

Supporting information

Stabilization of Lithium Anode with Ceramic-Rich Interlayer for All Solid-State Batteries

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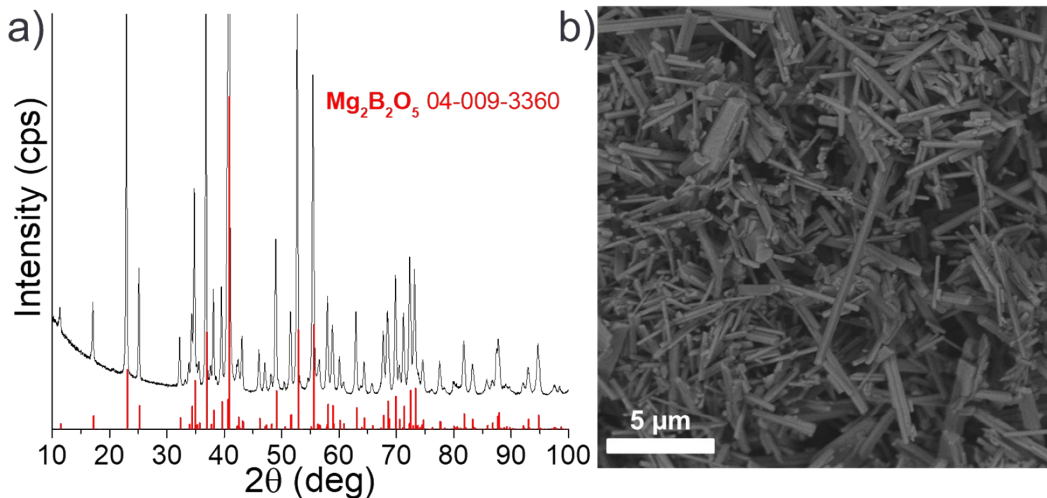


Figure S1. a) XRD pattern and b) SEM image of the $\text{Mg}_2\text{B}_2\text{O}_5$ powder. The corresponding JCPDS number is given and peaks position with their relative intensities marked with red rods.

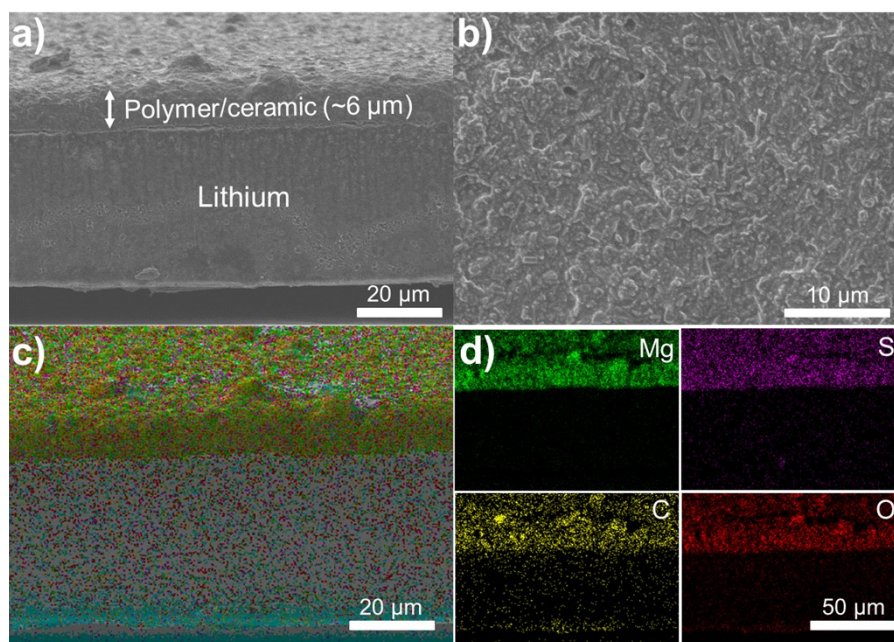


Figure S2. a) SEM cross-section and b) top views of an overcoating of 70% $\text{Mg}_2\text{B}_2\text{O}_5$ (~6 μm) on the surface of an aged LiAl and the c) corresponding elemental mapping of Mg (green), S (purple), C (yellow) and O (red).

