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Advanced Magnesium-Lithium-Ion Hybrid Batteries with Magnesium Metal Anode and Spinel $LiMn_2O_4$ Cathode

Baofei Pan,[a] Zhenxing Feng,[a] Niya Sa,[a] Sang-Don Han,[a] Qing Ma,[b] Paul Fenter,[a] John T. Vaughey,[a] Zhengcheng Zhang,[a] Chen Liao[a]

[a]Joint Center for Energy Storage Research, Chemical Science and Engineering Division, Argonne National Laboratory, Lemont, Illinois, 60439, USA

[b]DND-CAT, Synchrotron Research Center, Argonne National Laboratory, Lemont, Illinois 60439, USA

1. Experimental section

General considerations: Synthesis and characterization of the electrolytes were all carried out in argon-fi1lled glove boxes with oxygen and water concentrations below 1 ppm level. Chemicals were purchased commercially and used without further purification. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and magnesium powder were purchased commercially and used without further purification. Magnesium bis(trifluoromethylsulfonyl)imide ($Mg(TFSI)_2$, 99.5%) was purchased from Solvionic and used without further purification. Trimethylammonium 1-Carba-closo-dodecaborate ($[Me_3NH]^+[CB_{11}H_{12}]^-$) salt was purchased from Katchem and used without further purification. Anhydrous N-methyl-2-pyrrolidinone (> 99.5%) was purchased from Sigma-Aldrich and used without further purification. Anhydrous tetrahydrofuran (THF, > 99.9%), anhydrous dimethyl ether of diethylene glycol (diglyme, > 99.5%), anhydrous tetraethylene glycol dimethyl ether (tetraglyme, > 99%) were purchased from Sigma-Aldrich and dried with 3 Å molecular sieves for more than 12 hours before use. Lithium manganese oxide spinel ($LiMn_2O_4$, <0.5 µm particle size (BET), >99%), lithium cobalt oxide ($LiCoO_2$, 99.8% trace metals basis) and lithium nickel manganese cobalt oxide ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, <0.5 µm particle size, >98%) were purchased from Sigma-Aldrich and used without further purification.

1.1. Electrolyte preparation:

0.5 M $Mg(TFSI)_2$ in diglyme:

In a 20 mL vial, 1.17 g (2 mmol) $Mg(TFSI)_2$ salt was dissolved in 4.0 mL diglyme, and the mixture was stirred at room temperature for six hours to afford colorless 0.5 M $Mg(TFSI)_2$ in diglyme electrolyte.

0.25 M $Mg(TFSI)_2$-LiTFSI in diglyme:

In a 20 mL vial, 584.6 mg (1 mmol) $Mg(TFSI)_2$ and 287.3 mg (1 mmol) LiTFSI were mixed in 4.0 mL diglyme. The mixture was allowed to stir for six hours at room temperature to afford colorless 0.25 M $Mg(TFSI)_2$-LiTFSI in diglyme electrolyte before use. Similar procedure was used for the preparation of the equal molar ratio 0.50 M $Mg(TFSI)_2$-LiTFSI/diglyme and the 1:2 ratio 0.50 $Mg(TFSI)_2$-2LiTFSI/diglyme electrolytes.

0.25 M $Mg(CB_{11}H_{12})_2$ in tetraglyme:

A modified procedure from reported literature was used for the synthesis of $Mg(CB_{11}H_{12})_2$ in tetraglyme. In a 20 mL vial, 240 mg (10 mmol) magnesium power was suspended in 10 mL anhydrous THF, to which was added 406.3 mg (2 mmol) $[Me_3NH]^+[CB_{11}H_{12}]^-$ power. This mixture was allowed to stir at room temperature for overnight. After completion, a lot of gray solid precipitated from the mixture. The solid was collected via filtration through a medium size frit and washed with 5 mL *3 anhydrous THF solvent. The collected gray solid was dried in vacuum for 30 minutes to remove any THF solvent residue. In a 20 mL vial, the gray solid was suspended in 4 mL anhydrous tetraglyme, and the mixture was stirred vigorously at room temperature for more than 12 hours. After completion, filtration through a fine frit afforded clear solution of 0.25 M $Mg(CB_{11}H_{12})_2$/tetraglyme electrolyte.

0.25 M $Mg(CB_{11}H_{12})_2$-LiTFSI in tetraglyme

To 2 mL above prepared 0.25 M $Mg(CB_{11}H_{12})_2$ in tetraglyme solution was added 143.6 mg (0.5 mmol) LiTFSI, and the mixture was stirred at room temperature for six hours to afford the hybrid electrolyte before use.

