AlCl_3 + 3rTHF \rightarrow r/2[Mg_2Cl_3\cdot 6THF]^+/[AlCl_4]^- \quad (2)$$

However, the high conductivity of the electrolyte solution (σ_i = 0.23 mS cm^{-1}) in conjunction with the low Al concentration clearly shows that this cation-anion pair cannot represent the majority of the charge-carrier species in the electrolyte.

The above results demonstrate that although electrolyte **A** is similar to MACC in nature, it exhibits a very important difference owing to the synthesis method: namely a much higher Mg/Al content ratio (~13). This is five-fold greater than that of conditioned MACC. It has been reported that conditioning over ~ 100 cycles alters the speciation of Mg and Al in MACC, increasing the Mg/Al ratio from 2 to 2.6.[23-26] The ultra-low content of Al in electrolyte **A** suggests that much of the $[AlCl_4]^-$ generated in eq (2) further reacts with the Cr_pAl_q-covered Mg surface in the original one-pot synthesis to generate additional Mg^{2+}-dimer complex in the solution, concommitant with the reduction of $[AlCl_4]^-$ to Al:

$$4AlCl_4^- + 6Mg \rightarrow 4Al + 3[Mg_2Cl_3\cdot 6THF]^+ + 7[Cl]^- \quad (3)$$

We note that this reaction has been very recently invoked to explain irreversible Al deposition on the working electrode during MACC conditioning, which would release Mg dimer complex and free Cl^- into solution.[25] The freed Cl^- ions were detected on the surface of a Cu plate by surface enhanced Raman studies,[25] and are thought to enhance Mg electrodeposition along with the increased dimer concentration (*vis a vis* the unconditioned electrolyte).

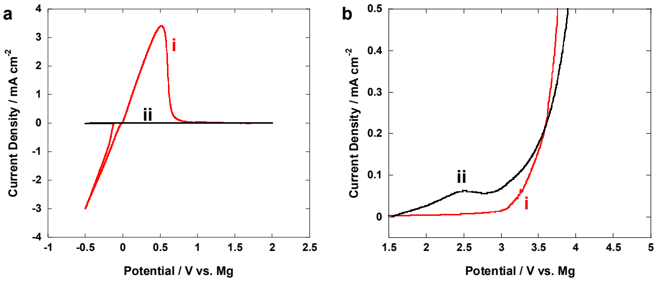

Fig. 2 (a) cyclic voltammograms (3rd cycle) and (b) linear sweep voltammograms for (i) electrolyte solution A and (ii) A′. Mg metal plates were used as reference and counter electrodes and a SS-316L current collector served as the working electrode (Pt for LSV). The scan rate for the CV was 1 mV s^{-1} and for the LSV, 25 mV s^{-1}.

In our case, a high Mg dimer concentration is directly produced in the initial synthesis steps; first by catalytic dissolution of Mg via eqns (1) and (2), and then additionally by eqn (3). The resulting "mixed anion" solution must be predominantly $[Mg_2Cl_3\cdot 6THF]^+/[Cl]^-$, (i.e., "$MgCl_2\bullet nTHF$") with some $[Mg_2Cl_3\cdot 6THF]^+/[AlCl_4]^-$ present (as determined above). EDS analysis carried out on dried electrolyte solutions confirms this hypothesis (**Fig S5**). Typical as-prepared MACC (ie, targetted composition of $Mg_2Cl_4\bullet AlCl_3$) exhibits a Mg: Al ratio of 1:0.5 and a Mg:Cl ratio of 3, close to that predicted. The deviation from the ideal stoichiometry reflects the non-stoichiometry of the product, and/or quantitative limitations of EDS analysis. In contrast, electrolyte **A** shows a Mg:Cl ratio

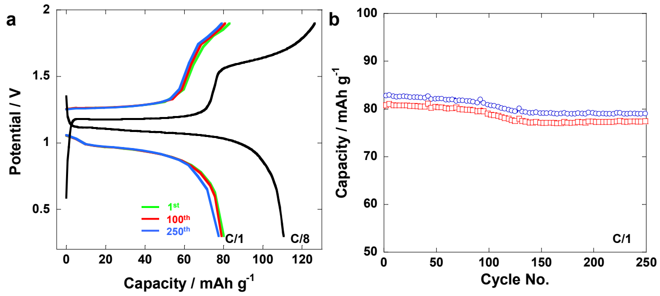

Fig. 4 (a) Discharge-charge profiles at the 1st, the 100th, and the 250th cycle and (b) capacity retention of Mg rechargeable batteries with the Chevrel phase cathode at 1C (=128 mA g^{-1}) for electrolyte **A** (blue circle = charge , red square = discharge).

of 2.2 - slightly higher than of $[Mg_2Cl_3{\cdot}6THF]^+/[Cl]^-$ - but what one would expect for the mixed anion composition described above with a minor contribution of the $[AlCl_4]^-$ anion. The Mg:Al ratio is 10 times greater that of the MACC electrolyte, confirming the roles of eqns 1 and 3 in generating a high Mg concentration in the electrolyte while greatly reducing the Al contribution and increasing the $[Cl]^-$ anion fraction. All of these factors contribute to a conditioning-free electrolyte. We deem this "MaCC" owing to its fundamentally low Al concentration.

MaCC demonstrates excellent properties in a conventional Mg cell. **Fig. 4** shows the discharge-charge profiles for the 1st, 100th, 250th cycles and the cycling capacity evolution, respectively, when electrolyte **A** (MaCC) was utilized in a cell with Chevrel Mo_6S_8 as the cathode and magnesium metal as the anode. It is well known that the magnesium ions can incorporate into the so called "inner ring" and "outer ring" sites of Chevrel phase, with up to two Mg^{2+} ions per Mo_6S_8 unit occupying one Mg per each site.[27-32] Each site is responsible for the half of the theoretical total capacity of 128 mAh g^{-1}. At a current rate of C/8 (**Fig 4a**), the capacity is 110 mAh g^{-1} which is close to theoretical. The performance at high current rates, where typically only the second Mg site is accessed, was evaluated by varying the rate from C/8 to 1C. The results (**Fig. S6** in ESI†) show a good current response. At a 1C rate (=128 mA g^{-1}), the discharge capacity was ~ 80 mAh g^{-1} (**Fig. 4b**) and outstanding cycling capacity retention is maintained up to 250 cycles. Furthermore, the XRD pattern of Chevrel Mo_6S_8 recovered from the cycled electrode shows no sign of structural degradation (**Fig. S7** in ESI†)

Conclusions

Catalytic dissolution of Mg metal in THF using $CrCl_3$ in the presence of $AlCl_3$ yields an electrolyte consisting of all inorganic species, where almost 100 % coulombic efficiency is obtained for Mg electro-deposition and stripping at the negative electrode on the first cycle with a stable electrochemical window up to 3.1 V. This novel approach represents a simple one-pot synthesis route to a "MACC"-like electrolyte. However, in distinct contrast to MACC, this electrolyte – "MaCC" - does not require a complex electrolytic conditioning due to the high initial Mg to Al content ratio in the electrolyte, which favours reversible Mg deposition.

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† Electronic Supplementary Information (ESI) available: Experimental details; Supplementary Note, Figures S1 to S9, Tables S1 to S3. See DOI: 10.1039/b000000x/

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