Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Target composition	Li	Mg	Al	O
$Li_{0.05}Mg_{0.9}Al_{2.05}O_4$ As Dep.	0.49% (0.7%)	9.5% (12.8%)	27.5% (29%)	62.6% (57%)
$Li_{0.15}Mg_{0.7}Al_{2.15}O_4$ As Dep.	1.5% (2.1%)	6.2% (10%)	32% (30.7%)	60% (57%)
$Li_{0.25}Mg_{0.5}Al_{2.25}O_4$ As Dep.	1.92% (3.6%)	5.3% (7.1%)	32.2% (32%)	61% (57%)

Table 1: ERD data of as deposited films of $Li_xMg_{1-2x}Al_{2+x}O_4$. Compared to the data shown in the manuscript a slightly higher lithium and magnesium content is shown here. The slightly higher Aluminum content is present even in the as deposited layers.

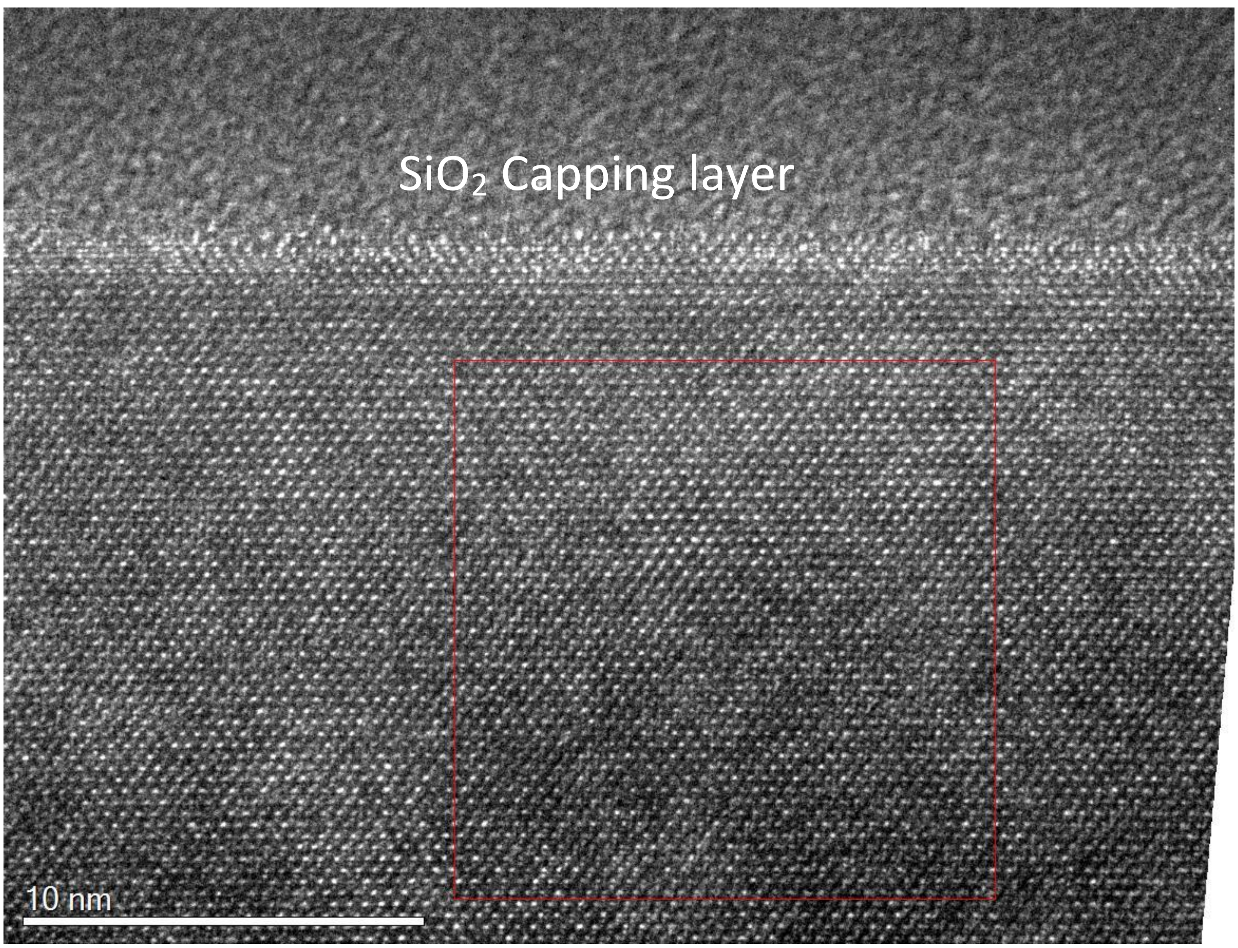

Figure1: Additional TEM data of the $Li_{0.25}Mg_{0.5}Al_{2.25}O_4$ layer showing the position where the fast Fourier transform was performed shown in ESI figure 2. Besides the $Li_{0.25}Mg_{0.5}Al_{2.25}O_4$ also the SiO_2 capping layer is visible.