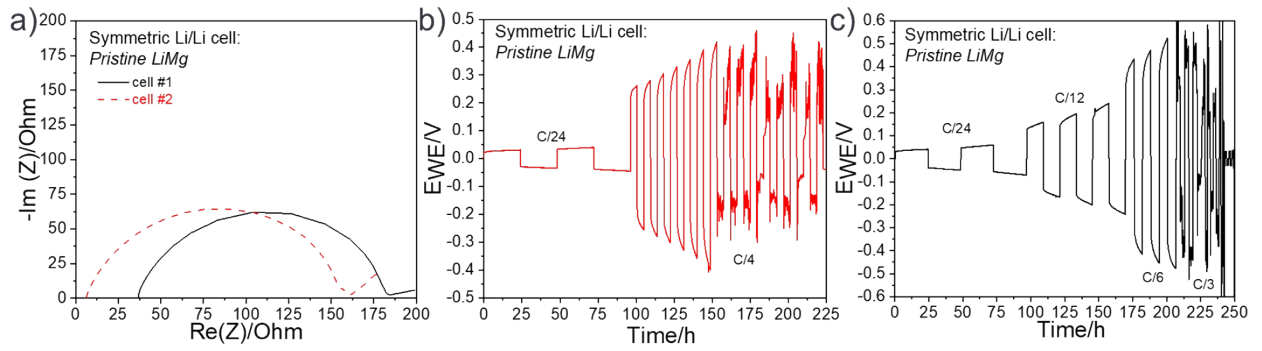


Figure S3. a) Nyquist plots, b) long cycling experiment at a C/4 rate and c) rate capability for symmetric Li/Li cell assembled with two pristine LiMg electrodes and a SPE. Electrochemical measurements were obtained at 50 °C.

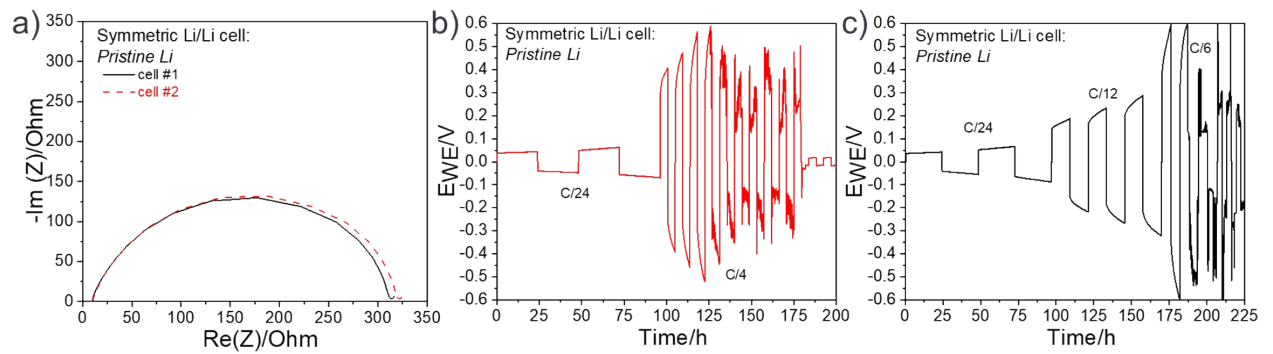


Figure S4. a) Nyquist plots, b) long cycling experiment at a C/4 rate and c) rate capability for symmetric Li/Li cell assembled with two pristine Li electrodes and a SPE. Electrochemical measurements were obtained at 50 °C.

