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COMMUNICATION

## Influence of Steric Bulk on the Oxidative Stability of Phenolate-Based Magnesium-Ion Battery Electrolytes

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**A compilation of electrolytes within the standard <sup>R</sup>PhOMgCl and AlCl<sub>3</sub> in THF electrolyte system with varying alkyl-based steric bulk about the phenol ring were prepared and cycled electrochemically. Most notable, 2,4,6-trimethylphenol-based solutions exhibit high conductivity (2.56 mS cm<sup>-1</sup>) and compatibility with the Chevrel-phase Mo<sub>6</sub>S<sub>8</sub> intercalation cathode (over 200 h cycle time at C/10 current).**

Batteries are deeply rooted within today's society— from portable electronics to hybrid electric vehicles. As the number of devices/vehicles increases and new technologies requiring secondary batteries emerge, less expensive and more abundant raw materials will be required. As a result, magnesium is high sought as a successor owing to decreased raw materials cost due to the high natural abundance of magnesium (4%) while contributing twice the theoretical volumetric density.<sup>1,2</sup> With additional improved safety due to dendrite-free deposition<sup>3</sup> in contrast to lithium's inherent dendritic growth,<sup>4</sup> magnesium-based systems offer desirable fundamental properties for commercial success as we move beyond lithium ion batteries.

Aurbach and coworkers accelerated magnesium-ion technology with the 1990 reported discovery of a Grignard-based electrolyte system (Mg(AlCl<sub>2</sub>BuEt)<sub>2</sub>) that shows chemical compatibility with the Chevrel-phase Mo<sub>6</sub>S<sub>8</sub> cathode material.<sup>5</sup> Removing possible β-H elimination degradation pathways by replacing the aliphatic hydrocarbons with phenyl in the electrolyte composed of two equivalents PhMgCl with one equivalent of AlCl<sub>3</sub> in THF (termed APC for all phenyl complex), resulted in expanding the electrochemical window to 3.3 V vs. Mg<sup>2+/0</sup>,<sup>6</sup> which now serves as standard for new electrolyte compositions. However, the nucleophilicity as well as air- and moisture sensitivity, hinder these Grignard-based systems from widespread adoption.

First recognized in 2012 by Hirano, phenolate-based magnesium precursors allow for electrolytes with anodic stabilities that are comparable to those prepared from Grignard reagents, while showing reversible magnesium deposition and stripping. Most notably, an electrolyte composed of 2-*tert*-butyl-4-methyl-phenolate showed an anodic stability of 2.6 V vs. Mg<sup>2+/0</sup>, with the ability to deposit and strip magnesium after 3 hours of air exposure.<sup>7</sup> While these studies featured a variety of substituted phenols, there was no insight into structure-function relationships to guide future electrolyte design presented therein. Subsequently, our group has demonstrated a strong electronic effect with para-substituted phenols within electrolyte salts composed of <sup>R</sup>PhOMgCl (R = CF<sub>3</sub>, <sup>t</sup>Bu, H, Me, and OMe all in the para-position) and AlCl<sub>3</sub>, suggesting that electron-withdrawing groups provide the greatest oxidative stability.<sup>8</sup> In that work, we discovered an increased oxidative stability of the 4-*tert*-butylphenolate salt that could not be explained by electronic arguments alone, rather suggesting a separate steric influence.

To begin this follow-up work, we probe the effects of steric bulk with respect to oxidative stability within the <sup>R</sup>PhOMgCl and AlCl<sub>3</sub> in THF electrolyte system. We generated five solutions, R = Me, Et, <sup>i</sup>Pr, <sup>s</sup>Bu, and <sup>t</sup>Bu (again, all in the para position) by first reacting ethylmagnesium chloride with the respective phenol, followed by adding an AlCl<sub>3</sub>-THF solution. Details of the synthesis are provided in the ESI<sup>†</sup>.

