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D3.2	**ALD coatings on cathodes**	WP3	IEE SAS	Report	P	Experimental results	M9

D 3.2 ALD layers on cathodes

Commercial cathodes (NEI Corporation) based on layered oxides $LiFePO_4$ (LFP) and $LiNiMnCoO_2$ (NMC811) are used as comparison materials for Li-ion battery cathodes. Both types of cathodes are used in today's Li-ion batteries due to their affordability and long-term cyclability (LFP) and high specific energy capacity (NMC). Within the project, we focused on improving the properties, especially on improving the capacity of the cathodes at higher charging rates (C=1, charging 0-100% in 1 hour, C=2, charging 0-100% in 30 min).

Growth of Al_2O_3 thin films using ALD

Very thin Al_2O_3 layers were deposited on LFP and NMC cathodes using atomic layer deposition (ALD). For ALD growth, the organometallic precursor trimethyl aluminum (TMA, $(CH_3)_3Al$) and water vapor, H2O, were used. Before starting ALD growth, the LFP and NMC cathode materials were placed in the ALD deposition chamber and held at 100 °C for 1 hour. For growth on LFP and NMC cathodes, we used a growth mode adapted for porous materials. Growth for porous materials consisted of prolonging the dosing of precursors and water vapor. We assume that due to the high pressure of TMA and H_2O, a significant part of the electrodes was covered during the process. The deposited Al_2O_3 was amorphous and continuous without pinhole defects.
Fig. 1 shows the dependence of Al_2O_3 layer thickness on the number of cycles for LFP and NMC electrodes. The layer thickness was determined by ellipsometry measurements on Si wafers placed together with the electrodes on a sample holder in the ALD chamber. The ALD deposition was set at 100 °C, where the growth is stable and the temperature is high enough to avoid condensation of precursors. ALD showed good saturation at pulse and purge times of 0.5s–40s–0.5s–80s.

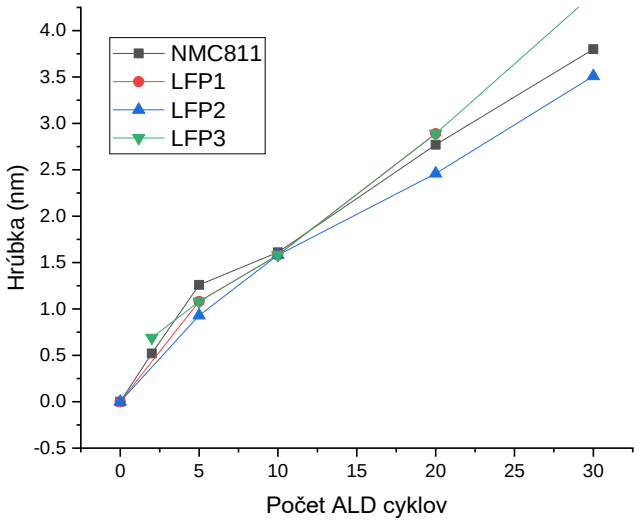


Fig. 1. Dependence of the thickness of Al_2O_3 layers on LFP and NMC electrodes on the number of ALD cycles.

The ALD growth per cycle (GPC) was 0.12 nm. Since determining the thickness of the Al2O3 layers directly on the porous electrodes was not possible, for simplicity we continued working with the thickness determined on these Si substrates.

Protective Al_2O_3 layers on $LiFePO_4$ cathode.

The surface and cross-sectional morphology of LFP cathodes was examined using a scanning electron microscope (SEM). The cross-section of the electrodes was made using a focused Ga+ ion beam with an accelerating voltage of 10 kV. Fig. 2 shows the surface of the LFP cathode before deposition (Fig. 2a) and after deposition of 5 ALD cycles of the Al_2O_3 layer (Fig. 2b). A comparison of Figs. 2a and 2b shows that the deposition of the Al_2O_3 layer did not change the morphology of the cathode. Figs. 2c and 2d show the cross-section of the original LFP cathode (Fig. 2c) and the cross-section of the LFP cathode with 5 ALD cycles of Al_2O_3. Again, it is shown that the deposition of the Al_2O_3 layer did not change the morphology of the cathode cross-section.