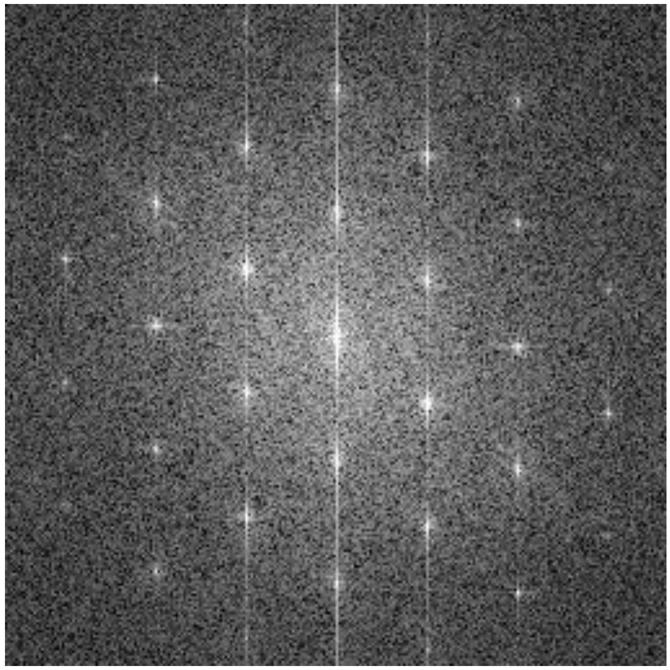

Figure 2: Shows the result of the fast Fourier transform. The found pattern allows extraction of a lattice parameter of 0.8 nm for a cubic lattice (spinel).

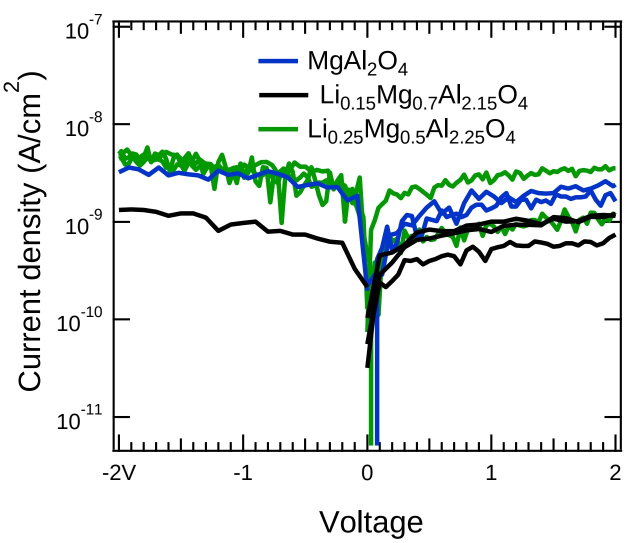

Figure 3: Shows the I-V characteristics of amorphous $Li_xMg_{1-2x}Al_{2+x}O_4$ layers. Leakage current density remains low throughout the entire voltage range probed here. Current density is approximately one order of magnitude lower than the current measured for crystalline layers.

