Supporting information to 'Plasma enhanced atomic layer deposition of a (nitrogen doped) Ti phosphate coating for improved energy storage in Li-ion batteries'

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Deposition of Nitrogen doped Ti-phosphate

To illustrate the different plasma polymerised species that might be formed at the surface during a DEPA plasma pulse, a set of different chemical structures is shown in figure S1. These structures are based on the peak positions and peak shapes that were found in the XPS study of different materials. The reaction products denoted in red remain speculative, as this was not tested in detail. Formation of other molecular products in the plasma (such as more than one -OH bond for one DEPA molecule) is possible, but this is not shown here. It also has to be noted that only the triply coordinated nitrogen is illustrated here, as the doubly coordinated nitrogen bonds are thought to originate mainly from the nitrogen plasma that is pulsed after DEPA*.

Figure S1: Visualisation of the possible species formed at the substrate surface when DEPA is turned into a plasma. Speculated reaction products are shown in red.

In figure S2, the ERD depth profile is shown as well as the complete composition for both films deposited using TMP* or DEPA*.

Figure S2: ERD depth profile for N-doped Ti phosphate, using (a) TMP as phosphorus precursor and (b) DEPA as source.

To complete the XPS comparison of the different deposition processes, the important peaks of a thin film resulting from the surface polymerisation of DEPA* at low substrate temperature are shown in figure S3.

Figure S3: XPS study of a thin film grown by decomposition of DEPA* at 150°C. Each peak was fitted using at least two components, of which the peak position is labelled next to the component.

The crystallinity of the material was also studied, both before and after annealing the (un)doped Ti phosphate. The appearance of crystalline peaks after anneal is illustrated in figure S4.

Figure S4: XRD data before and after annealing up to 950°C in He atmosphere. The stars denote peak positions of crystalline TiP_2O_7 (JCPDS #00-038-1468).

Electrochemical characterisation

The cyclic voltammogram of the (un)coated electrodes is shown in figure S5a. From this graph, the lithiation peak of the underlying TiO_2 electrode does not seem to be affected by the coatings, meaning that they are not hampering Li-ions to diffuse into the electrode. It can also be seen that, in lithiating the (un)coated electrodes (figure S5b), the coating improves the capacity at every C-rate (similar to what was seen during de-lithiation in figure 5). The de-lithiation peak in the cyclic voltammogram seems to be smoothed due to the coating, but that does not mean that the coating is hampering the diffusion of Li-ions into the electrolyte. This was clear from the capacity at different C-rates from figure 5, which even showed an improvement due to the coating. As it does not show to hamper the battery kinetics, this smoothing was not studied further.

Figure S5: (a) Cyclic voltammetry of the (un)coated TiO_2 electrode at a scan rate of 10 mV/s. The coating thickness is approximately 9 nm for both coatings. (b) The capacity of the (un)coated electrodes during discharge at different rates. TiPO is used to refer to undoped Ti-phosphate, while TiPON is used for N-doped Ti-phosphate.

The use of the peak potential and peak current of an (un)coated TiO_2 electrode at different scan rates for determining the effective transversal ionic conductivity is also shown here (figure S6).

Figure S6: Calculation of the resistance for both approximately (a) 9 nm of Ti phosphate and (b) 9 nm of N-doped Ti phosphate. The measured resistances are $(7.1 \pm 2.3) \text{ k}\Omega$ for the electrode coated with undoped Ti phosphate (denoted as TiPO) and $(8.7 \pm 2.9) \text{ k}\Omega$ for the electrode coated with N-doped Ti phosphate (denoted as TiPON). The resistance of the uncoated TiO_2 electrode is $(3.3 \pm 0.6) \text{ k}\Omega$.

Electronic conductivity on TiN

In the system using TiN as the electrode and a ferrocene solution as the electrolyte, the electronic behaviour of the coating can be studied. In a very similar way as with the effective transversal ionic conductivity, the peak current and potential of the system were measured at different scan rates, from which the final coating resistance was then calculated. This is shown in figure S7. The peak potential was determined with respect to the electrochemical potential of the ferrocene redox couple.