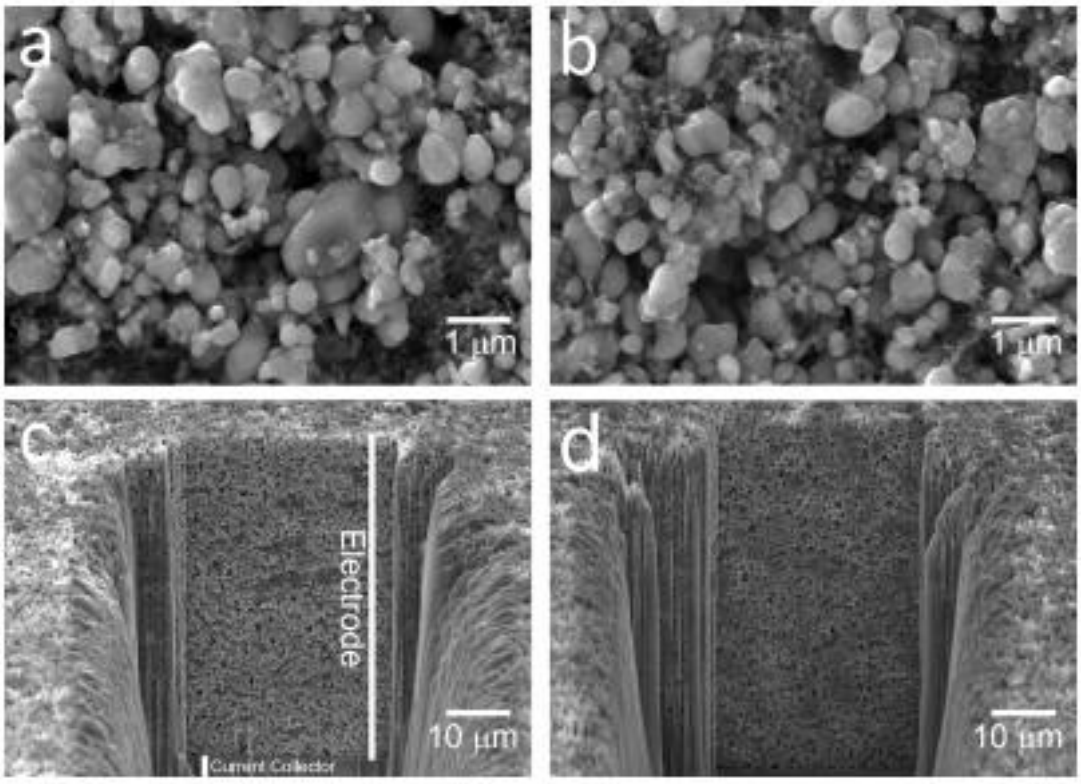


Fig. 2. Surface of the original LFP cathode (a) and the cathode with 5 ALD cycles of Al_2O_3.