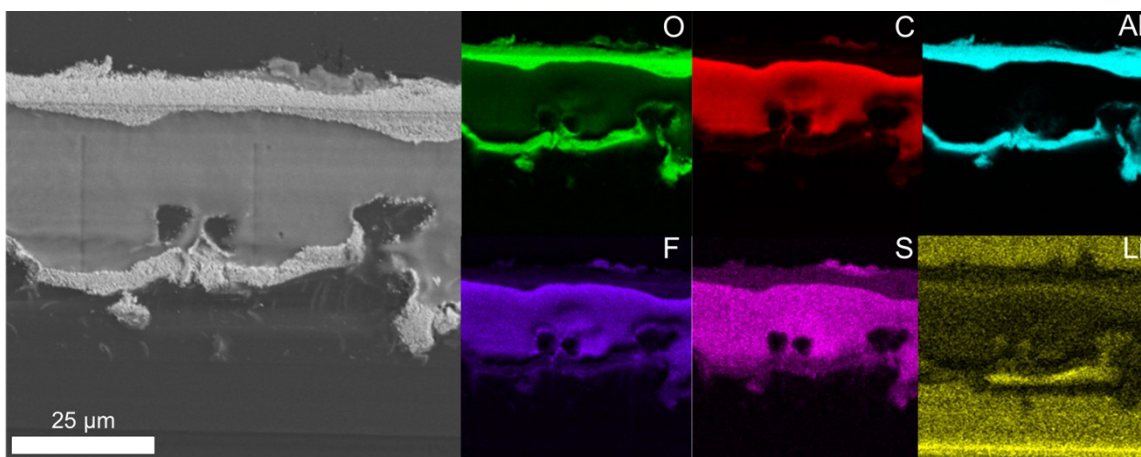


Figure S5. SEM cross-section view and corresponding elemental mapping of a LiAl/SPE/LiAl stack with a $\sim 4\text{-}\mu\text{m}$ thick $85\%\text{Al}_2\text{O}_3\text{-sph}$ ceramic layer on the surface of the lithium foils. The cell assembled with this stack was short-circuited and evident traces of dendrites growth are visible.

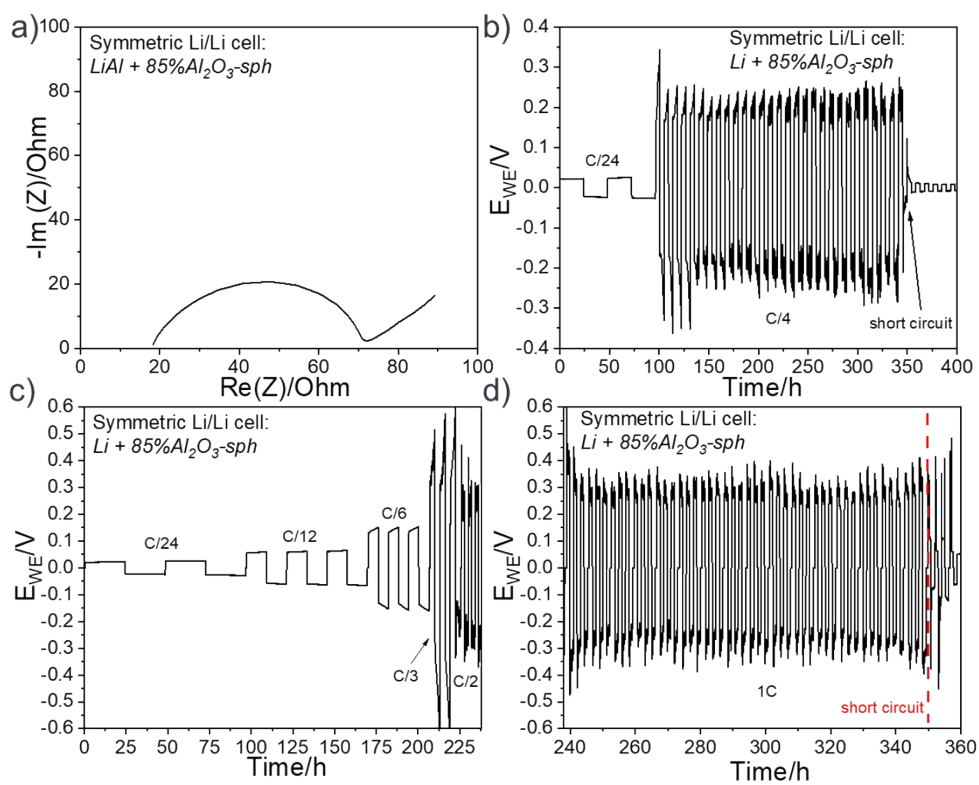


Figure S6. a) Nyquist plot and b) long-term stability experiment at a C/4 rate for a symmetric Li/Li cell assembled with a SPE and two Li electrodes modified with a $\sim 4\text{-}\mu\text{m}$ thick $85\%\text{Al}_2\text{O}_3\text{-sph}$ ceramic layer. c) Rate capability for a symmetric Li/Li cell assembled with a SPE and two Li electrodes modified with a $\sim 4\text{-}\mu\text{m}$ thick $85\%\text{Al}_2\text{O}_3\text{-sph}$ ceramic layer and d) the subsequent long-term stability experiment at a 1C rate. Electrochemical measurements were obtained at $50\text{ }^\circ\text{C}$.

