Modification of composites by Dielectric Barrier Discharge (DBD) at atmospheric pressure for electrochemical applications

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Abstract: Nanometric thin layers made by plasma processes at atmospheric pressure have received a lot of interest because of their potential in different industrial applications. Water stability, dielectric and barrier proprieties of such coatings are now essential features used in automotive and electronic industries. However, the use of these advanced coatings to control the performances of electro-chemical devices, such as electrochemical cells, remain limited despite the rise of this industrial sector in recent years. In this study, organosilicon coatings are synthetized on a composite conductive layer by atmospheric pressure DBD operating with Helium. Different organosilicon molecules have been studied to highlight the effect of different growth mode as well as chemical functionalities on the operation of the final electrochemical device. The physical and chemical modification of plasma on the conductive layer as well as the water stability of the coatings were investigated in this study.

Keywords: organosilicon, chemical stability, electrochemical conductivity, discharge, atmospheric pressure

1.Introduction

Cell manufacturing will be the most essential step for the future battery value chain. Estimated to account for up to 40% of battery industry it will contribute to the expected 14.1% grow of this market (USD 108.4 billion in 2019 [1]) in the next five years. In this context, lithium-ion based solutions will most likely dominate the products in the future. Today, market growth is attributed to the high demand for rechargeable and non-rechargeable batteries used in electric vehicles (EV). In this context, high-power and stationary large-scale energy storage systems, such as lithium-ion batteries (LiBs), are essential electrochemical devices to make electricity quickly accessible to the power grid[2], [3]. This is particularly true for renewable energy sources or power plants located in remote areas. Despite their advantages, commercial LiBs are today limited by their environmental and safety hazards. Reactive electrodeelectrolyte interactions occurring at the interfaces of the electrochemical layers often provoke thermal runaway under abusive cycling or high temperature conditions [4]. Moreover, conventional organic electrolytes remain highly flammable and release toxic compounds upon heating or when exposed to air [5]. These limitations force this sector to use and study new technologies for safe recycling operations and control of the discharge cycling depending on the external conditions [6]. Currently, research efforts are focused on the development of new advanced materials, composite design as well as advanced interfacial layers to control and modify charge transport mechanisms. Extensive research has been devoted to modify the surface wettability of these interfaces using different approaches. In this context, surface modification by cold plasma has

been reported as one of the most promising solutions [7]. In comparison to wet chemical methods, plasma processes offer dry and low-temperature medium with which a wide variety of substrate materials, even thermosensitive materials such as paper, can be treated [8]-[10]. In addition, these techniques are today considered economical and ecological friendly due to low consumption of chemicals and the absence of solvents. Although these processes have been widely used to modify separators in batteries [11] and/or to synthesize active materials for electrodes [12], [13], rare are the studies using cold discharges at atmospheric pressure to control the chemical proprieties of interfaces inside electrochemical assembly. In this work, the physical phenomena underlying the efficient operation of the plasma-modified electrodes in dilute aqueous electrolytes were reported. Electrochemical stability of plasma-treated composites containing LiFePO₄ were analysed in detail. Finally, the mechanisms governing the transport of species through the nanomembrane were also studied.

2. Experimental Procedure

Composite conductive layer was easily prepared in water by combining 84 wt % of active material (LiFePO₄ and FePO₄) with 9 wt % of carbon black (Timcal C65) and 7 wt % of CMC (Sigma Aldrich). Then, the substrates were exposed to a cold discharge at atmospheric pressure. Experiments were performed in a plane-to-plane discharge cell housed in a stainless-steel chamber. The homogeneous glow-like discharge was formed by two electrodes (2.5 cm



Figure 1 Schematic of the plasma-treated electrodes assembled in the final electrochemical cell.