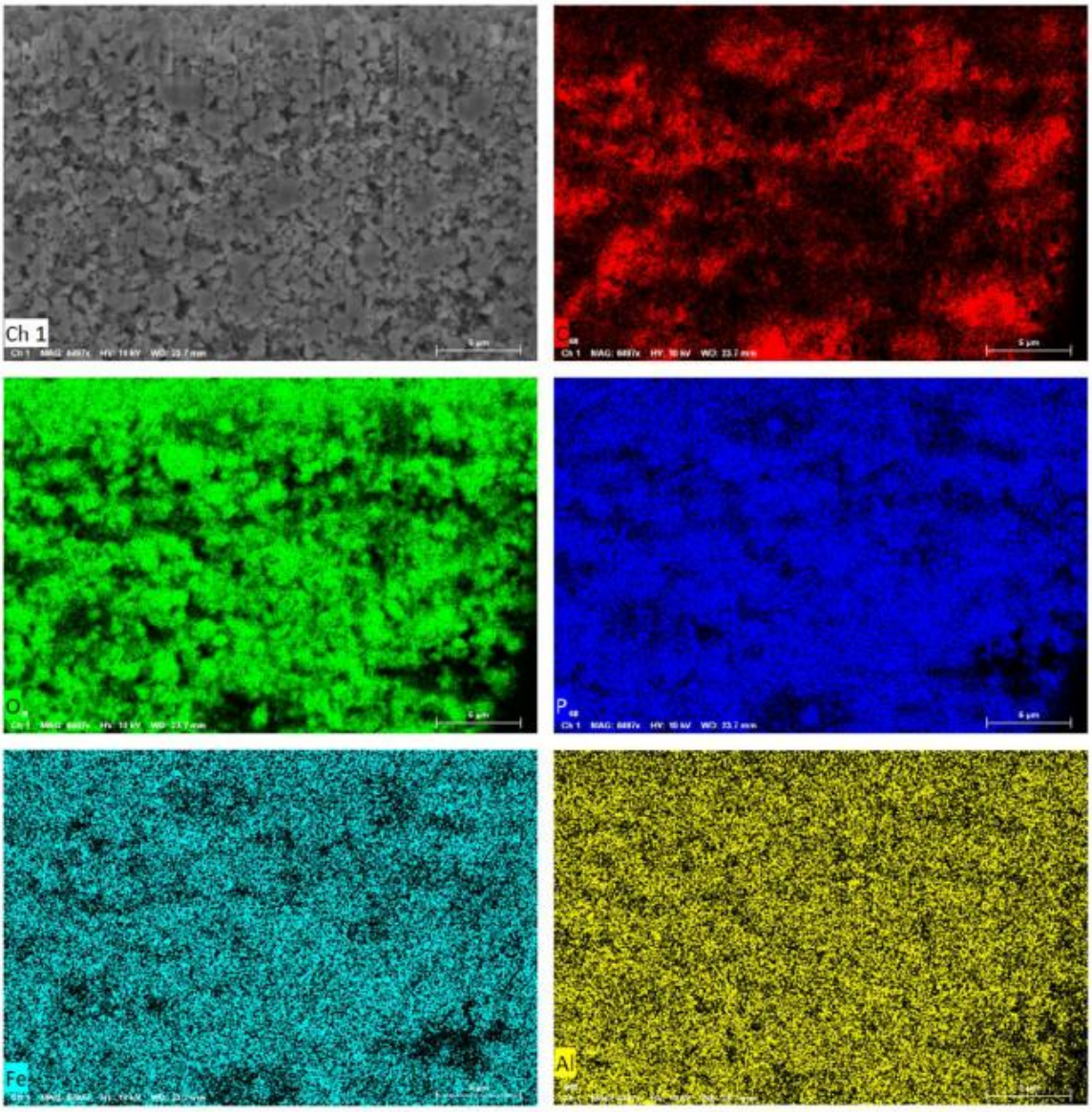


Fig. 3. Distribution of elements C, O, P, Fe and Al across the cross-section of a $LiFePO_4$ cathode.

Fig. 3 shows the distribution of the elements C, O, P, Fe and Al along the cross-section of the LiFePO4 cathode. From the distribution of the elements along the cross-section, it can be seen that all elements are homogeneously distributed along the cross-section, including the distribution of Al. The representation comes from the deposition of a thin layer of Al2O3 using ALD. This means that the Al2O3 has penetrated the entire layer due to the porous nature of the LFP cathode.

