Electronic Supplementary Information for

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

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Detailed Experimental Section

Synthesis. All electrolyte solutions were prepared within a N_2-filled glove box (Vacuum Atmospheres) analogous to the following procedure represented for 0.5 M ^{R}PhOMgCl and 0.25 M $AlCl_3$ (R = ^{t}Bu). 2 M ethylmagnesium chloride in THF (8 mmol, 4 mL) was slowly added via syringe to a solution of 4-*tert*-butylphenol (8 mmol, 1.20 g) dissolved in dry THF (4 mL). The mixture was allowed to stir overnight, forming ^{R}PhOMgCl (R = ^{t}Bu). Then, a 0.5 M solution of $AlCl_3$ (4 mmol, 8 mL) in THF (0 °C) was prepared in a 20 mL scintillation, warmed to room temperature, and added to the phenolatemagnesium chloride. This solution was stirred for 8 hours, providing a clear colorless solution of 0.5 M ^{R}PhOMgCl and 0.25 M $AlCl_3$ (R = ^{t}Bu).

Electrolyte Analysis. ^{27}Al NMR was performed on a Varian VNMRS-700 MHz spectrometer in THF with chemical shifts reported relative to a solution of $AlCl_3$ in D_2O with a drop of concentrated HCl. Peak assignments were made with reference to previous work in the Bartlett group.[1] Cyclic voltammograms were recorded using a CH Instruments Electrochemical Workstation 1000A or 660C while using a Pt-disk working and Mg-foil counter- and reference electrodes. Measurements were performed starting at open circuit potential and scanned cathodically within a custom-designed, three-necked, sealed glass cell. Conductivity measurements were obtained using a YSI Model 3200 meter equipped with a 3253 conductivity cell at room temperature. A slurry of Mo_6S_8 was prepared by mixing an 8:1:1 (by weight) ratio of Mo_6S_8, super-P carbon powder, and polyvinylidine fluoride (PVDF) binder, suspended in N-methyl-2-pyrrolidinone (NMP). The active material loading was approximately 2 mg/cm^2. The slurry was doctor bladed onto a stainless steel current collector and dried in an over at 120 °C, placed in a 2016-type coin cell with a Mg-foil anode and a soaked glass fiber separator in 0.5 M ^{R}PhOMgCl and 0.25 M $AlCl_3$ (R = 2,4,6-Me$_3$) in THF electrolyte. Cycling was carried out on a Vencon UBA4 battery analyzer charger and conditioner (Toronto, Canada) with cut-off voltages of 1.6 and 0.2 V vs. Mg$^{2+/0}$. Transference numbers (t_+) were estimated assuming deposition directly from Mg^{2+}, as described in a previous report.[2] In brief, chronopotentiometry was used to deposit Mg metal using a Pt disk working electrode, and Mg strips as reference and counter electrodes, with 1 mL of electrolyte. A controlled amount of charge was passed between the electrodes, and magnesium deposits were then digested in 10 mL of 0.1 M HNO_3 solution. The prepared solution was analyzed with ICP-AES for Mg^{2+} using a Perkin-Elmer Optima 2000DV. Samples were referenced to an yttrium internal standard and concentrations of magnesium were determined from the maximum intensity compared to those of standard reference solutions.