1.2. Cathode preparation:

A slurry was made with $LiMn_2O_4$ spinel, Timcal Super C45 carbon black and poly(tetrafluoroethylene) (PTFE) in an 8:1:1 weight ratio by N-methyl-2-pyrrolidinone as the solvent. The generated slurry was casted onto carbon coated aluminum sheet, and then dried at 75 ℃ in air for 2 hours and then at 75 ℃ in vacuum oven for 12 hours before cut into laminates with diameter of 7/16 inches. The obtained laminates were further dried in vacuum oven at 75 ℃ in glovebox for 2 hours before use. Each electrode laminate contains the active material varying from 1.0 mg to 1.2 mg. The same procedure was used for the preparation of $LiCoO_2$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ on carbon coated aluminum electrode laminates.

1.3. Electrochemical characterization

Cyclic voltammetry (CV) measurement of the electrolytes was carried out using a house-made three electrode set-up. Platinum disc ((2 mm in diameter, CH instruments, Austin, TX) was used as working electrode, and freshly polished magnesium ribbons (99.9% purity, Sigma-Aldrich) were used as counter and reference electrodes. A multi-channel potentiostat (Parstat MC, Princeton Applied Research, TN) was applied for the measurement.

Battery cycling test: 2032-type coin cells were assembled using metal oxide laminate as cathode and freshly polished magnesium metal foil as anode, and the cycling performance was carried out using Maccor series 4000 cycler at room temperature.

1.4. X-ray absorption spectroscopy (XAS) measurement

XAS experiments were carried out at beamline 5BM-D of the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) at the Advanced Photon Source (APS) of Argonne National Laboratory (ANL). $LiMn_2O_4$ cathode materials on carbon coated aluminum at pristine, charged and discharged states are cleaned, dried and sealed in Kapton tapes for measurements. All data were collected in transmission mode. The Si(111) monochromator was detuned to 65% of the maximum intensity at the Mn K-edge (6539 eV) to minimize higher harmonics. Data reduction and analysis were performed with the Athena software. Standard procedures were used to extract the XAS data from the measured absorption spectra. The pre-edge was linearly fitted and subtracted. The post-edge background was determined by using a cubic-spline-fit procedure and then subtracted. The data were normalized by the height of the absorption edge.

1.5 Ionic conductivity measurement

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.

2. Supporting figures

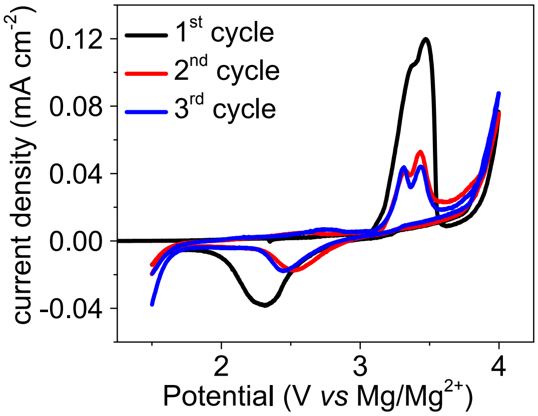

Figure S1. Cyclic voltammetry measurement (0.05 mV s^{-1}) of a coin cell using $LiMn_2O_4$ spinel on carbon coated aluminum as working electrode, freshly polished magnesium metal foil as counter and reference electrode, and 0.5 M $Mg(TFSI)_2$-LiTFSI/diglyme as the electrolyte, with the cutoffs at 1.5 V and 4.0 V (*vs* Mg/Mg^{2+}), respectively.

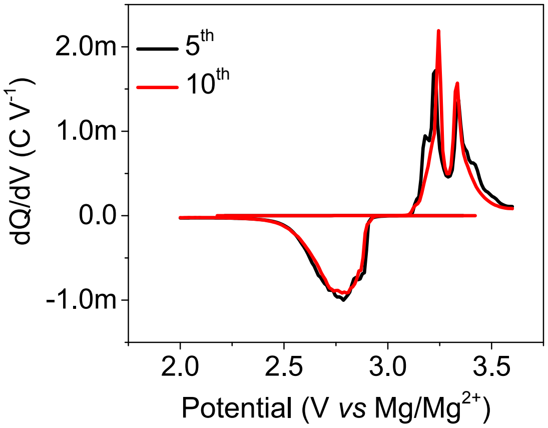

Figure S2. Representative differential capacity curves (the 5th and 10th cycles) for Mg-$LiMn_2O_4$ battery cell using 0.5 M $Mg(TFSI)_2$-LiTFSI/diglyme as electrolyte at the current rate of 0.2C with cutoffs at 2.0 V and 3.6 V, respectively.