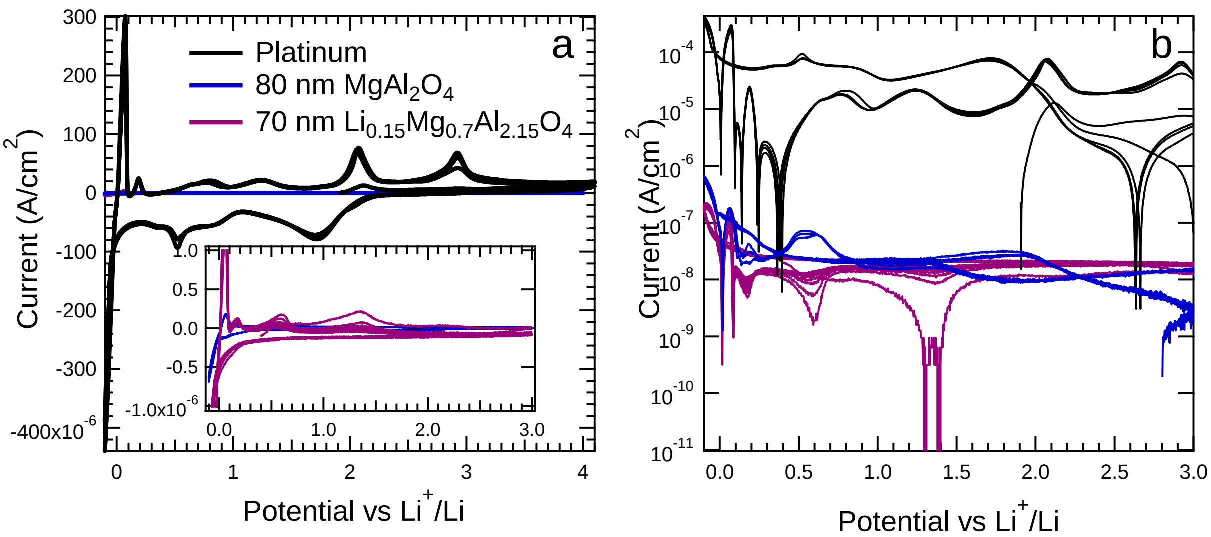

Figure 4: Shows cyclic voltammetry experiments on amorphous layers of $MgAl_2O_4$ and $Li_{0.15}Mg_{0.7}Al_{2.15}O_4$. **a.** Plating and stripping peaks are also visible in the unannealed sample. The inset shows only the $MgAl_2O_4$ and $Li_{0.15}Mg_{0.7}Al_{2.15}O_4$ the platinum dealloying peaks can be seen at 0.2 V. **b.** Shows the graph of a on Log scale. At 0.2 and 0.6 V clear dealloying peaks can be seen again indicating Li transport through the layer.

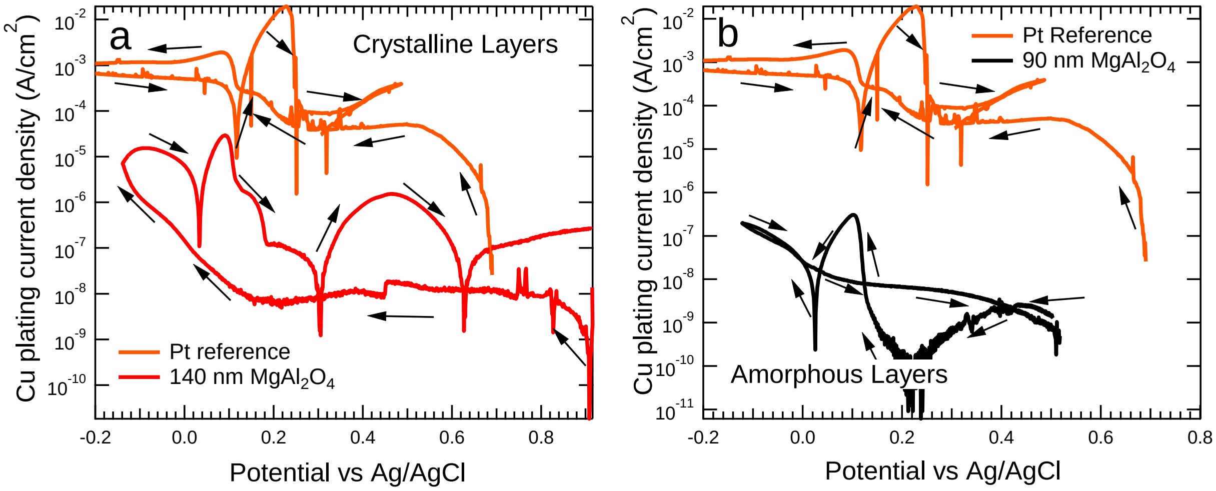

Figure 5 ***a****.Result of Copper plating experiments for annealed samples. The current is roughly a factor 100 lower than the platinum reference sample.* ***b*** *Resuls of plating experiment for unannealed sample. The current is a factor 10000 lower than the Pt reference*

Copper plating and stripping cyclic voltammetry experiments were conducted using a Ag/AgCl reference electrode and a gold wire as counter electrode at scan rate of 10mV/s. An aqueous solution of 10 mM of $CuSO_4$ was used during the experiment. The results of these measurements are depicted in figure 3. On lowering the potential, a copper plating peak is seen, on increasing the potential above 0 V copper stripping initiates. The plating current for crystalline $MgAl_2O_4$ layers is on average a factor of one hundred lower than the bare platinum reference. In the amorphois $MgAl_2O_4$ layers, the plating current is over 4 orders of magnitude lower than the platinum reference. The current value measured here roughly corresponds to the electronic leakage determined through both the amorphous and crystalline material.