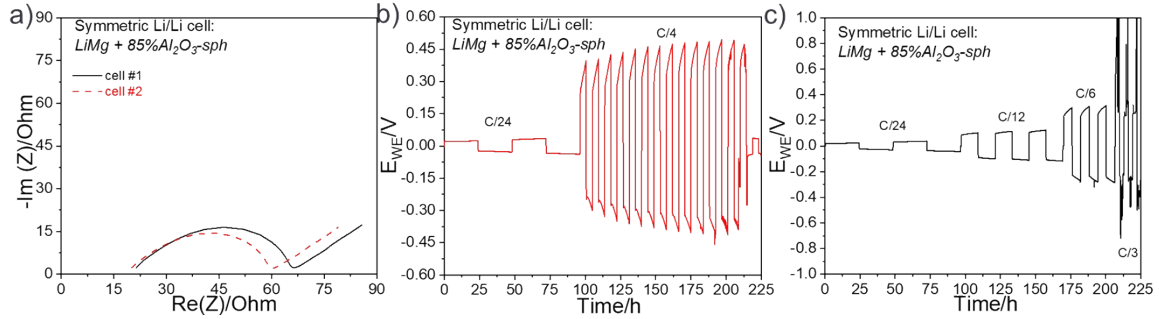


Figure S7. a) Nyquist plots, b) long cycling experiment at a C/4 rate and c) rate capability for symmetric Li/Li cells assembled with a SPE and two LiMg electrodes modified with a $\sim 4\text{-}\mu\text{m}$ thick $85\%\text{Al}_2\text{O}_3\text{-sph}$ ceramic layer. Electrochemical measurements were obtained at $50\text{ }^\circ\text{C}$.

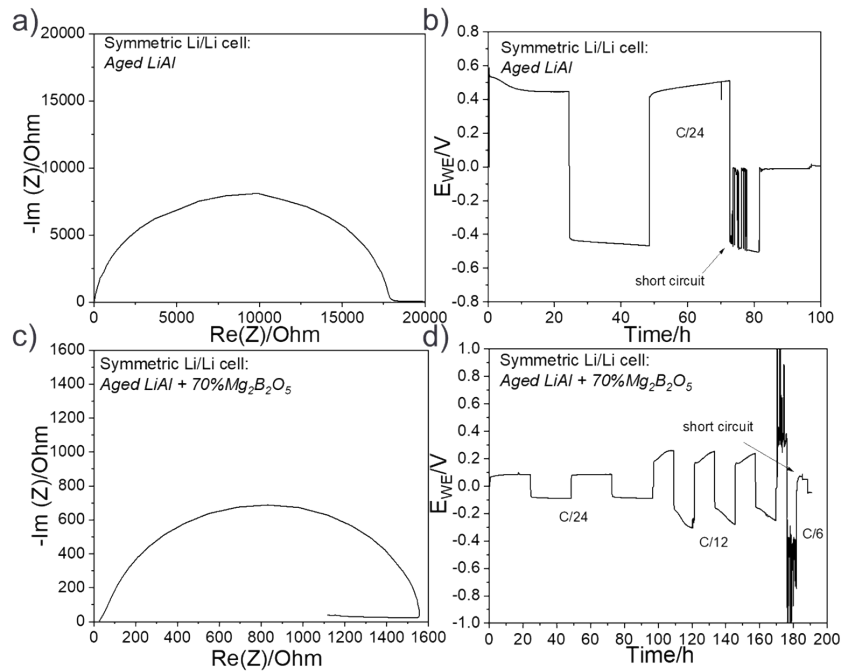


Figure S8. a,c) Nyquist plots and b,d) rate capability for symmetric Li/Li cells assembled with a,b) two aged LiAl electrodes and a SPE and c,d) two aged LiAl electrodes modified with a $\sim 6\text{-}\mu\text{m}$ thick $70\%\text{Mg}_2\text{B}_2\text{O}_5$ ceramic layer and a SPE. Electrochemical measurements were obtained at $50\text{ }^\circ\text{C}$.