By cyclic voltammetry of a THF solution composed of 0.5 M <sup>R</sup>PhOMgCl and 0.25 M AlCl<sub>3</sub> the para-substituted phenols show anodic stability that increases by 150 mV (2.58 – 2.73 V) in the order R = Me, Et, <sup>i</sup>Pr, <sup>s</sup>Bu, and <sup>t</sup>Bu (Table 1), with solution conductivities comparable to previous reports.<sup>7,8</sup> The most anodically stable salt composed having R = <sup>t</sup>Bu also shows high deposition/stripping efficiency on a Pt-working disc electrode (94%). The <sup>27</sup>Al NMR spectra display solution speciation dominated by R<sub>2</sub>AlCl<sub>2</sub><sup>-</sup> and RAlCl<sub>3</sub><sup>-</sup> for all para-substituted electrolytes, consistent with our previous findings (Fig. S2, ESI<sup>†</sup>).<sup>8</sup> We surmise that in solution, magnesium is present as the typically observed [Mg<sub>2</sub>(μ-Cl)<sub>3</sub>(thf)<sub>6</sub>]<sup>+</sup> complex cation.

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Table 1. Anodic stability (potential vs.  $\text{Mg}^{2+/0}$ ), conductivity, Taft steric substituent constant and coulombic efficiency for deposition–dissolution of para-substituted (top) and multi-substituted phenol-based electrolytes (bottom).

electrolyte (R)	$E_a^a$ / V	$\sigma$ / $\text{mS cm}^{-1}$	$-E_s$	CE/%
4-Me	2.58	1.25	1.24	81
4-Et	2.59	1.21	1.31	81
4- <sup>i</sup> Pr	2.62	1.17	1.71	82
4- <sup>s</sup> Bu	2.69	1.16	2.37	89
4- <sup>t</sup> Bu	2.73	1.18	2.78	94
2,4,6-Me <sub>3</sub>	2.56	2.56		92
2,4,6- <sup>t</sup> Bu <sub>3</sub>	2.72	1.29		70
2,6-Me <sub>2</sub>	2.52	2.48		95
2,6- <sup>t</sup> Bu <sub>2</sub>	2.35	1.66		84

<sup>a</sup>  $E_a$  defined as the potential at which 5  $\mu\text{A}$  anodic current observed

With electrochemical results suggesting a steric influence, we sought quantification of steric bulk for direct comparison relative to oxidative stability. A linear relationship between anodic stability and Taft's steric bulk parameter ( $-E_s$ )<sup>9,10</sup> was observed (Figure 1), suggesting inductive charge dissipation from the site of oxidation of the coordinated phenol within the (<sup>R</sup>PhO)<sub>x</sub>AlCl<sub>4-x</sub> ( $x = 1 - 2$ ) anion, allowing for an expansion of the electrochemical window. Consistent with previous studies, destabilization of positive charge and the subsequent withdraw from, in this case the site of oxygen-aluminum coordination, increases oxidative stability.<sup>11-13</sup>

Further insight regarding the effects of steric bulk was gained by preparing electrolytes starting from 2,4,6-trimethylphenol and 2,4,6-tri-*tert*-butylphenol to give R = Me<sub>3</sub> and tBu<sub>3</sub> respectively, groups. Collective electrochemical properties and cyclic voltammetry can be found in Table 1 (bottom) and Figure 2 (top) respectively.

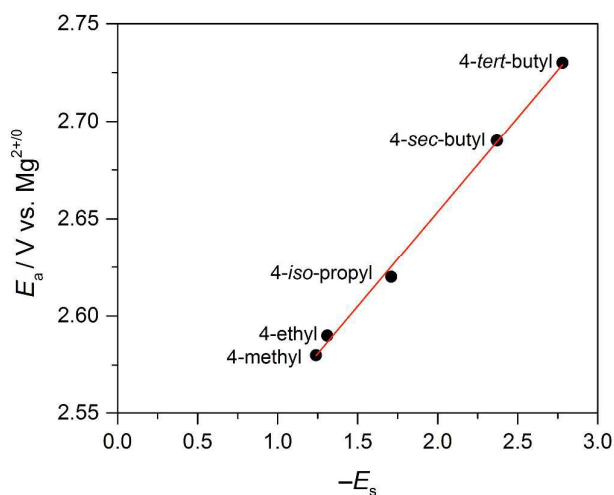


Fig. 1. Anodic stability defined as potential for onset 5  $\mu\text{A}$  of anodic current vs. Taft's steric bulk parameter ( $-E_s$ ) of para-substituted phenols (relative to unsubstituted phenol). The linear fit is shown in red.