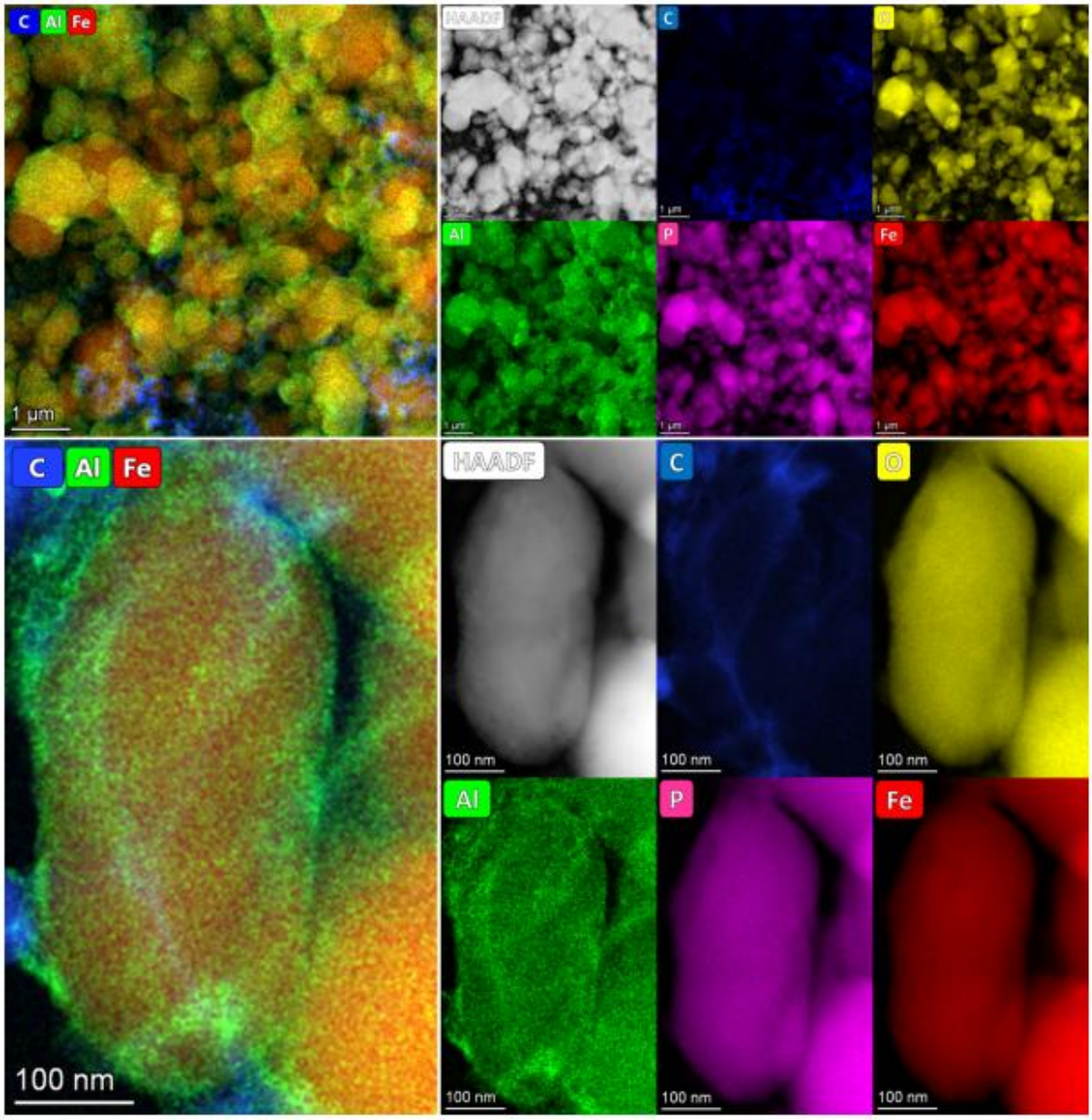


Fig. 4. High-angle angular dark-field scanning transmission electron microscopy (HAADF-STEM) of a $LiFePO_4$ electrode covered with a thin layer of Al_2O_3. The upper part shows a map of the elements present C, O, Al, P, Fe. The lower part shows a single LFP particle obtained by mechanical preparation - scraping.

High-angle angular dark-field scanning transmission electron microscopy (HAADF-STEM) of an LFP cathode with a thin Al2O3 layer deposited by ALD technology is shown in Fig. 4. The elemental distribution of the transmission electron microscopy image shows the presence of Al_2O_3 mainly at the boundaries of the $LiFePO_4$ particle, thus demonstrating the role of the protective layer also in the bulk of the porous LFP electrode.

Electrochemical properties of $LiFePO_4$ cathodes covered with a protective Al_2O_3 layer.