A large IR drop is present for the plating and stripping experiments on the $MgAl_2O_4$ coated platinum substrates. The IR drops shifts the Cu plating peaks away from the peaks determined in the platinum reference. The shift is over 0.3 V, even at these low current densities. This again indicates the good insulating properties of the $MgAl_2O_4$ layers. From these experiments we cannot exclude some contribution of grain boundaries and defects, however this contribution is less than the electronic leakage.

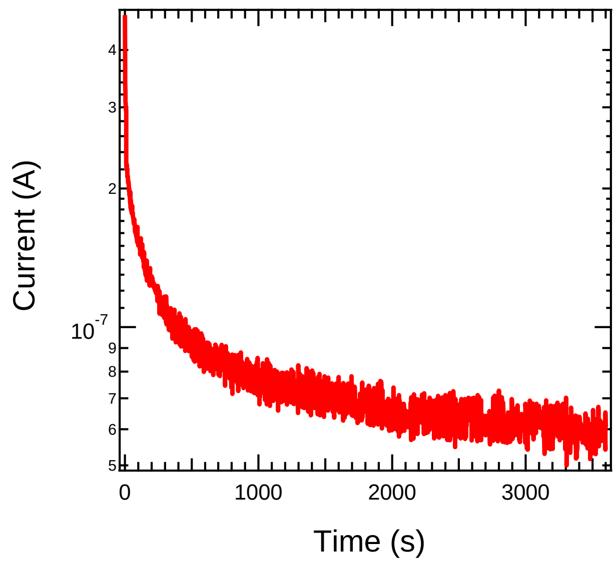

Figure 6 Typical relaxation behavior of the current after application of a potential step. Charge under this curve is calculated by integration.

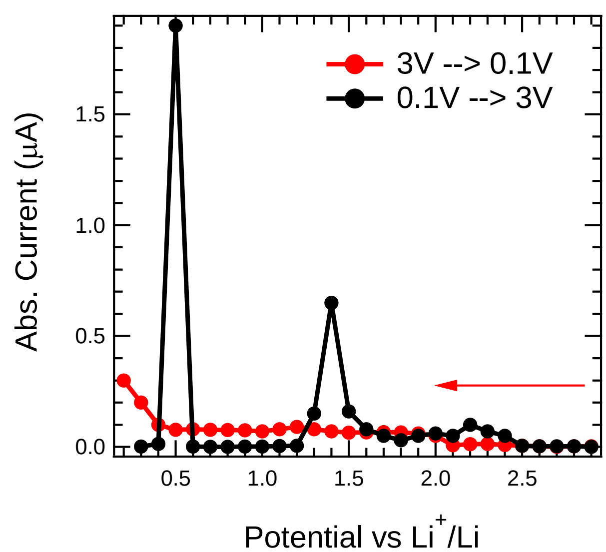

Figure 7 Evolution of the resulting current (at the end of a typical relaxation curve shown in ESI figure 6). It can be seen that the change of the resulting current cannot account for the 3orders of magnitude in the resistance. The distinct peaks seen when increasing the potential correspond to distinct platinum-lithium dealloying peaks