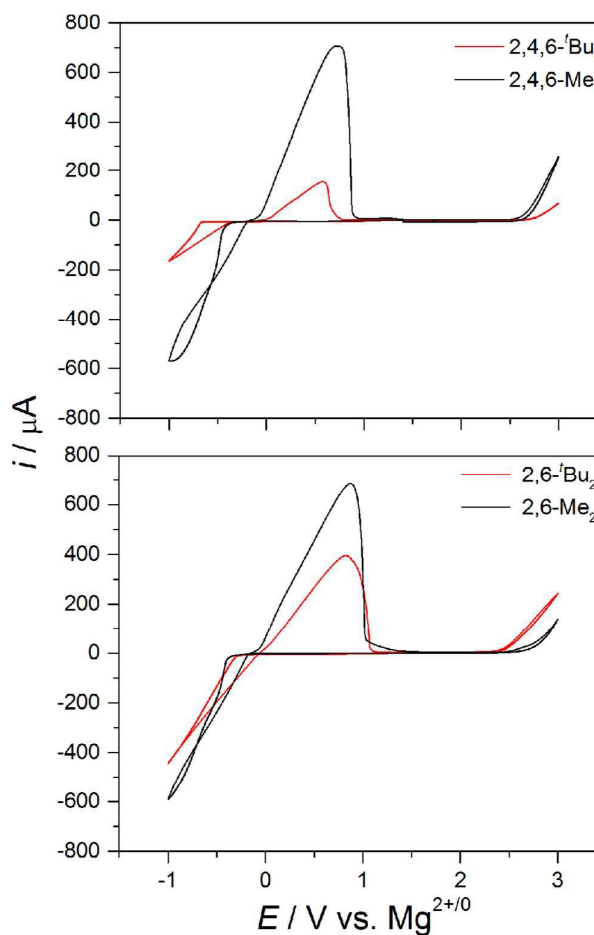


Fig. 2. Cyclic voltammograms for 0.5 M RPhOMgCl and 0.25 M AlCl<sub>3</sub> electrolyte solutions, substitutions designated in figure legend.

Adding identical ortho-substituents to the para-phenol equivalent negligibly contributes to anodic stabilities. However, substituting at the ortho positions does lead to increased conductivity presumably due to weaker ion pairing between the magnesium cations and the phenolic aluminum anions. A two-fold increase in solution conductivity is observed for electrolytes starting composed of 4-methylphenol and 2,4,6-trimethylphenol both at room temperature (Table 1) and at  $-10$  °C (0.63 and 1.3  $\text{mS/cm}$ , respectively). The steric bulk of the substituent plays a larger role than does the number of substituted sites. That is, the solution conductivity of the electrolytes comprising methyl-derivatized phenols is consistently greater than that of the *tert*-butyl-derivatized phenols.<sup>27</sup> Al NMR spectra reveal increased speciation in the R = Me<sub>3</sub>- and Me<sub>2</sub>-containing electrolytes, consisting of each species [<sup>R</sup>PhO<sub>x</sub>AlCl<sub>4-x</sub>]<sup>-</sup> ( $x = 1 - 4$  (Fig. S3, ESI<sup>+</sup>)). With a conductivity of 2.56  $\text{mS/cm}$ , the electrolyte composed of 0.5 M RPhOMgCl and 0.25 M AlCl<sub>3</sub> (R = 2,4,6-Me<sub>3</sub>) in THF is comparatively one of the most conductive electrolytes to date.<sup>8,12,14</sup> Further insight is provided from measuring the cation transference numbers,  $t_+$  (Table S1, ESI<sup>+</sup>). We find that electrolytes composed of R = 4-Me and 2,4,6-Me<sub>3</sub> demonstrate transference numbers of 0.38 and 0.78, respectively. As size of

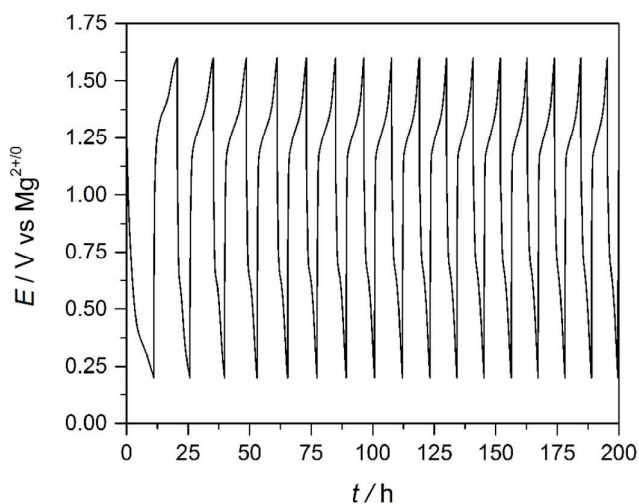


Fig. 3. Reversible galvanostatic cycling of Mo<sub>6</sub>S<sub>8</sub> vs. Mg-foil at C/10 in 0.5 M <sup>R</sup>PhOMgCl and 0.25 M AlCl<sub>3</sub> (R = 2,4,6-Me<sub>3</sub>) in THF electrolyte.