The electrochemical properties of LiFePO4 cathodes covered with a protective Al_2O_3 layer were first realized in the so-called half cell configuration, i.e. when the properties of the LFP cathode were measured against a Li+ anode using the PAT-cell test kits from EL-CELL GmbH. The cathodes were covered with 5 ALD cycles of Al_2O_3. The LFP properties of the Al_2O_3-coated cathodes were always compared with the original cathode without a protective layer.

The cathode formation was performed by measuring the current-voltage dependences (CV measurement) at a rate of 0.1 mV/s in the range of 2.4–4.1 V, Fig. 5a, b. Comparison of the CV characteristics of the uncoated (pristine) and coated $LiFePO_4$ cathodes with 5 ALD cycles shows oxidation-reduction maxima at the indicated voltages. The CV characteristics indicate a well-defined and stable redox reaction. The oxidation-reduction maxima are narrower for the cathode coated with the Al_2O_3 layer, indicating a positive effect of the coating.

Galvanostatic charge/discharge measurements at different rates of the pristine and Al_2O_3 coated $LiFePO_4$ cathode were performed in the range of 2.5–4.1 V vs. Li/Li+, Fig. 5c. The following charge/discharge rates C were used: 0.2, 0.5, 1, 2. A charge/discharge rate of 1C means charging/discharging the battery in 1 hour.

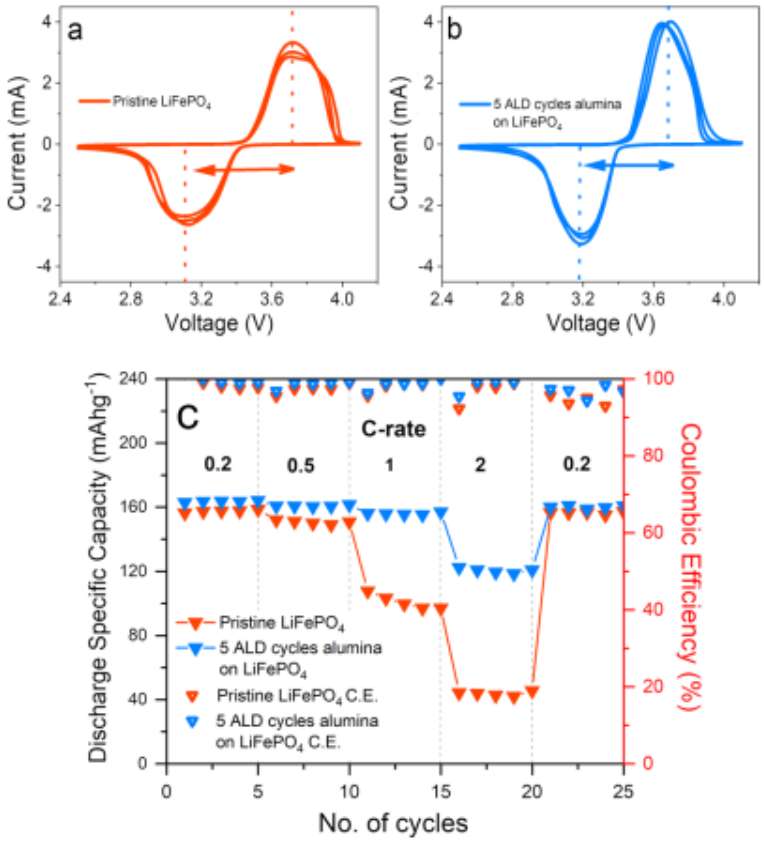


Fig. 5. Electrochemical measurements of $LiFePO_4$ cathode uncoated (pristine) and coated with 5 ALD cycles of Al_2O_3 in a configuration with a Li anode (half-cell configuration).

For low charge/discharge rates C=0.2, the $LiFePO_4$ capacity reaches 160 mAh/g, close to the theoretical capacity as stated by the manufacturer (170 mAh/g). Fig. 5 shows that at higher charge/discharge rates C=1 and C=2, the LiFePO4 cathode reaches up to 3 times higher capacity. This value indicates the positive effect of covering the LiFePO4 cathode with an ultra-thin Al_2O_3 layer using ALD.

