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Supporting Information

Reverse Schlenk Equilibrium Magnesium Electrolytes for Rechargeable Magnesium Ion Battery

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1. Materials and Synthesis

All chemicals used in the synthesis of RSE magnesium electrolyte were purchased from commercial suppliers and used without further purification. Magnesium hexamethyldisilazane, magnesium dichloride, anhydrous tetrahydrofuran (THF) were purchased from Aldrich. Magnesium isopropyl amide was purchased as the 0.7 M solution in THF. The THF was removed to prepare a pure salt of magnesium isopropyl amide solid. Newly synthesized RSE compounds were characterized by ^{1}H, ^{13}C, and ^{25}Mg NMR spectroscopy, using a 300 MHz spectrometer. All chemical shift values (d) are reported in ppm, referenced relative to TMS (^{1}H and ^{13}C) or $MgCl_2$ (^{25}Mg).

2. Electrochemical Measurements

Cyclic voltammetry (CV) was characterized on a three-electrode configuration with working electrode such as a platinum disk (2 mm in diameter, CH instruments, Austin, TX), counter electrode and reference electrode as Mg ribbons (99.9% purity, Sigma-Aldrich). The working electrodes such as platinum disk, gold disk and glassy carbon, were polished with a corundum suspension and rinsed with dry acetone before use. Three continuous scans of CV were collected to evaluate the deposition and dissolution performance of the $MgHDMS\cdot 4MgCl_2$ electrolyte. Potential was swept from -1 V to +3 V *vs* Mg/Mg^{2+} with the scan rate of 25 mV/sec.

Ionic conductivity was measured by impedance spectroscopy, and an aqueous solution of 0.1 M KCl was used as a reference to calibrate the house-made ionic conductivity cells.

Chronocoulometry (CC) method was applied to evaluate the diffusion coefficient of the cations in the electrolyte with the same experimental setup for the CV characterization. Potential at the working electrode was set at -0.5 V *vs* Mg/Mg^{2+} for 120 sec allowing the reduction of Mg^{2+} based cations at the surface of the working electrode. All the electrochemical characterizations mentioned in this paper were carried on a multi-channel potentiostat (Parstat MC, Princeton Applied Research, TN) under pure argon atmosphere in a glove box. Integration of the faradic current density over time was obtained and plotted against the square root of time as shown in Figure 2a. Diffusion coefficient at each concentration was determined by fitting Q versus $t^{1/2}$ with eq. 1 derived from the Cottrell equation.

$$Q = \frac{2nFAC_0D^{1/2}}{\pi^{1/2}}t^{1/2} + Q_{dl} + Q_{ads} \qquad \text{eq. 1}$$

The corresponding parameters of eq. 1 are defined as follows: n as the number of electrons for the reduction reaction occurred at the working electrode (n=2); F is the Faraday constant; A as the electrode area (0.0314 cm^2 in this case), Q_{dl} as capacitive charge and Q_{ads} as charge contributed from the absorbed species.

The Cell cycling tests and cyclic voltammetry were conducted using 2032 coin cells. All cells were cycled with C/10 current on a Maccor series 4000 cycler within a voltage range of 0.2–1.6 V at room temperature.

3. NMR Spectroscopy

^{1}H and ^{13}C NMR experiments were performed by single pulse experiments and ^{25}Mg NMR experiments were performed by Hahn-echo experiments at 11.7 T using a Bruker Avance III spectrometer. ^{1}H, ^{13}C and ^{25}Mg NMR signals were referenced to TMS and 5M $MgCl_2$ (aq) at

0 ppm, respectively. A deuterium-lock was obtained by using a sealed D_2O capillary to avoid unwanted magnesium coordination.

4. Theory

All theoretical calculations were performed using density functional theory (DFT). All structure optimizations were performed using the B3LYP (Ref 1) method and 6-31+G(d) basis sets as implemented in the Gaussian 09 suit (Ref 2). Since all reactions occur in solution, the Polarizable Continuum Model (PCM) with tetrahydrofuran as the solvent was used to add solvation free energy correction to each species. The free energy of each species is the summation of enthalpy, entropy and solvation energy terms and the reaction free energies ΔG are calculated accordingly. Oxidation potential of a molecule C relative to Mg/Mg^{2+} reference electrode can be calculated from equation:

$$E_C = \frac{G_{C^{n+}} - G_C}{nF} - 1.9 \text{, (Eqn S1)}$$

where n is the number of electrons involved in the oxidation event, F is the Faraday's constant, G_C and $G_{C^{n+}}$ are the free energies of the molecule C and the oxidized C with $n+$ charge.