the phenol increases, both the transference number and the solution conductivity increase. Notable is that only a divalent cation ( $z_+ = 2$ ) gives rise to meaningful transference numbers. Thus, it is unlikely that  $[\text{Mg}_2(\mu\text{-Cl})_3(\text{thf})_6]^+$  contributes directly to magnesium deposition and stripping. This phenomenon is an ongoing area of investigation for phenolate-based magnesium electrolytes with AlCl<sub>3</sub>. Nevertheless, our higher transference numbers compared to those reported<sup>15</sup> suggests enhanced cation mobility due to looser ion pairing to the larger aluminate anion.

Electrolytes starting from 2,6-di-methylphenol (R = Me<sub>2</sub>) and 2,6-di-*tert*-butylphenol (R = <sup>t</sup>Bu<sub>2</sub>) were also prepared for evaluating the specificity of charge dissipation distance and its influence on anodic stability. Removing the para-substitutions in both the methyl and *tert*-butyl systems results in decreased anodic stability stabilities (Fig. 2, bottom). When R = <sup>t</sup>Bu<sub>3</sub> or <sup>t</sup>Bu<sub>2</sub>, only [<sup>R</sup>PhOAlCl<sub>3</sub>]<sup>-</sup> is observed, likely due to the steric hindrance of the *tert*-butyl groups (Fig. S4, ESI<sup>†</sup>). This effect was more pronounced with *tert*-butyl than methyl being that its initial increased stabilization was a result of the large inductive contribution in para-equivalent systems. Accordingly, removing it proves to be more detrimental. The combination of removing the source of added stability, which allowed for maximum charge dissipation, and decreased electrochemical species, electrolyte composed of R = <sup>t</sup>Bu<sub>2</sub> demonstrates the lowest anodic stability among all of our electrolyte solutions, thus providing further support for the relationship between preferred distances of charge delocalization and oxidative stability.

Demonstrating the ability to facilitate ion insertion and extraction is shown in Chevrel-phase Mo<sub>6</sub>S<sub>8</sub> containing batteries. We prepared Chevrel-phase Mo<sub>6</sub>S<sub>8</sub> cathode material by a known solid-state method.<sup>16</sup> 2016-type coin cells, prepared in an argon-atmosphere containing mechanically polished Mg foil as the anode in THF electrolyte with a soaked glass fiber separator, were cycled at room temperature at C/10 current. The galvanostatic cycles in Figure 3 along with the

charge–discharge curves (Figure S5, ESI<sup>†</sup>) show gravimetric capacities consistent with reversible Mg<sup>2+</sup> insertion into Chevrel-phase Mo<sub>6</sub>S<sub>8</sub>. Although our capacities (~63 mAh/g) are significantly lower than the theoretical capacity of Mo<sub>6</sub>S<sub>8</sub> Chevrel (~130 mAh/g), they are on par with those reported for Grignard-based Mg and AlCl<sub>3</sub> electrolytes. We also note that the capacities we observe upon charging are greater than those observed upon discharge, likely due to parasitic corrosion of Chevrel that occurs at higher potentials. Similar behavior is also observed in the original report.<sup>5</sup>