The electrochemical properties of $LiFePO_4$ cathodes covered with ALD Al_2O_3 layers were also measured in the configuration with a graphite anode, the so-called full cell-configuration, Fig. 6. Similar to the configuration with a Li/Li+ anode, CV measurements showed the corresponding redox maxima. The cathode covered with 5 ALD cycles of Al_2O_3, (Fig. 6b) is characterized by a narrower maximum and a higher current value in this maximum. Again, we can state that the CV characteristics indicate a well-defined and stable redox reaction. Oxidation-reduction characteristics thus indicate a positive effect of Al_2O_3 coverage.

For galvanostatic determination of the capacity at different charging and discharging rates of the original and Al_2O_3 coated $LiFePO_4$ cathode, measurements were performed in the range of 2.5 – 4.1V, Fig. 6c. The following charging/discharging rates C were used: 0.2, 0.5, 1, 2. For low charging/discharging values C=0.2, the capacity of $LiFePO_4$ in the configuration with a graphite anode reaches a value of approximately 120 mAh/g. Fig. 6c

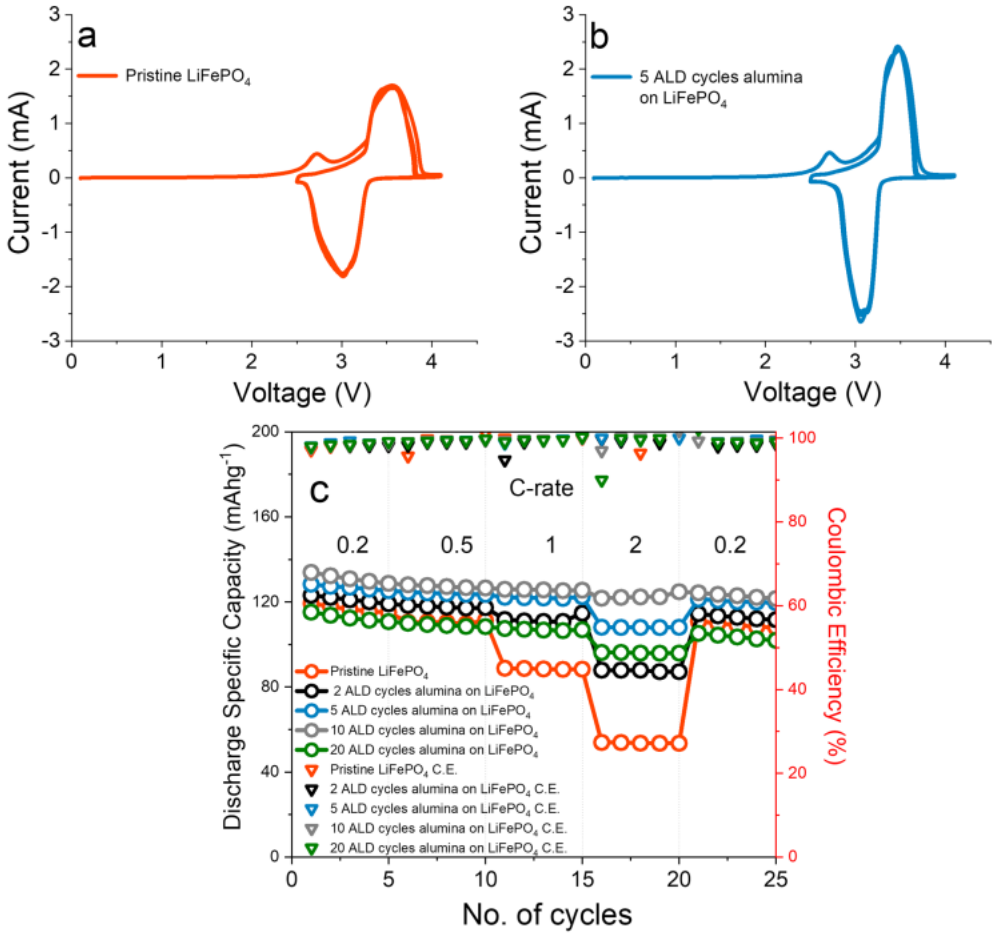


Fig. 6. Electrochemical measurements of a $LiFePO_4$ cathode uncoated (pristine) and coated with 5 ALD cycles of Al_2O_3 in a configuration with a graphite anode (full-cell configuration).