Results

1. Simulation

All possible reactions we considered between $Mg(HMDS)_2$ and $MgCl_2$ with their corresponding reaction free energies are reported in Figure S1. It can be shown that the pathway shown in black arrows (also reported in equation 1-3 in our main text) is the most favorable pathway.

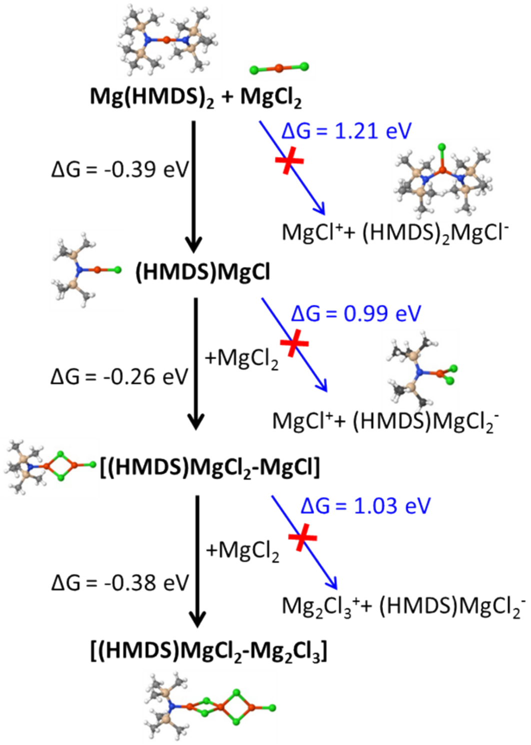
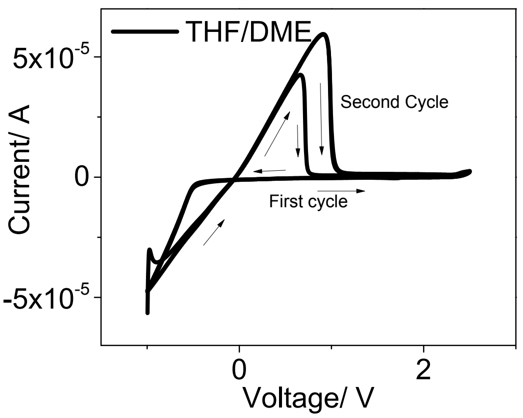


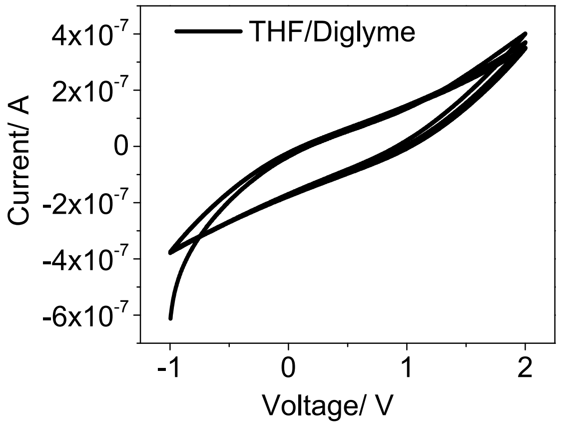
Figure S1. Main reaction pathway (in black arrow) and other less possible reactions we calculated. Reaction free energies (corresponding to 1 mole of each reactant) of these steps are reported.

