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Enhanced oxidative stability of non-Grignard magnesium electrolytes through ligand modification<sup>†</sup>

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A series of non-Grignard Mg-electrolytes with various parasubstituents was synthesized starting from commercially-available phenols. More electron-withdrawing substituents shift the anodic stability of the electrolyte by 400 mV. The *p*-CF<sub>3</sub> substituted phenol exhibits the highest stability of 2.9 V vs. Mg<sup>2+/0</sup>, and cycles reversibly with the Chevrel-phase Mo<sub>6</sub>S<sub>8</sub> Mg-ion cathode.

Since Gaston Planté invented the lead-acid battery in 1859, research in rechargeable batteries has matured to fold several chemistries into our everyday lives. Notably, nickel-cadmium and nickel-metal hydride, as well as lithium-ion batteries power devices on all size scales-from portable electronics to hybrid electric vehicles (HEVs). At present, lithium-ion is the leading technology for HEVs, but they are still not able to meet all the energy density requirements for all-electric vehicles (EVs) to become competitive in driving range and cost compared to traditional internal combustion engine vehicles. A promising candidate for high energy density batteries is Mg-ion batteries. Mg-ion batteries are still in the early stages of development, with the earliest research happening in the 1990s and early 2000s.<sup>1,2</sup> Magnesium is of interest due to its relatively negative potential (Mg<sup>2+/0</sup> is -2.37 V vs. NHE) and high volumetric capacity (3832 mA h cm<sup>-3</sup> for the 2-electron couple). Magnesium also has the benefits of improved safety as there is no dendrite formation upon deposition,<sup>3</sup> and it is low cost compared to lithium due to high natural abundance (2.76% by weight of crustal rocks compared to 18 ppm for lithium).<sup>4</sup>

Finding an electrolyte that displays both reversible Mg deposition and a wide electrochemical window is a major obstacle that constrains research in rechargeable Mg batteries. Aurbach and co-workers discovered a breakthrough with Mg organohalo-aluminate salts Mg(AlCl<sub>4-n</sub>R<sub>n'</sub>R'<sub>n''</sub>)<sub>2</sub>.<sup>2</sup> The optimized composition (AlCl<sub>3</sub>-(PhMgCl)<sub>2</sub>) exhibits anodic stability to 3.3 V vs. Mg<sup>2+/0</sup> and reversible Mg deposition–dissolution characteristics.<sup>5</sup> However, these electrolytes are nucleophilic and quite sensitive to air and moisture due to the Grignard components (RMgX and MgR<sub>2</sub>). These drawbacks decrease the likelihood of their adoption in battery production, and exclude their potential application in next-generation Mg/S<sub>8</sub> and Mg/O<sub>2</sub> batteries.<sup>6</sup> The first non-nucleophilic electrolyte, [Mg<sub>2</sub>Cl<sub>3</sub>·6THF][HMDSAlCl<sub>3</sub>] (HMDS = hexamethyldisilazide), is compatible with sulfur, however stability to 3.2 V vs. Mg<sup>2+/0</sup> can only be achieved through single-crystal formation.<sup>7</sup>

Prior efforts in non-Grignard reagents based on phenolate Mg salts show good anodic stability to 2.6 V vs.  $Mg^{2+/0}$ , reversible Mg deposition–dissolution, and chemical compatibility with the  $Mo_6S_8$  Chevrel-phase cathode.<sup>8</sup> It also shows resistance to air/moisture decomposition, with no loss in anodic stability after stirring in air for 3 hours. The authors acknowledge an influence of alkyl substituents on the electrochemical performance, but do not develop a hypothesis or predictive model to guide new synthesis.<sup>8</sup> Herein, we build a model rooted in physical organic chemistry and a detailed examination of solution speciation to elucidate the role of the ligand in enhancing electrochemical stability. We show an expanded electrochemical window of these air stable electrolytes by 400 mV, bringing them close to the air sensitive Grignard stability window, and cycle them as reversible Mg-ion batteries.

We synthesized a series of six ROMgCl salts: [RO = 4-methoxyphenolate (MPMC), phenolate (PMC), 4-methyl-phenolate (MPMC), 4-*tert*-butyl-phenolate (BPMC), 4-(trifluoromethyl)-phenolate (FMPMC), and pentafluorophenolate (PFPMC)]. These phenolate salts were then reacted with an AlCl<sub>3</sub>-THF solution to form the electrolytes. Detailed synthesis is presented in the ESI.†