1. E. G. Nelson, J. W. Kampf and B. M. Bartlett, *Chem. Commun.*, 2014, **50**, 5193-5195.
2. Benmayza, A.; Ramanathan, M.; Arthur, T. S.; Matsui, M.; Mizuno, F.; Guo, J.; Glans, P. A.; Prakash, J. *J. Phys. Chem. C*, 2013, **117**, 26881.
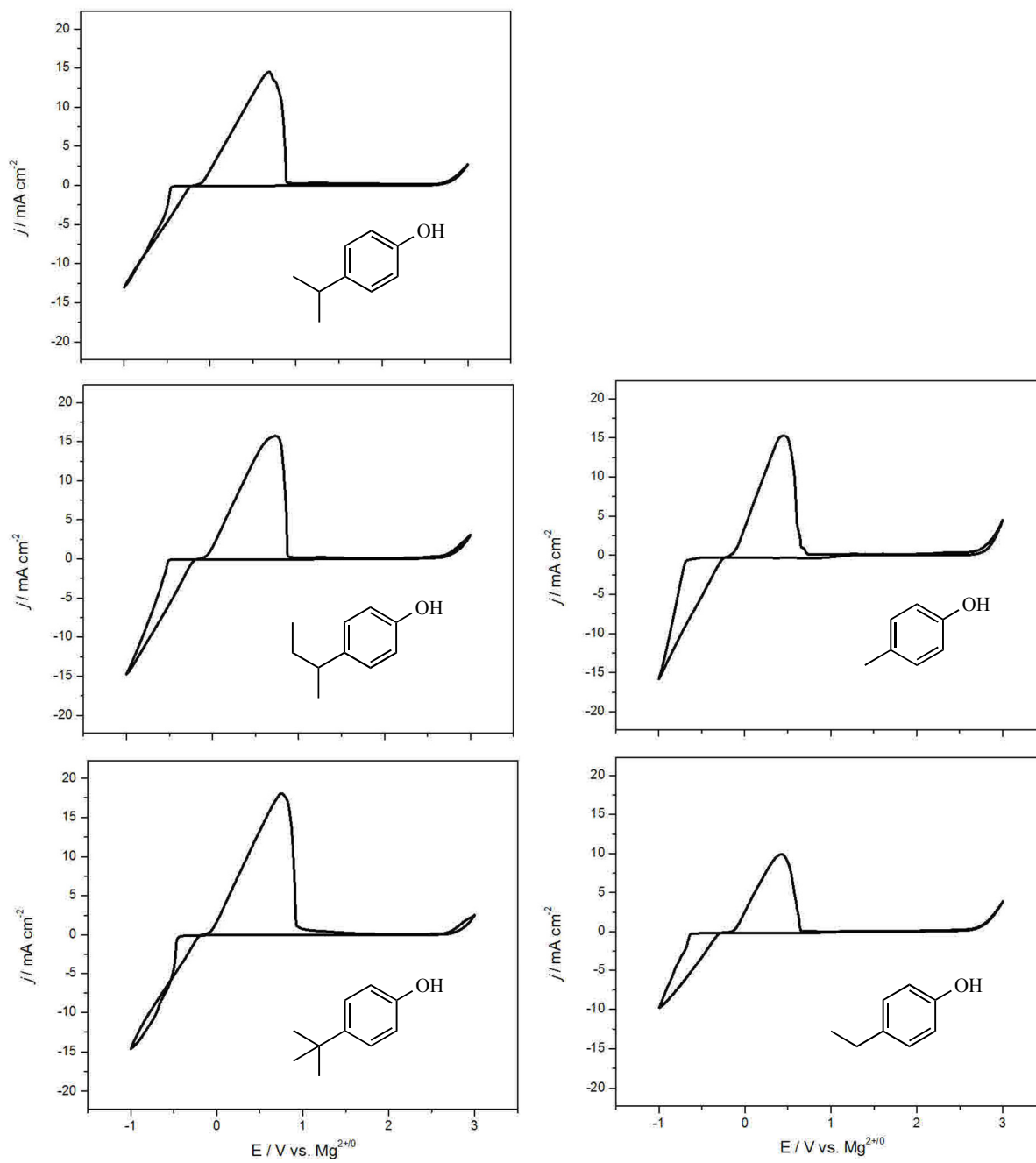
Figure S1. Cyclic voltammograms of 0.5 M ^{R}PhOMgCl and 0.25 M AlCl$_3$ R = 4-Me, 4-Et, 4-^{i}Pr, 4-^{s}Bu, and 4-^{t}Bu.
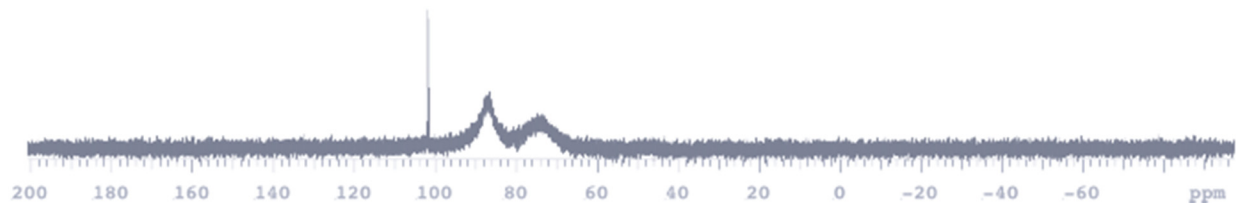
Figure S2. ^{27}Al NMR chemical shifts and assignments for 0.5 M ^{R}PhOMgCl and 0.25 M AlCl$_3$ (R = 4-Me, 4-Et, 4-^{i}Pr, 4-^{s}Bu, and 4-^{t}Bu).
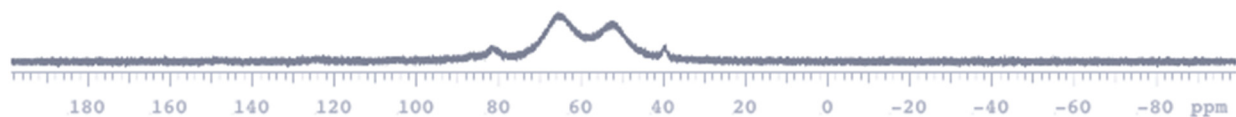
Figure S3. Typical ^{27}Al NMR spectrum for 0.5 M ^{R}PhOMgCl and 0.25 M AlCl$_3$ (R = 2,4,6-Me$_3$ and 2,6-Me$_2$).
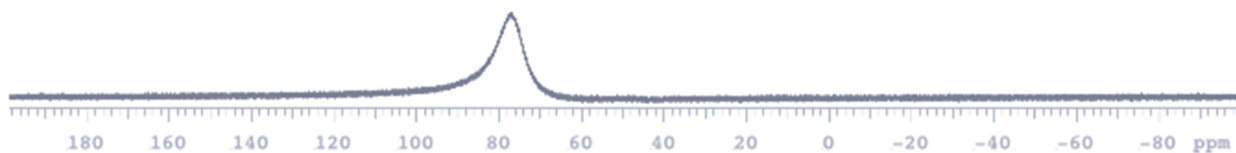
Figure S4. Typical ^{27}Al NMR spectrum 0.5 M ^{R}PhOMgCl and 0.25 M AlCl$_3$ (R = 2,4,6-^{t}Bu$_3$ and 2,6-^{t}Bu$_2$).