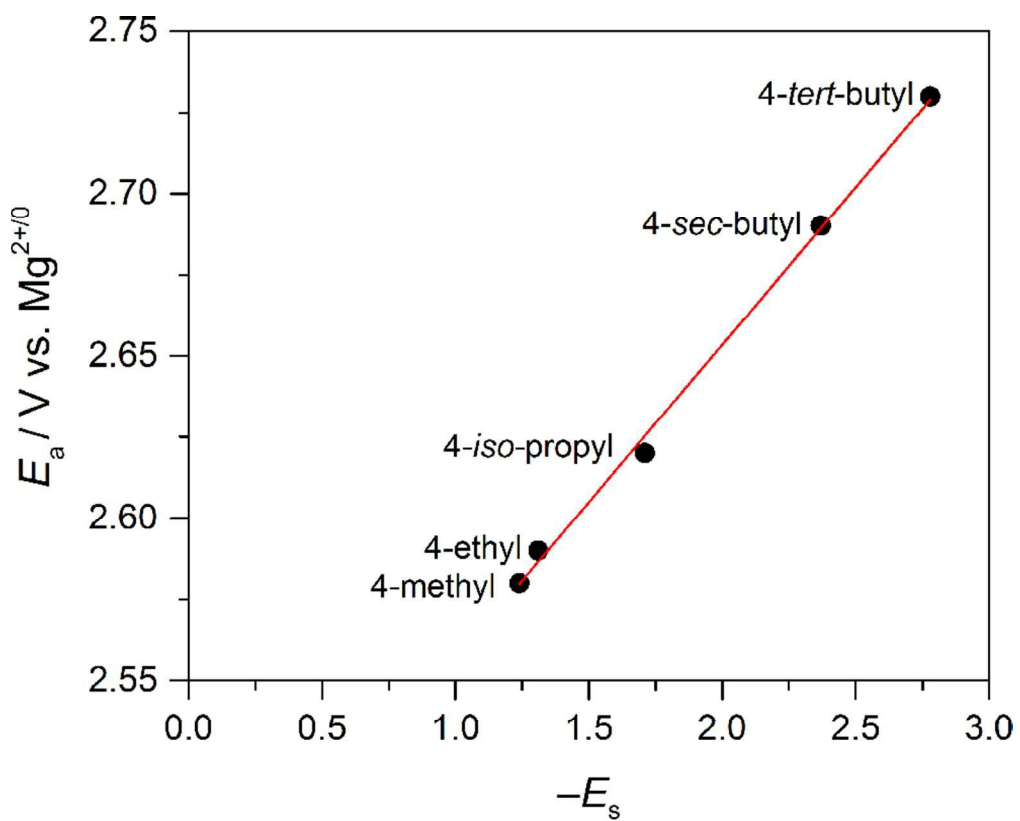
In summary, with the systematic substitution of a variety of alkyl-based phenols within the standard <sup>R</sup>PhOMgCl and AlCl<sub>3</sub> in THF electrolyte system, we have demonstrated charge dissipation from the site of oxidation that results from the inductive effect of branching alkyl groups, allowing for an expansion of the electrochemical window to 2.73 V vs. Mg<sup>2+/0</sup>. Additionally, including alkyl substituents at the 2 and 6 positions yield similar anodic stabilities with a nearly two-fold enhancement in solution conductivity, allowing for future development of highly conductive and highly stable magnesium-ion electrolytes as we move beyond-lithium ion technologies.

#### Acknowledgement

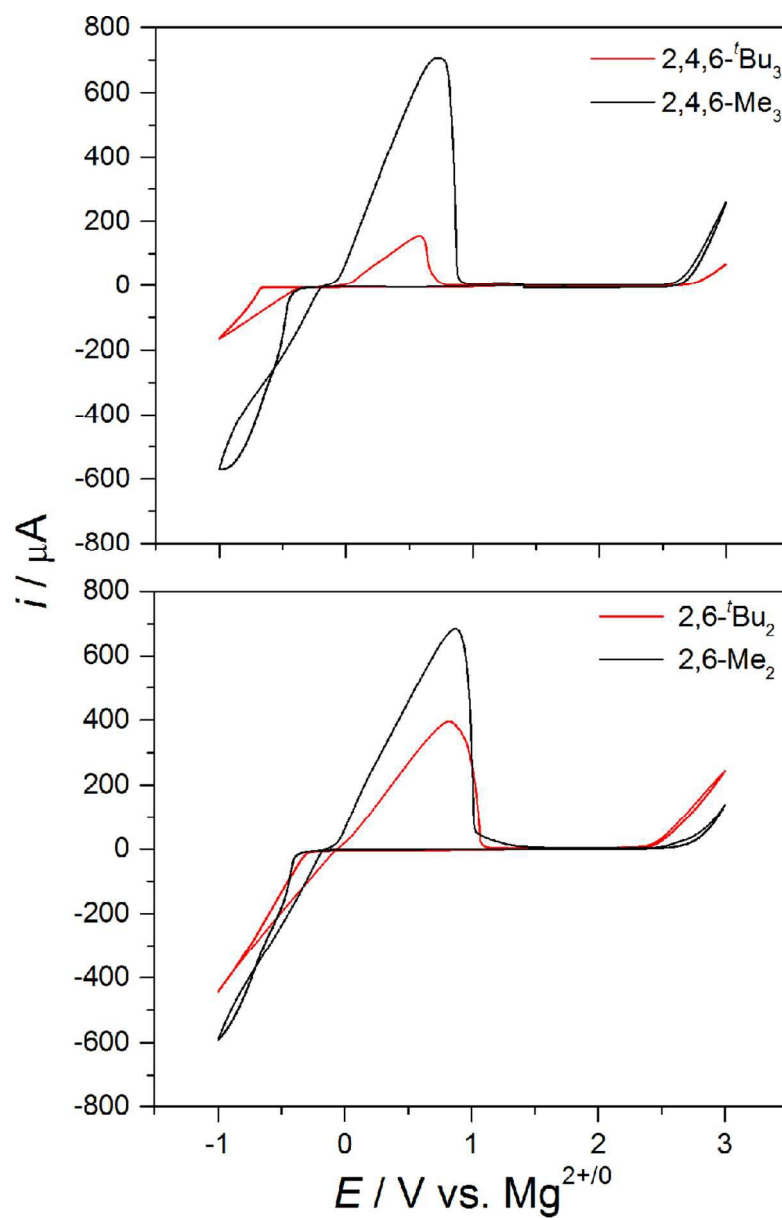
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#### Notes and references