Fig. 1 presents the cyclic voltammograms of  $(MPMC)_2$ -AlCl<sub>3</sub>/THF (electron-donating),  $(PMC)_2$ -AlCl<sub>3</sub>/THF, and  $(FMPMC)_2$ -AlCl<sub>3</sub>/THF (electron-withdrawing); voltammograms for the other electrolytes are presented in Fig. S1 of the ESI.† The  $(FMPMC)_2$ -AlCl<sub>3</sub>/THF electrolyte is referenced to the ferrocene Fc<sup>+/0</sup> couple in Fig. S2 (ESI†). Reversible Mg deposition-dissolution is observed for all electrolytes with the exception of  $(MPMC)_2$ -AlCl<sub>3</sub>/THF, and the anodic stability of the solutions (shown in Table 1)

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Fig. 1 Typical cyclic voltammograms of Pt electrodes in (a) 0.5 M (FMPMC)<sub>2</sub>-AlCl<sub>3</sub>/THF, (b) (PMC)<sub>2</sub>-AlCl<sub>3</sub>/THF, and (c) (MPMC)<sub>2</sub>-AlCl<sub>3</sub>/THF solutions. The scan rate is 25 mV s<sup>-1</sup> and the dashed lines are added as guides to the eye.

Table 1 Conductivity, voltage, anodic current, and Hammett  $\sigma^+$  values for the substituted phenolate electrolyte complexes

Substituent	$\sigma^{\scriptscriptstyle +}$ value	$E_{\rm on}{}^a/{\rm V}$	$I_a^{\ b}/\mu A$	$ ho^c/\mu S \ cm^{-1}$
ОМе	-0.78	2.31	257.08	1052
Ме	-0.31	2.58	158.94	1119
t-Bu	-0.26	2.74	74.95	736
Н	0	2.71	64.66	877
CF <sub>3</sub>	0.61	2.90	9.474	2240
F <sub>5</sub>	—	3.05	3.90	2448

<sup>*a*</sup> Potential  $\nu$ s. Mg<sup>2+/0</sup> at which the onset of anodic current is first observed. <sup>*b*</sup> Anodic current at 3 V  $\nu$ s. Mg<sup>2+/0</sup>. <sup>*c*</sup> Conductivity measured at 25 °C at 0.5 M (based on Mg<sup>2+</sup>).

ranks as:  $(FMPMC)_2-AlCl_3/THF > (BPMC)_2-AlCl_3/THF > (PMC)_2-AlCl_3/THF > (MePMC)_2-AlCl_3/THF > (MPMC)_2-AlCl_3/THF. The measured conductivity of the electrolyte solutions does not follow this trend; rather, all were ~ 1 mS cm<sup>-1</sup> with the exception of (FMPMC)_2-AlCl_3/THF, which exhibits a conductivity almost twice the others at 2.24 mS cm<sup>-1</sup>. The higher conductivity is likely due to the stabilization of the overall negative charge on the aluminate anion, creating a weaker ion pair.$ 

The electrochemistry illustrates the strong dependence of phenolate substitution on electrical performance. The Hammett plot in Fig. 2 of onset potential *vs.*  $\sigma^+$  values ( $\sigma^+$  representing Hammett parameters for phenol) show a linear negative slope, consistent with positive charge build up during oxidation.<sup>9</sup> Withdrawing groups destabilize positive charge increasing the difficultly of oxidation.<sup>10,11</sup> This same trend is observed with the anodic current recorded at



Fig. 2 Hammett plot of *para*-substituted phenols *vs.* oxidation onset potential of non-Grignard electrolytes.



Fig. 3 Cyclic voltammograms of (FMPMC)\_2–AlCl\_3/THF before (—) and after (---) exposure to air for 6 hours. Scan rate is 25 mV  $s^{-1}\!$ .

3 V vs. Mg<sup>2+/0</sup> (Fig. S3, ESI<sup>†</sup>). The (BPMC)<sub>2</sub>–AlCl<sub>3</sub>/THF electrolyte does not follow the main trend of  $\sigma^+$  values, suggesting that the steric bulk of the alkyl substituents contributes an additional factor to the oxidative stability, though further studies are needed. Fig. 3 shows that the oxidative stability of the electrolyte (FMPMC)<sub>2</sub>–AlCl<sub>3</sub>/THF remains unchanged after exposure to air for 6 hours. Reversible Mg deposition–dissolution is still observed. However, the decrease in efficiency and increased polarization is likely due to the slow oxidation of the Mg–Cl bonds, as has been previously reported.<sup>8</sup>

Further support of imparting greater oxidative stability through electron-withdrawing substituents comes from preparing the pentafluorophenolate complex. Although the  $\sigma^+$  Hammett values for all positions on the phenol ring are not known, the increased number of electron-withdrawing groups results in an ~100 mV enhancement in the anodic stability, increasing the electrochemical window to 3 V for non-Grignard magnesium electrolytes (Fig. S5, ESI†). This result represents the largest stability window for non-Grignard electrolytes, and is 400 mV more positive than what has been previously reported,<sup>8</sup> moving the non-Grignard systems close to the stability window of the Grignard electrolytes.<sup>5</sup> The conductivity of (PFPMC)<sub>2</sub>–AlCl<sub>3</sub>/THF is 2.44 mS cm<sup>-1</sup>, similar to that of



Fig. 4 Reversible galvanostatic cycling of  $Mo_6S_8$  vs. Mg-foil in 0.5 M (FMPMC)<sub>4</sub>-AlCl<sub>3</sub>/THF electrolyte at C/5.