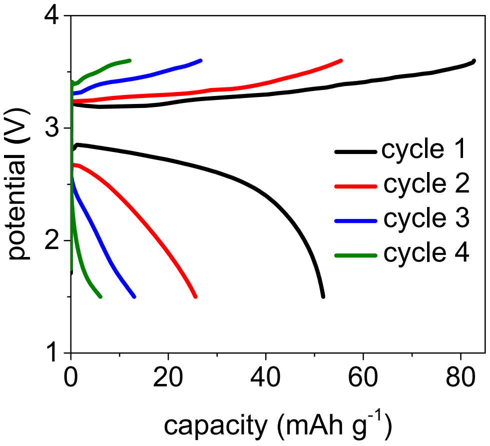

Figure S3. Galvanostatic cycling curves in the first four cycles of Mg-$LiCoO_2$ battery using 0.5 M $Mg(TFSI)_2$-LiTFSI/diglyme as the electrolyte at the current rate of 0.1C with cutoffs at 1.5 V and 3.6 V, respectively.

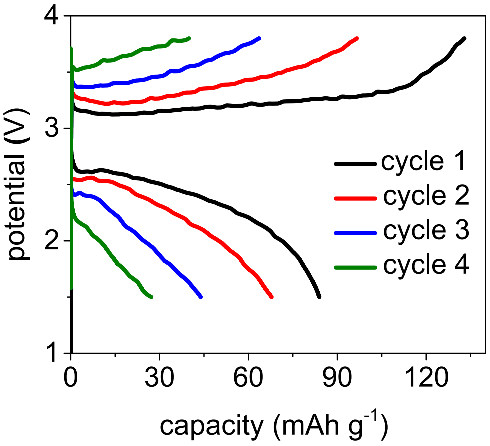

Figure S4. Galvanostatic cycling curves in the first four cycles of Mg-$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ battery using 0.5 M $Mg(TFSI)_2$-LiTFSI/diglyme as the electrolyte at the current rate of 0.1C with cutoffs at 1.5 V and 3.8 V, respectively.

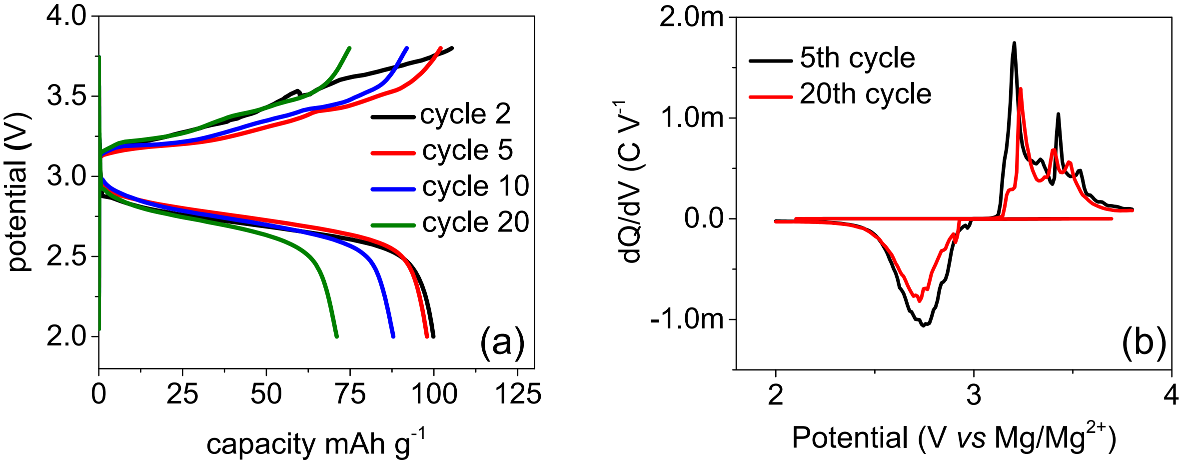

Figure S5. Cycling performance of Mg-$LiMn_2O_4$ battery using 0.25 M $Mg(CB_{11}H_{12})_2$-LiTFSI/tetraglyme as electrolyte at the current rate of 0.1 C with the cutoffs at 2.0 V and 3.8 V, respectively: (a) galvanostatic curves for representative cycles; (b) differential capacity curves at representative cycles