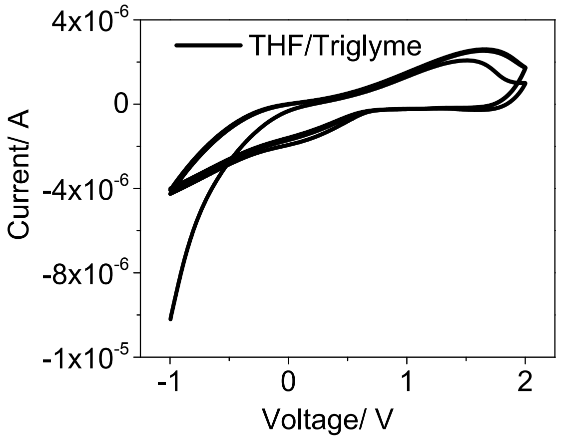
We also calculated oxidation potentials of $(HMDS)MgCl_2^-$ and $[MgHMDSCl_2\_MgCl]$ using Eqn S1. The oxidation potentials calculated are 3.2 and 3.9 V, respectively, relative to Mg/Mg^{2+} reference electrode.

2. Typical cyclic voltammograms

0.5 M Mg(HMDS)2-4MgCl2 in different solvent THF/DME (1:1). The working electrode is Pt electrode, and Mg ribbon is used both as the reference and the counter electrode. The scan rate is 100 mV s^{-1} and the number of cycles is marked on the graph.


THF/DME
Second Cycle
First cycle
5x10^{-5}
0
-5x10^{-5}
Current/ A
0
2
Voltage/ V


THF/Diglyme
4x10^{-7}
2x10^{-7}
0
-2x10^{-7}
-4x10^{-7}
-6x10^{-7}
Current/ A
-1
0
1
2
Voltage/ V


THF/Triglyme
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0
-4x10^{-6}
-8x10^{-6}
-1x10^{-5}
Current/ A
-1
0
1
2
Voltage/ V

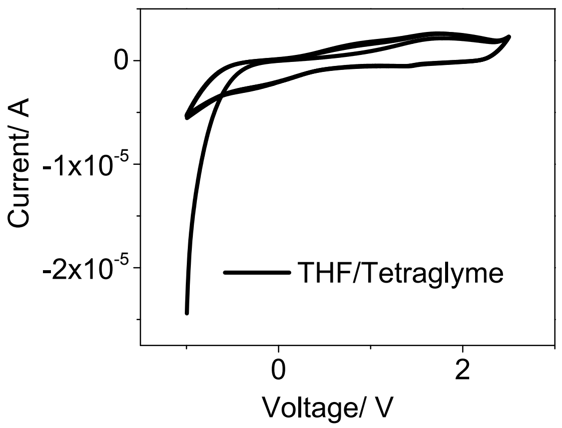

Figure S2. Cyclic Voltammetry of 0.5 M Mg(HMDS)2-4MgCl2 in THF/DME (1:1), THF/Diglyme (1:1), THF/triglyme (1:1), THF/tetraglyme (1:1). The working electrode is Pt electrode, and Mg ribbon is used both as the reference and the counter electrode. The scan rate is 100 mV s-1 and the number of cycles is marked on the graph.

3. Typical cyclic voltammograms with Pt electrodes of THF solution containing $Mg(HMDS)_2$-$3MgCl_2$

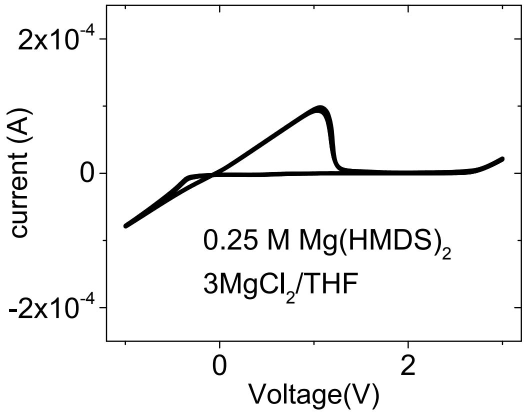

Figure S3. Cyclic Voltammetry of 0.25 M $Mg(HMDS)_2$-$3MgCl_2$ in THF. The working electrode is Pt electrode, and Mg ribbon is used both as the reference and the counter electrode. The scan rate is 100 mV s^{-1} and the number of cycles is marked on the graph.

Reference

1) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 98, 5648 (1993).

2) Frisch, M. J.; Trucks, G. W. S., H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. ; Gaussian, Inc.: Wallingford CT, 2009.