shows that while the capacity of the uncoated cathode at higher charge/discharge rates decreased quite significantly, at higher charge/discharge rates C=1 and C=2 the capacity of the $LiFePO_4$ cathode covered with 10 ALD cycles of Al_2O_3 practically did not decrease at all. This phenomenon again points to the positive effect of covering the LiFePO4 cathode with an ultra-thin Al_2O_3 layer using ALD.

Next, we investigated the long-term stability of the $LiFePO_4$ cathode at charge/discharge rates C=1, Fig. 7. All $LiFePO_4$ cathodes covered with Al_2O_3 are characterized by higher capacity values compared to the uncoated electrode. Cathodes covered with 5 and 10 ALD cycles have the highest capacity value and also excellent long-term stability.

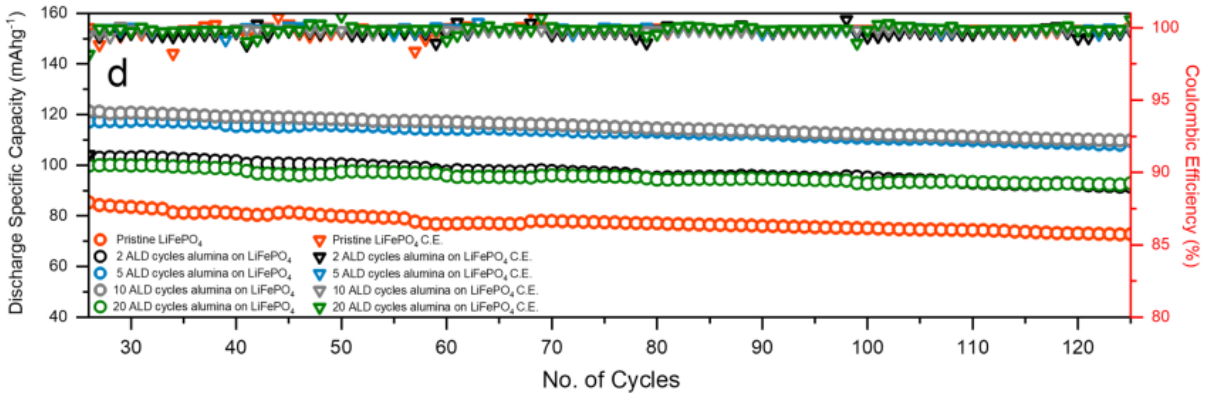


Fig. 7. Long-term stability of $LiFePO_4$ cathodes at a charge/discharge rate of C=1.

Protective Al_2O_3 layers on $LiNiMnCoO_2$ cathode (NMC811)

The protective Al_2O_3 layers were prepared on $LiNiMnCoO_2$ cathode (NMC811) under the same conditions as on LFP cathode. Fig. 8 shows the dependence of specific capacity at different discharge rates depending on the number of charge/discharge cycles.

A significant effect is the increase in capacity of Al_2O_3 coated layers at higher charge values ($C \geq 1$) compared to the uncoated cathode. Cathodes covered with layers of 5-10 ALD cycles have the best properties and we can therefore conclude that the thickness of 5-10 ALD cycles is optimal from this point of view. It was also shown that the long-term stability of Al_2O_3 coated $LiNiMnCoO_2$ cathodes is very good compared to the uncoated cathode.