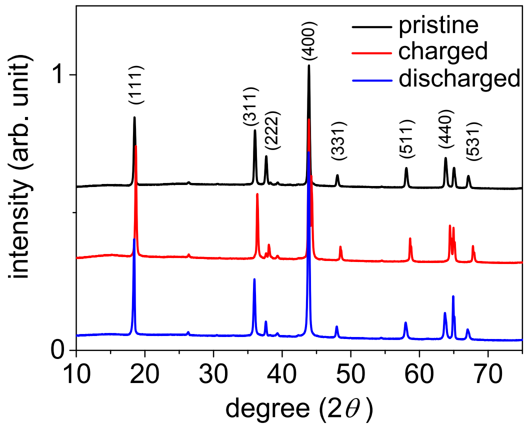

Figure S6. *Ex situ* XRD patterns for pristine, charged and discharged $LiMn_2O_4$ on carbon coated aluminum laminates from Mg-$LiMn_2O_4$ battery cell using 0.25 M $Mg(CB_{11}H_{12})_2$-LiTFSI/tetraglyme as the electrolyte

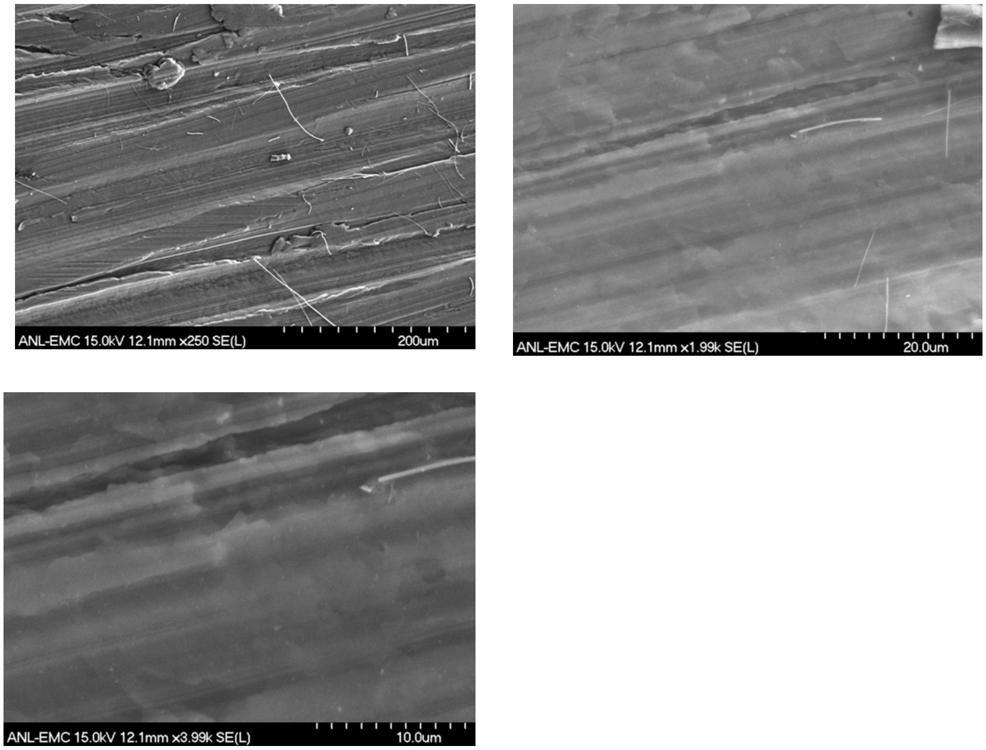

Figure S7. SEM images at different scale (200 μm, 20 μm, and 10 μm) of the magnesium anode from Mg-$LiMn_2O_4$ battery cell (cycled after 20 cycles) using 0.25 M $Mg(CB_{11}H_{12})_2$-LiTFSI/tetraglyme as the electrolyte