Figure S7: CV-analysis of the coatings in the ferrocene system, showing the calculation of the resistance for (a) 9 nm of Ti-phosphate (b) 7 nm of N-doped Ti-phosphate. The coating resulted in a total electronic resistance of (8.0 ± 0.5) k Ω for the electrode coated with undoped Ti-phosphate and (2.1 ± 0.1) k Ω for the electrode coated with N-doped Ti-phosphate. The resistance of the uncoated electrode is (0.35 ± 0.01) k Ω .

PE-ALD nitrogen-doped Ti-phosphate films as functional coatings

To prove that a coating is present on the surface of the NMC particles, a SEM/EDX measurement was performed on NMC coated with 20 nm of the N-doped Ti-phosphate. This measurement is shown in figure S8.

In addition to the electrochemical tests that are shown in figure 6, other electrode formula-

Figure S8: 20 nm of N-doped titanium phosphate on NMC powder, studied with (left) SEM and (right) EDX. The EDX spectrum was measured for 500s with a 10 kV acceleration voltage.

tions were studied to get a more detailed view on the coating properties. In figure S9a, an electrode formulation with higher active material loading (but a similar porosity to the electrodes in figure 6) is characterised. There is still a significant increase in the rate capability, meaning that a decrease in the total number of contact points between the NMC particles and the carbon black additives might be counteracted by the added electronic pathways from the coating. When the porosity is decreased (figure S9b), the contact between the electrolyte and

Figure S9: Energy density of (un)coated NMC powder electrodes at different C-rates for an electrode formulation with (a) an active material loading of 16.5 mg/cm² and (b) 13.5 mg/cm² but with a lower porosity.

the NMC particles is decreased. From the fact that the undoped Ti-phosphate coating still results in an improved rate capability, it is shown that besides aiding electronic conductivity of the electrode, it can also act as an extra pathway for Li-ions. The N-doped Ti-phosphate coated electrode has slightly worse behaviour than the uncoated electrode, meaning that this coating should mainly be used as an electronic pathway with Li-ion transparency.

To study the protective nature of both coatings towards the challenging conditions at a high potential in particular, additional impedance measurements were performed. The electrode was again kept at 50°C, and the cell voltage was kept at 4.5 V vs. Li^+/Li for one day. After this, the electrode was discharged down to 4.2 V vs. Li^+/Li at which the impedance was measured. The battery was again cycled up to 4.5 V vs. Li^+/Li at which it was then kept for three days to study the effect of a more prolonged time at high potential and temperature on the impedance. This procedure was repeated one more time by now keeping the electrode at high potential for five days, finally resulting in the impedance measurements shown in figure S10. The labels denoting short, medium and long exposure for each electrode refer to maintaining the electrode at elevated potential and temperature for respectively a one, three and five day period. In these measurements, relatively similar results are found as

Figure S10: Impedance measurements when the electrode has been kept at high voltage and temperature for low, medium and long times for (a) uncoated NMC (b) Ti phosphate coated NMC and (c) N-doped Ti phosphate coated NMC. The amount of time at which the electrode was kept at elevated potential and temperature is denoted by 'short', 'medium' or 'long' exposure.

in figure 7. For the uncoated electrode, the resistance in the electrode is clearly increasing showing degradation of the electrode at high temperature and voltage. When the electrode is coated with N-doped Ti phosphate, it can be seen that the increase in resistance is actually worse meaning that the coating is not well suited for prolonged cycling at high temperatures and voltages. As mentioned before, the coating can thus be used for improved capacity at high charging speeds, but should not be regarded as protection against the harsh environment at these given conditions. The resistance of the electrode coated with undoped Ti phosphate is however much lower and barely increases. This shows that this coating has a lot of potential to improve the amount of capacity that can be stored at high charging speeds while preventing loss of capacity, especially from prolonged cycling at high voltage and temperatures.