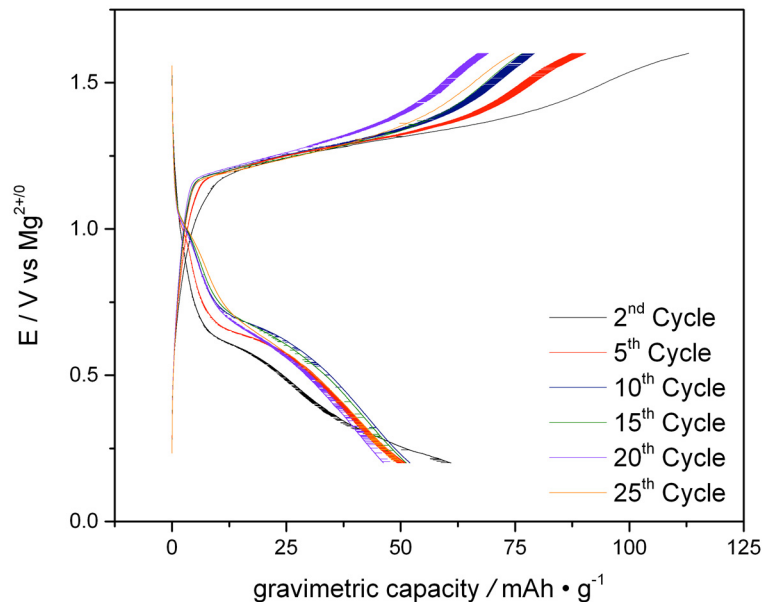| Electrolyte (R)	Chemical Shift /ppm)	Assignment
4-Me, 4-Et, 4-^{i}Pr, 4-^{s}Bu, and 4-^{t}Bu	74	[(^{R}PhO)$_2$AlCl$_2$]$^-$
	87	[(^{R}PhO)AlCl$_3$]$^-$
	102	Al$_2$Cl$_6$
2,4,6-Me$_3$ and 2,6-Me$_2$	42	[(^{R}PhO)$_4$Al]$^-$
	55	[((^{R}PhO)$_3$AlCl]$^-$
	68	[(^{R}PhO)$_2$AlCl$_2$]$^-$
	84	[((^{R}PhO)AlCl$_3$]$^-$
2,4,6-^{t}Bu$_3$ and 2,6-^{t}Bu$_2$	79	[(^{R}PhO)AlCl$_3$]$^-$

Figure S5. Charge–Discharge curves of Mo_6S_8 *vs.* Mg-foil in 0.5 M $^RPhOMgCl$ and 0.25 M $AlCl_3$ (R = 2,4,6-Me$_3$) in THF at *C*/10.

Table S1. Chronopotentiometric deposition details and estimated transference numbers.

$$t_+ = 1 - (z_+ F \Delta C^* V / q)$$

Transference number (t_+) for Mg^{2+}-containing complex cation with a valency (z_+) of 2, Faraday's constant ($F = 26.801$ Ah/mol), change in bulk magnesium ion concentration (ΔC^* / mmol L^{-1}), V is the volume of electrolyte (1 mL), and charge passed (q / mAh). We note from Faraday's law that the theoretical Mg^{2+} concentration is 23.58 ppm for a monovalent cation ($z_+ = 1$) being responsible for Mg metal deposition. However, a more reasonable value, 5.89 ppm results for a divalent cation ($z_+ = 2$) being responsible for Mg metal deposition.

Electrolyte / R	Charged passed / mAh	Concentration / ppm	ΔC / mM	t_+
4-Me	0.13	3.674	1.512	0.38
2,4,6-Me$_3$	0.13	1.325	0.545	0.78