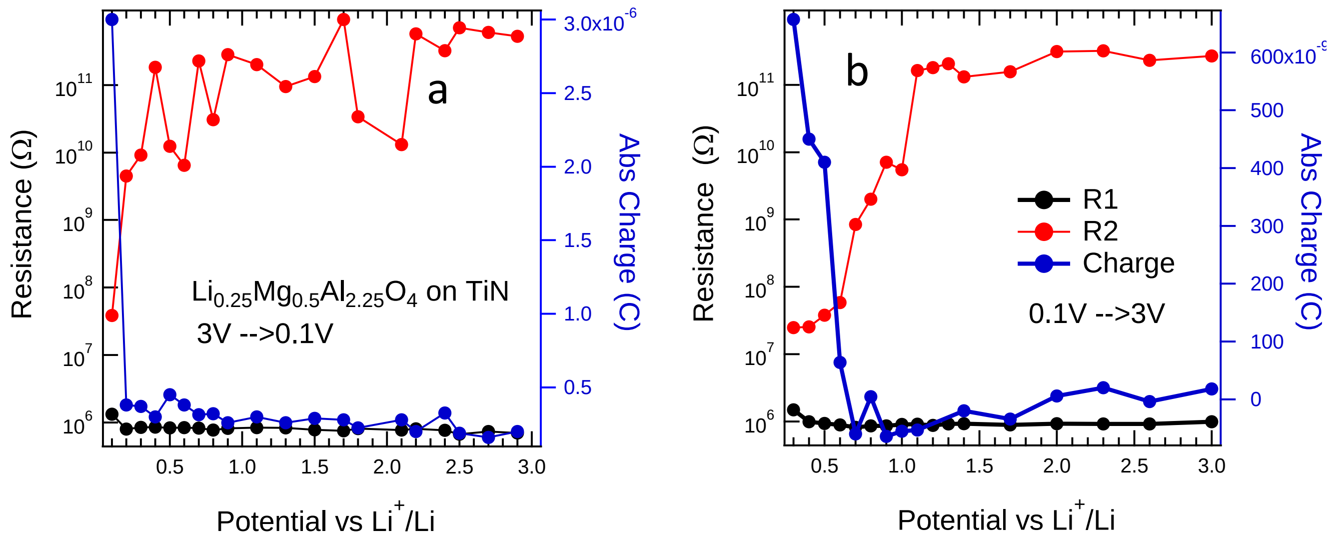

Figure 8 Impedance analysis for amorphous 100 nm $Li_{0.25}Mg_{0.5}Al_{2.25}O_4$ layer on TiN substrate. ***a*** *shows the evolution of R_1, R_2 and the charge upon lowering the potential.* ***b*** *shows the same but on increasing the potential. Behavior similar to the one on Pt current collector is seen. However the typical hysteresisis clearly reduced compared to the layers on Pt.*

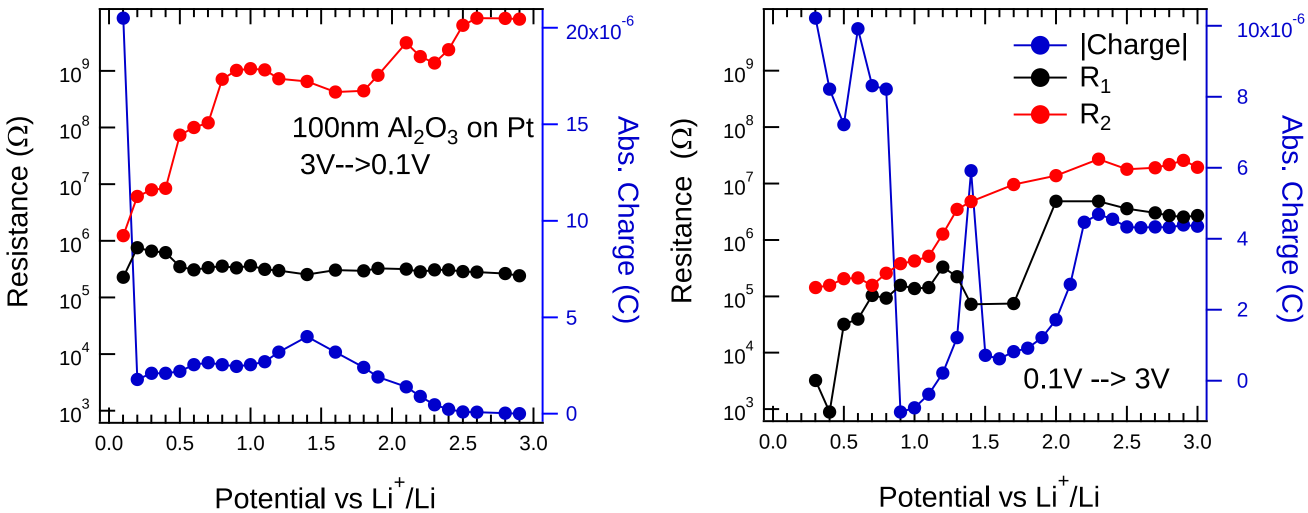

Figure 9 Impedance analysis of 100 nm Al_2O_3 on Pt. A reduction in resistance with potential is seen. The behavior closely resembles the $Li_xMg_{1-2x}Al_{2+x}O_4$ layers. However, the original resistance values are not obtained on increasing the potential. The charge in the up trace closely resembles the cyclic voltammorgram of Pt in figure 4 in the regular text.