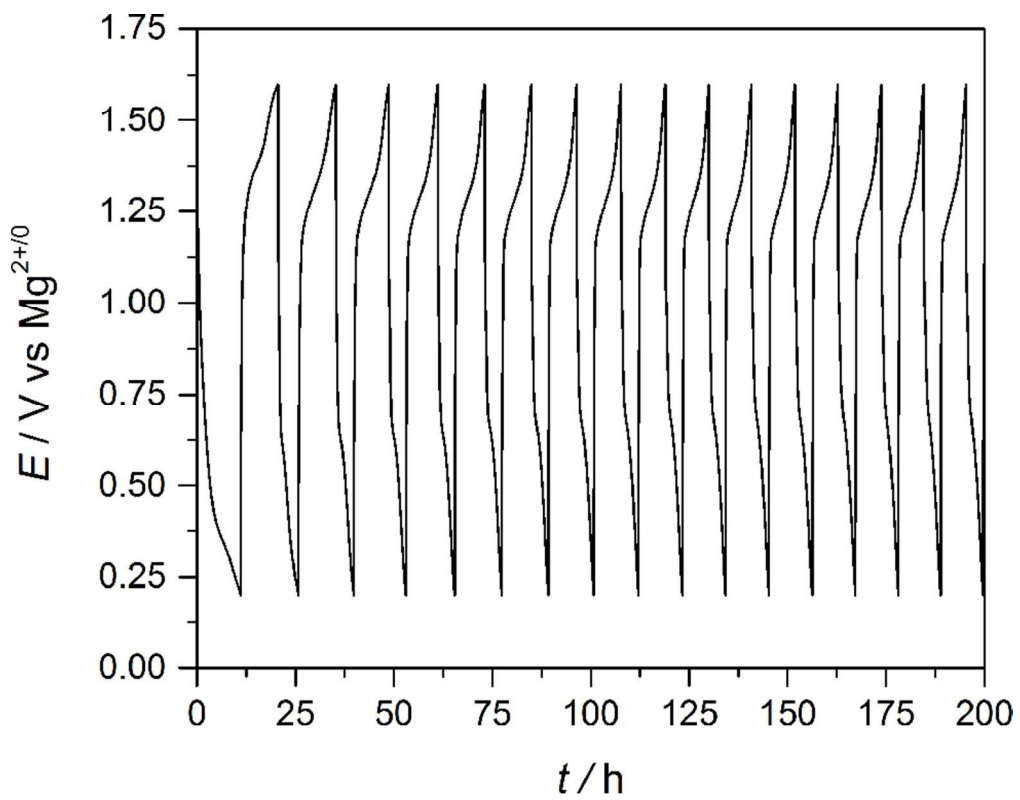
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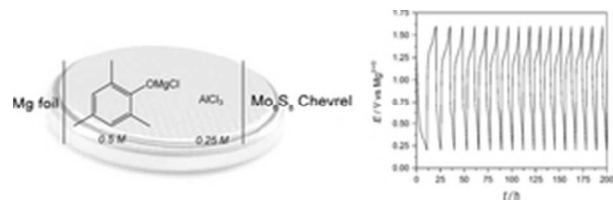


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