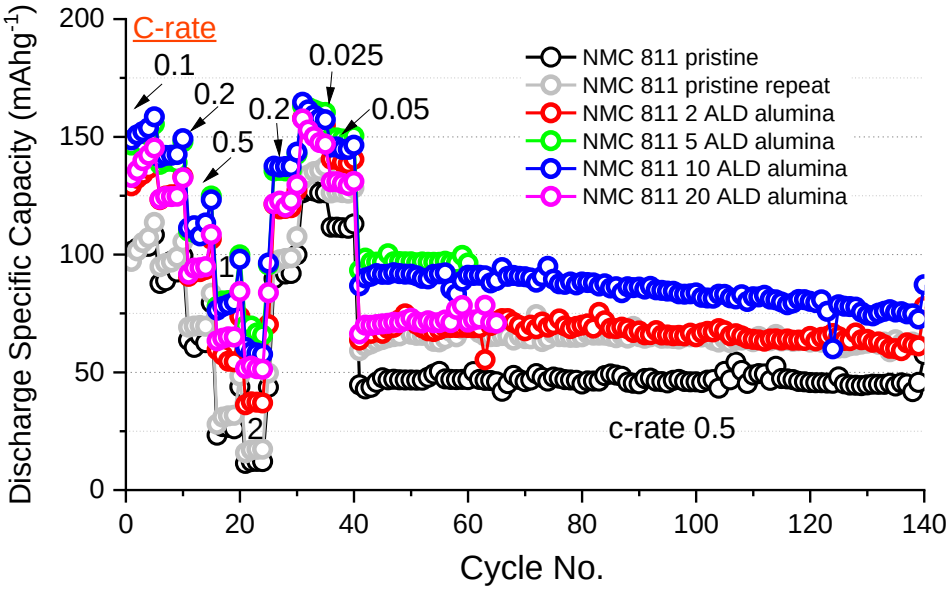


Fig. 8. Electrochemical measurements of the specific capacitance of the $LiNiMnCoO_2$ cathode (NMC811) uncoated (pristine) and coated with 2, 5, 10 and 20 ALD cycles of Al_2O_3 in a configuration with a Li anode (half-cell configuration).

Summary of Results

The results of electrochemical measurements of $LiFePO_4$ cathodes covered with Al_2O_3 layers using atomic layer deposition (ALD) showed a positive coating effect. Ultra-thin Al_2O_3 layers have a positive effect on the electrochemical properties of LiFePO4 cathodes, mainly by acting as protective layers between the cathode and the electrolyte and reducing the structural degradation of LiFePO4. A significant effect is the increase in the capacity of Al_2O_3-coated layers at higher charging values (C≥1) compared to the uncoated cathode. Cathodes covered with layers of 5-10 ALD cycles have the best properties and we can therefore conclude that the thickness of 5-10 ALD cycles is optimal from this point of view. It was also shown that the long-term stability of Al_2O_3-coated $LiFePO_4$ cathodes is very good compared to the uncoated cathode. The use of protective Al_2O_3 layers with a thickness of ~ nm has been shown to be an effective way to enhance the electrochemical properties of $LiFePO_4$ cathodes. The results of this study were published by the authors in a renowned international scientific journal [1].

Similar results were also achieved for $LiNiMnCoO_2$ cathodes covered with thin ALD layers of Al_2O_3. At higher charging values (C≥1), up to 5 times higher capacity of $LiNiMnCoO_2$ cathodes covered with 10 ALD cycles of Al2O3 was shown compared to the uncoated electrode.

Overall, we can conclude that the coating of $LiFePO_4$ and $LiNiMnCoO_2$ cathodes for Li-ion batteries increases their capacity compared to uncoated electrodes, especially at higher charge/discharge rates, and thus significantly contributes to increasing the safety of using these cathodes in Li-ion batteries.

References

[1] P. P. Sahoo, B. Hudec, M. Mičušík, M. Mikolášek, M. Precnerová, P. Švec Jr., P. Nadáždy, S. Mičky, M. Zubair, P. Šiffalovič, K. Frohlich: Enahnced performance of $LiFePO_4$ cathodes with alumina nanocoating by atomic layer deposition: insight from electrochemical, operando X-ray diffracton, and X-ray photoelectron spectroscopy analyses. ACS Appl. Energy Mater. 2025, 8, 10594-10607. https://doi.org/10.1021/acsaem.5c01523