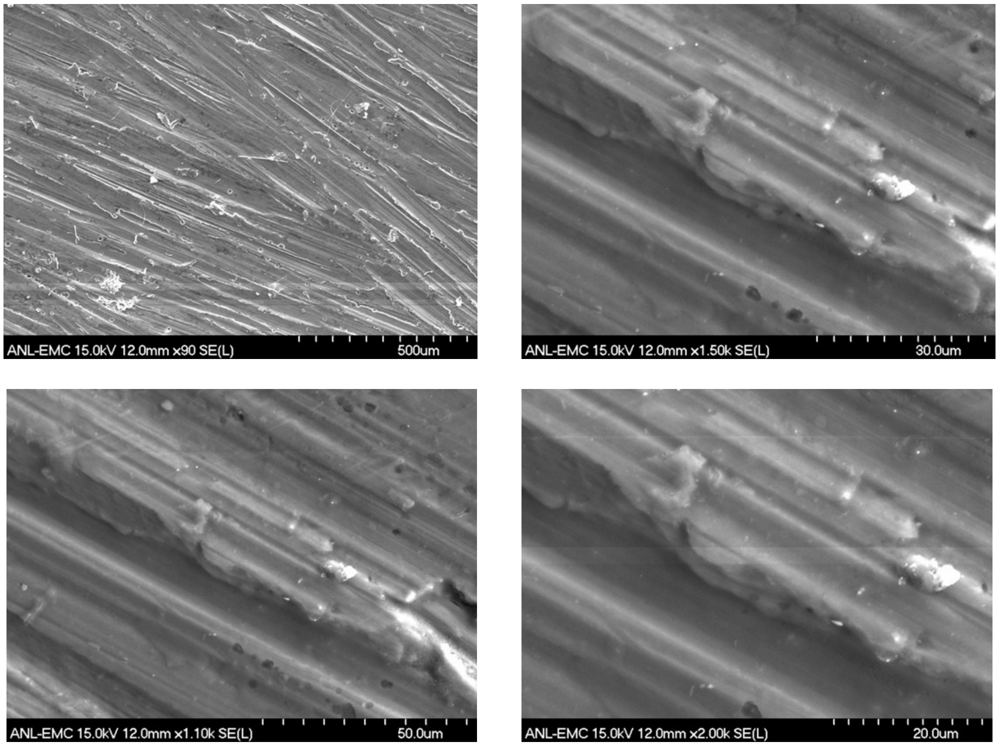

Figure S8. SEM images at different scale (200 μm, 50 μm, 30 μm, and 20 μm) of the magnesium anode from Mg-$LiMn_2O_4$ battery cell (cycled after 20 cycles) using 0.5 M $Mg(TFSI)_2$-LiTFSI/diglyme as electrolyte

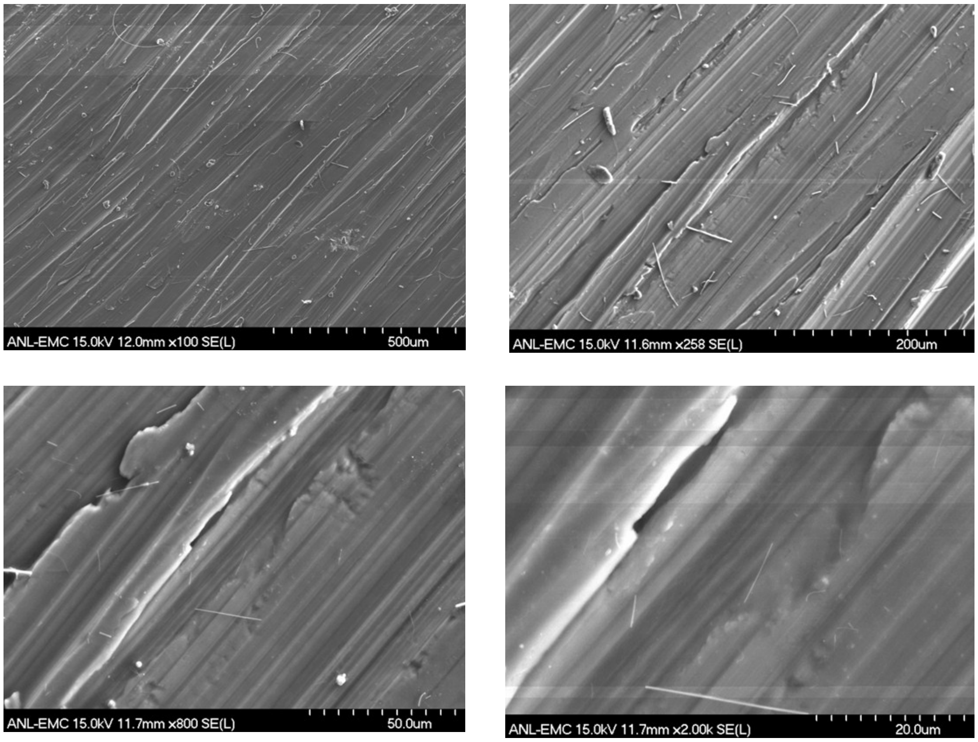

Figure S9. SEM images at different scale (500 μm, 200 μm, 50 μm, and 20 μm) of the magnesium anode from Mg-$LiCoO_2$ battery cell (cycled after 20 cycles) using 0.5 M $Mg(TFSI)_2$-LiTFSI/diglyme as electrolyte

