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Supplementary Information for

$MgCl_2/AlCl_3$ Electrolytes for Reversible Mg Deposition/Stripping: Electrochemical Conditioning or not?

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Experiment section

Materials and electrolyte synthesis: Anhydrous $MgCl_2$ and $AlCl_3$ were bought from Sigma-Aldrich with purity >99.99%. Dimethoxyethane (DME) was purchased from TCI America and was distilled over Na and benzophenone under Nitrogen. Water content in DME was measured to below 10 ppm using a Karl Fischer titration meter. All glassware was dried at 150 °C in an oven for at least 12 h before introduction into a glovebox. All the electrolytes were prepared inside an Argon-filled glove box with oxygen and water content below 1 ppm. In a typical synthesis of 2.0 ml 0.1 M $MgCl_2/AlCl_3$-DME electrolyte, 26.7 mg $AlCl_3$ (0.2 mmol) was slowly dissolved into 2.0 ml DME (under stirring) in a 5.0 ml glass vial and then 19.0 mg $MgCl_2$ (0.2 mmol) was slowly added to the above mixture. The mixture was stirred at 30 or 45°C in an oil bath for 6 hours, and was cooled down to room temperature. A clear solution was obtained with no precipitate. Other electrolytes were prepared via a similar procedure.

Conductivity test: Ion conductivity of the electrolytes was collected by a S230 SevenCompact™ conductivity meter (METTLER TOLEDO) in an Ar glovebox.

Electrochemical test: All the electrochemical tests were conducted in a glove box with oxygen and water content below 1 ppm. Cyclic voltammetry (CV) tests were performed on a computer controlled Gamry Interface 1000 electrochemical workstation in a homemade vial cell utilizing a glassy carbon working electrode (or Pt working electrode), a graphite counter electrode and a Mg strip reference electrode at a scan rate of 50 mV/s. Overpotential (η) was calculated from the potential difference between the onset potential of Mg deposition and stripping in CV curve. Coulombic efficiency (CE) was calculated by dividing the electrical charge collected during the Mg deposition process by that of the stripping processes. Bulky electrolysis for Mg deposition was conducted at 2 mA/cm^2 for 1 h to produce an Mg film using a 0.4 M 1:1 $MgCl_2/AlCl_3$-DME electrolyte. The deposited Mg film was then characterized by SEM and EDX (FEI Quanta FEG 650).

Electrochemical conditioning process: 20 μL DME solution with water content of 2.5×10^3 ppm (prepared by mixing suitable amount of H_2O with totally dried DME) was added into a fresh 1:1 $MgCl_2/AlCl_3$-DME electrolyte at 0.1 M. According to the procedure reported by Gewirth *et al.*[1] and Aurbach *et al.*,[2] the resulting electrolyte was conditioned with a Pt working electrode (2 mm in diameter) and Mg strip counter/reference electrodes. CV was conducted at 5 mV/s from -1 to 1 V until overpotential recovered to original value. After each 10 cycles, all the electrodes were polished and CV was conducted at 50 mV/s from -1 to 2 V to monitor the overpotential change. A control experiment showed that glassy carbon working electrode is not effective as Pt working electrode for electrochemical conditioning.

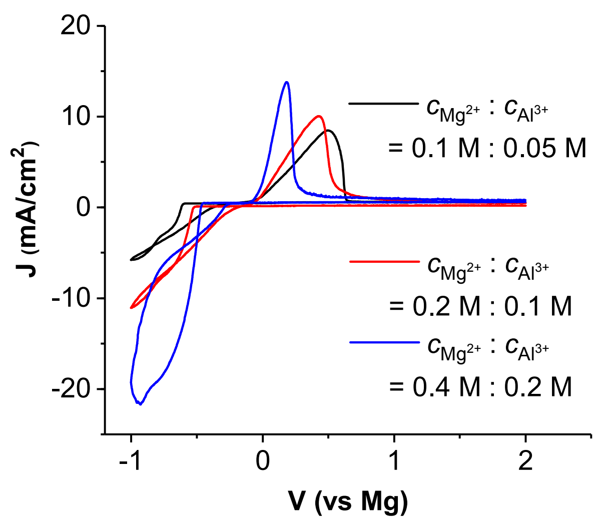

Figure S1. CV curves of $MgCl_2/AlCl_3$-DME electrolytes with ratio of 2:1 at different concentrations.

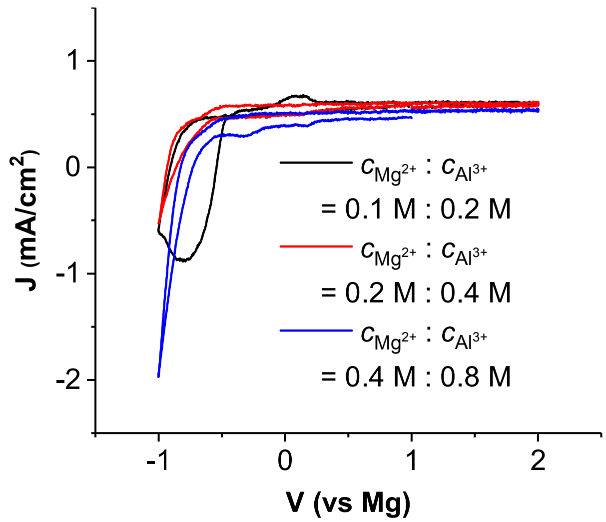

Figure S2. CV curves of $MgCl_2/AlCl_3$-DME electrolytes with ratio of 1:2 at different concentrations.