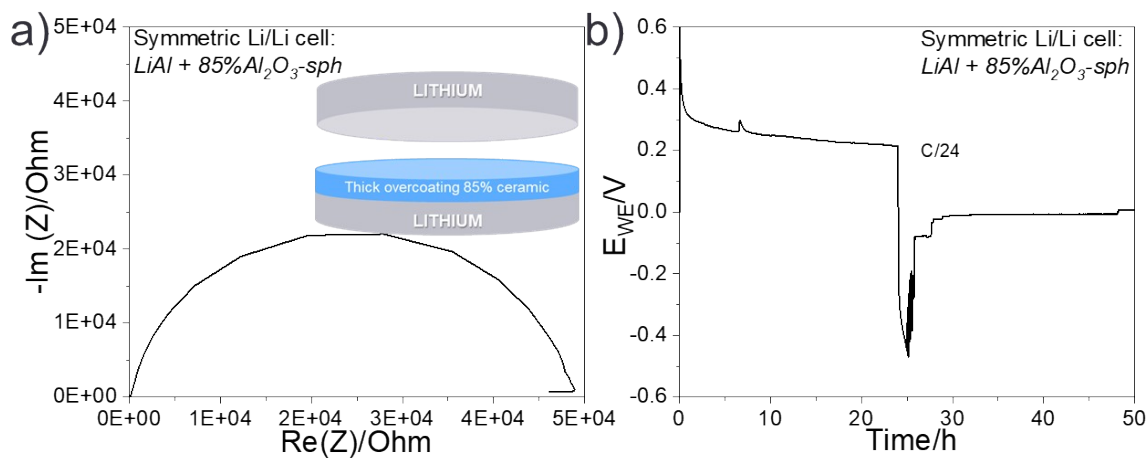


Figure S9. a) Nyquist plot with a schematic representation of the cell assembly and b) first stripping/plating cycle at a C/24 rate for a symmetric Li/Li cell assembled with a pristine LiAl electrode and a LiAl electrode modified with a thick $85\%\text{Al}_2\text{O}_3\text{-sph}$ ceramic layer ($\sim 15\text{ }\mu\text{m}$). Electrochemical measurements were obtained at $50\text{ }^\circ\text{C}$.

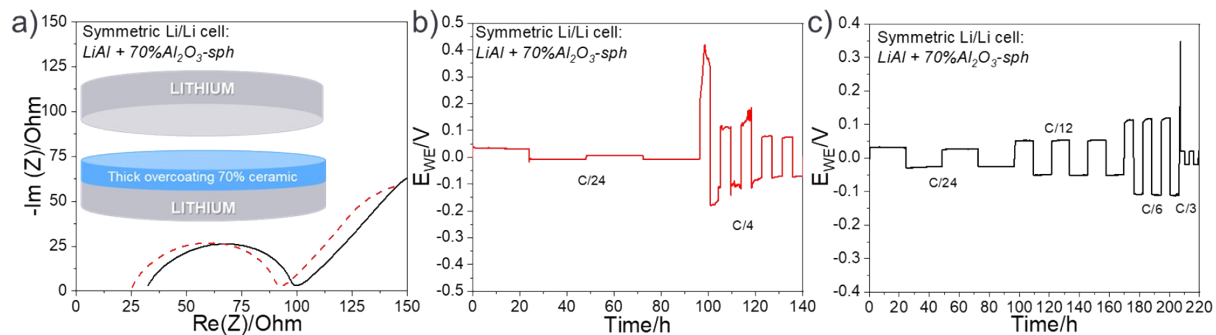


Figure S10. a) Nyquist plots with a schematic representation of the cell assembly, b) long cycling experiment at a C/4 rate and c) rate capability for symmetric Li/Li cells assembled with a pristine LiAl electrode and a LiAl electrode modified with a thick

70%Al₂O₃-sph ceramic layer (~15-20 μm). Electrochemical measurements were obtained at 50 °C.

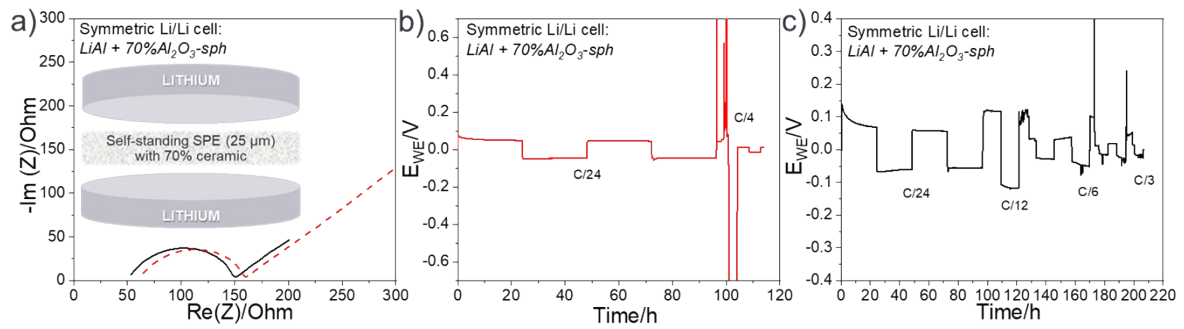


Figure S11. a) Nyquist plots with a schematic representation of the cell assembly, b) long cycling experiment at a C/4 rate and c) rate capability for symmetric Li/Li cells assembled with two pristine LiAl electrodes and a SPE (25 μm) made with 70% of Al₂O₃-sph ceramic. Electrochemical measurements were obtained at 50 °C.