(FMPMC)<sub>2</sub>–AlCl<sub>3</sub>/THF. The voltammogram of (FMPMC)<sub>2</sub>–AlCl<sub>3</sub>/ THF is also recorded under near steady-state conditions (scan rate of 1 mV s<sup>-1</sup>) and presented as Fig. S6 (ESI<sup>†</sup>), and no new features emerge. In order to verify the compatibility of the (FMPMC)<sub>2</sub>–AlCl<sub>3</sub>/THF electrolyte with a Mg-ion intercalation cathode, Mo<sub>6</sub>S<sub>8</sub> was synthesized by known solid-state methods,<sup>12</sup> and galvanostatic cycling (*C*/5 rate = 50  $\mu$ A cm<sup>-2</sup>) *versus* a Mg-foil auxiliary electrode shows reversible cycling in Fig. 4 (discharge curves presented as Fig. S7, ESI<sup>†</sup>).

In solution, a mixture of complexes is present in a dynamic equilibrium, previously reported for aluminium alkoxides.<sup>13,14</sup> In an effort to assign the <sup>27</sup>Al NMR spectra of the as-synthesized electrolyte, we prepared a series of solutions comprised of differing ratios between the Lewis acid (AlCl<sub>3</sub>) and base (FMPMC). Details are presented in the ESI,† and spectral assignments are based on prior work.<sup>15–17</sup>

The electron-withdrawing phenolates, FMP and PFP show the greatest number of (RO)<sub>x</sub>AlCl<sub>4-x</sub> species in solution, with x = 1 - 4species all present. The remaining electrolytes do not show the tetrakis-ligated aluminum species; the <sup>27</sup>Al NMR spectrum of the most electron-donating complex (MPMC)2-AlCl3/THF shows only the bis- and mono-ligated complexes in smaller intensities relative to the Al<sub>2</sub>Cl<sub>6</sub> species (Tables S1 and S2, ESI<sup>†</sup>). One possible explanation for this observation is that ligand exchange between MPMC and AlCl<sub>3</sub> is slower or incomplete. The X-ray crystal structure of the compound crystallized from (MPMC)<sub>2</sub>-AlCl<sub>3</sub>/THF (Fig. S8, ESI<sup>+</sup>) shows that ligand exchange is incomplete, resulting in a Mg cubane-like structure with bridging methoxyphenolate ligands. In contrast, the X-ray crystal structure of (FMPMC)<sub>2</sub>-AlCl<sub>3</sub>/THF shows the expected ligand exchange reaction forming [Mg<sub>2</sub>Cl<sub>3</sub>(THF)<sub>6</sub>]<sup>+</sup> cations and [(FMP)AlCl<sub>3</sub>]<sup>-</sup> anions (Fig. S9, ESI<sup>+</sup>). The <sup>27</sup>Al NMR assignments are further supported by the mass spectrometry and by Raman spectra (assignments based on prior work<sup>18-20</sup>) presented in the ESI<sup>†</sup> (Fig. S10 and S11).

In an effort to distinguish which solution species is responsible for the wider potential window, bulk electrolysis of  $(FMPMC)_2$ -AlCl<sub>3</sub> was carried out at 3.5 V vs.  $Mg^{2^{+/0}}$  for 90 minutes. Comparing the <sup>27</sup>Al NMR spectra before and after electrolysis shows decomposition of the *in situ* formed aluminium complex (Fig. S12, ESI<sup>†</sup>) and suggests that Lewis acids are responsible for the anodic stability of these non-Grignard electrolytes, similar to what has been reported for their Grignard congeners.<sup>17,21</sup> In summary, through a controlled study of substituted phenols, we have shown that the anodic stability of  $ROMgCl:AlCl_3$ -THF non-Grignard electrolytes can be pushed ~400 mV past the phenolate electrolytes previously published by placing very electronwithdrawing substituents on the phenolate ring. This brings these non-Grignard electrolyte systems close to the stability of previously published Grignard based electrolytes. Using phenolate ligands allows for improved stability in air and lower nucleophilicity, opening the door to exploring high density cathodes such as Mg-air and Mg-sulfur. The use of physical organic design principles and a general synthesis method will allow us to further open the stability window of these types of Mg electrolytes.

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