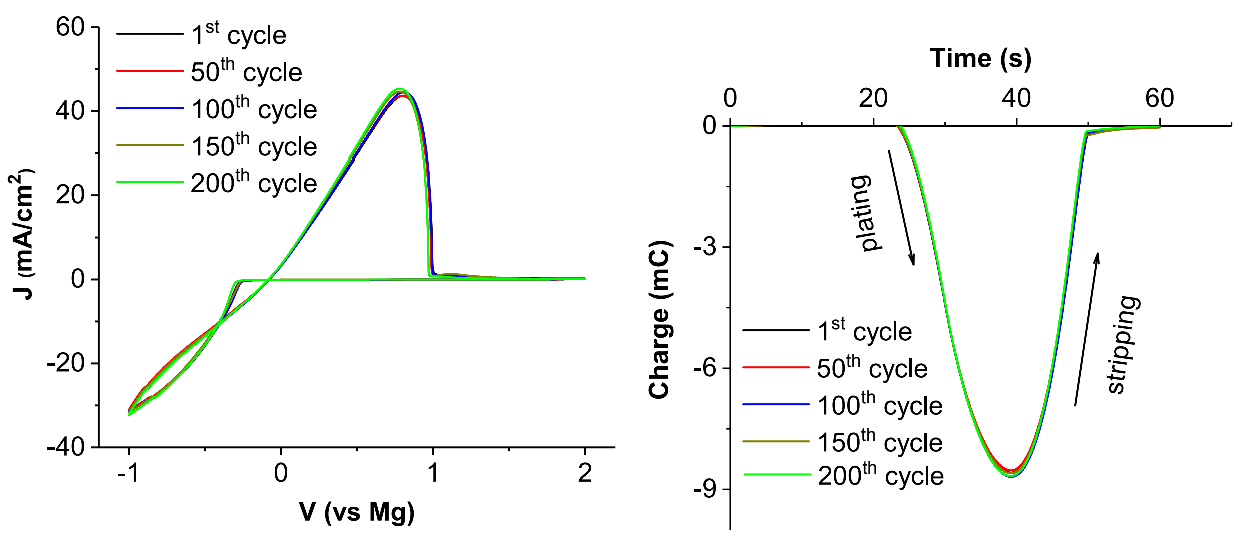

Figure S3. Overlapped CV curves (left) and corresponding plots (right) of charge over time for the 1st, 50th, 100th, 150th and 200th CV curves in a continuous cyclic voltammogram study of a 0.4 M 1:1 ratio electrolyte on Pt. The scan rate is 100 mV/s.

Table S1 Comparison of conductivity and overpotential for different Mg battery electrolytes

Electrolyte	Conductivity (mS/cm)	Overpotential (mV)	ref.
0.4 M $MgCl_2$/0.4 M $AlCl_3$-DME	5.51	271	This work
0.6 M $MgCl_2$/0.6 M $AlCl_3$-DME	8.75	261	This work
0.7 M $MgCl_2$/0.7 M $AlCl_3$-DME	9.98	251	This work
0.25 M $MgCl_2$/0.125 M $AlCl_3$/DME	~2	<200	3
0.28 M $MgCl_2$/0.02 M $AlCl_3$-THF	0.23	<200	4
0.4 M $MgCl_2$/0.267 M $AlEtCl_2$-THF	2.09	252	5
0.4 M $MgCl_2$/0.4 M $AlEtCl_2$-THF	4.1	220	5
0.4 M $MgCl_2$/0.4 M $AlEtCl_2$-diglyme	2.29	404	5
0.4 M $MgCl_2$/0.4 M $AlEtCl_2$-triglyme	1.19	466	5
0.4 M $MgCl_2$/0.4 M $AlEtCl_2$-tetraglyme	0.95	384	5
0.4 M $MgCl_2$/0.2 M $AlEtCl_2$-DME	2.1	216	5
0.4 M $MgCl_2$/0.27 M $AlEtCl_2$-DME	2.72	202	5
0.4 M $MgCl_2$/0.4 M $AlEtCl_2$-DME	3.9	220	5
0.4 M $MgCl_2$/0.6 M $AlEtCl_2$-DME	4.32	360	5
0.8 M $MgCl_2$/0.8 M $AlEtCl_2$-DME	6.72	209	5
0.4 M $MgCl_2$/0.4 M $Mg(TFSI)_2$-DME	/	~400	5
0.43 M $MgCl_2$/$AlPh_3$-THF	2.96	~200	6

0.5 M (DTBP)$MgCl/MgCl_2$-THF	0.66	~200	7
0.5 M RPhOMgCl/0.25 M $AlCl_3$-THF (R = 2, 4, 6-Me_3)	2.56	~200	8
0.5 M (BMP–$MgCl)_2/AlCl_3$-THF	2.1	~300	9
0.5 M $(BMPMC)_2AlCl_3$-THF	2.56	~400	10
0.67 M $MgCl_2/AlEtCl_2$-THF	6.99	~200	6
1 M Et2AlCl/MgCl2-THF	3.2	/	11
1 M $Et_2AlCl/MgCl_2$-diglyme	3.0	/	11
1 M $Et_2AlCl/MgCl_2$-tetraglyme	0.9	/	11
1 M (*tert*-BuOMgCl)$_6/AlCl_3$-THF	1.33	~200	9

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