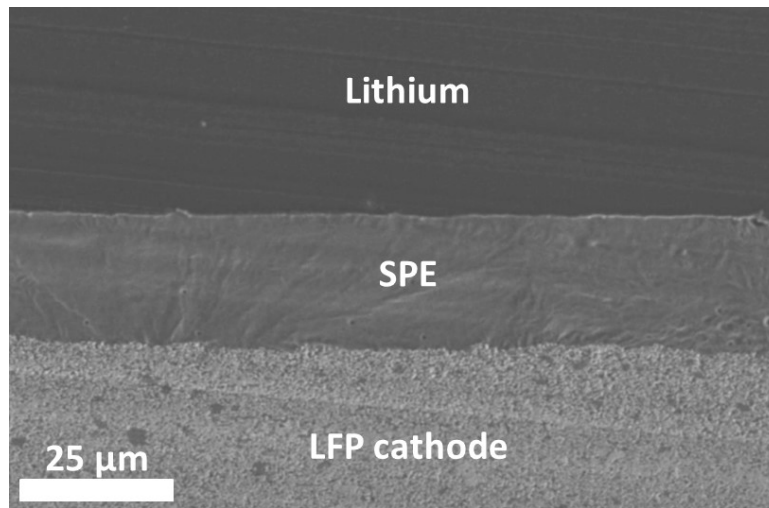


Figure S12. SEM image of the cross-sectional view of LFP/SPE/Li stacking.

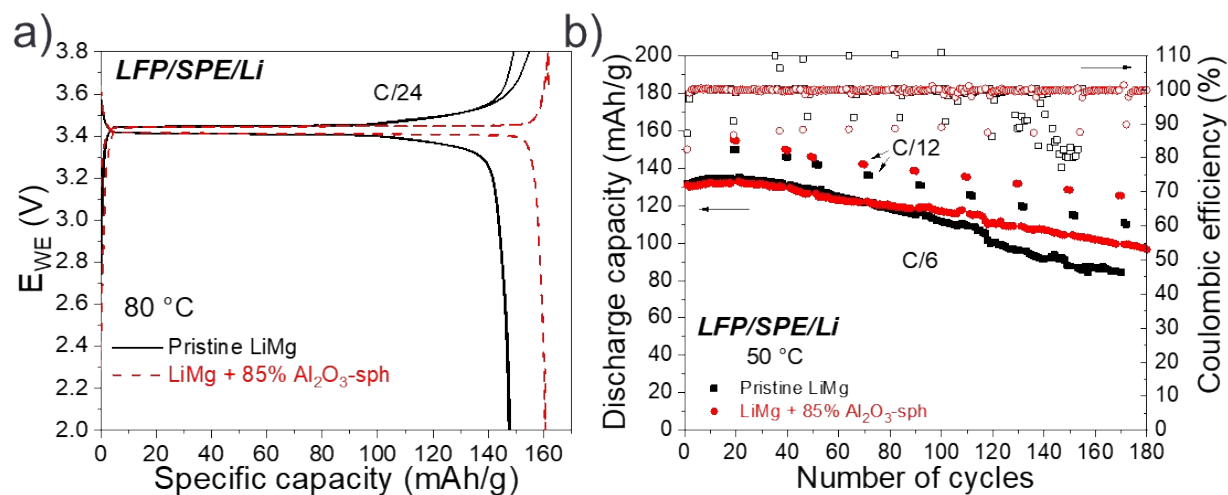


Figure S13. a) Charge/discharge profiles obtained at $80\text{ }^\circ\text{C}$ for the two first cycles at C/24 and b) long cycling experiments conducted at $50\text{ }^\circ\text{C}$ with a constant charge/discharge current of C/6 between 2.0 and 3.8 V vs. Li/Li⁺ for LFP/SPE/Li batteries made with a pristine LiMg electrode and a modified LiMg electrode with a $\sim 4\text{-}\mu\text{m}$ thick $85\%\text{Al}_2\text{O}_3\text{-sph}$ ceramic layer.