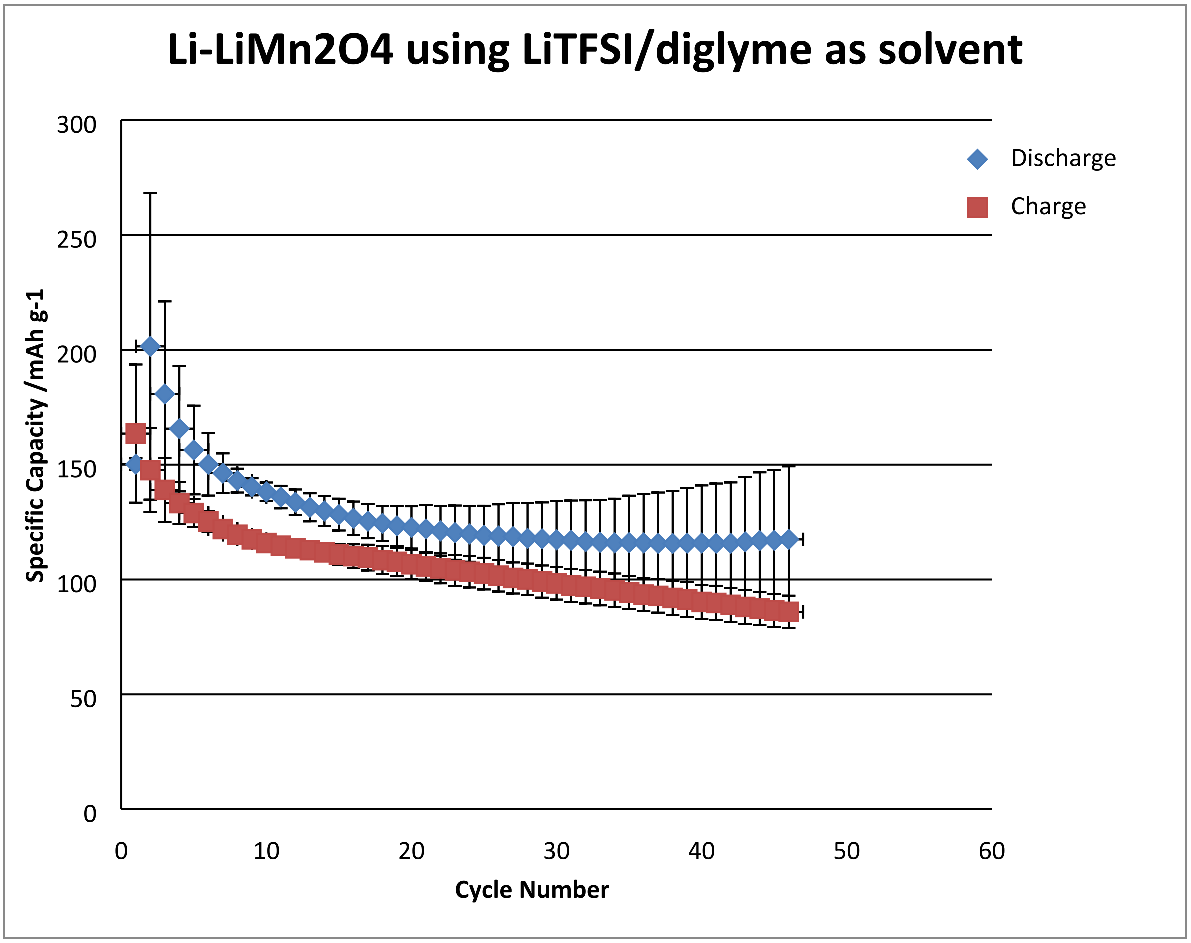

Figure S10. The cycling performance of three averaged Li-$LiMn_2O_4$ battery cells using 0.5 M LiTFSI/diglyme as electrolyte