 \times 5.5 cm) made between two metallized paint (Pt-Ag alloy) deposited on dielectric plates (alumina, 635 µm thick). The gap between the electrodes was set to 1 mm using two glass slides. Helium (He, 4.5 L/min) was used as a carrier gas 120 of along with mg/h precursor (i.e., hexamethyldisiloxane or HMDSO, tetraethylorthosilicate or TEOS, 2,4,6,8-tetramethylcyclotetrasiloxane or TMCTS). Prior the discharge, the chamber was pumped down to remove all impurities. A sinusoidal voltage (2kV_{pp}, 20kHz) was used to ignite the discharge. The electrical characteristics were measured with a highvoltage probe (Tektronix P6015A) and a wide-band terminated current transformer (LILCO Ltd. 13W5000), respectively. After the plasma treatment, all the modified LiFePO₄/FePO₄ lithium-ion cells were assembled in a 1 mol/kg LiTFSI aqueous electrolyte. Figure 1 depicted the schematic of the electrochemical cell assembled after the plasma treatment. Cycling of the modified device was performed between -0.6 and 0.6 V (i.e., 2.8 V and 4.0 V vs. Li+/Li) with a C-rate of C/10. The same composite electrodes without plasma-deposited organosilicon protection were cycled in LiPF₆ in EC: DEC organic electrolytes. To study the diffusion of the species through the modified surfaces, an Indigo-Carmine (IC; Sigma Aldrich) electrode was also prepared. In this case the slurry of combined ingredients was blended for 20 min using a Kurabo Mazerustar KK-50S planetary mixer-deaerator. Finally, all treated surfaces were characterized using an electronic microscope (HITACHI TM3030Plus) and their cross-sections were studied with a JEOL FE-SEM 7600 Field Emission Gun scanning electron microscope (SEM; 10 kV accelerating voltage, ~4 mm working distance, 5-50 kX). The chemical composition of the surfaces was analyzed before and after plasma treatment using Attenuated Total Reflectance Fourier Transform InfraRed (ATR-FTIR) spectroscopy (Vertex 70; Bruker®)

3.Results and Discussion

Figure 2a shows the SEM images of the plasma-treated surfaces. A homogeneous coating is formed on the top of the composite material. The modified surface does not highlight cracks or delamination of the plasma coating, indicating a robust modification. It is worth mention that some sub-micrometer pores appear. These features are most likely linked to the relatively low energy provided to the substrate during thin film growth in cold discharge at atmospheric pressure. The cross section of the plasmatreated electrode is also visible in Figure 2b. The images suggest a good coverage of the layer on the rough surface. The chemical mapping of the coating (Si signal, Figure 2c) clearly highlights the distribution of the thin layer over the composite. The results show that the plasma modification does not penetrate the composite part of the electrode. The modified thin layer remains conformal with the roughness of the pristine electrode. From the mapping one can also note that the thickness of the membrane remains close to 0.5 µm. Further analyses were performed by ATR-FTIR to determine the chemical composition of the untreated and plasma-treated layers (not reported in this document). All spectra from the modified surfaces highlight the presence of CH₃ bands related to the Si-CH₃, structure. Similarly, strong bands between 700 and 900 cm⁻¹ have been observed confirming the presence of C-H rocking and Si-C s-stretching from the Si-(CH₃)₃[14].



Figure 2 Morphological and chemical characterization of the plasma-modified electrodes: (a) surface, (b) cross section and (c) chemical signature of the Si obtained by EDX from a high magnification of the cross section.

Overall, results from the FT-IR analysis suggest the low oxidation of organosilicon fragments created in the gas phase and the growth of soft plasma-polymers over the composite material. At this stage, no degradation of the composite material is detected by ATR-FTIR suggesting the preservation of the chemical and microstructural properties for the active material after the discharge. Further analysis will be necessary to confirm the previous hypothesis. Since the electro-chemical device has been designed to cycle in aqueous conditions, the wettability of the plasma-treated surface with water is a key element for visible at x=0.5 (ca. 90 mV). This indicates an increase of the resistance when an organosilicon layer is used. This phenomenon is clearly visible of the membranes having a thickness close to 20 μ m. The analysis of the coulombic efficiency (not reported in this document) indicates that the plasma-protected CMC-based electrode delivers a stable capacity of 140 mAh/g with efficiency close to 99% over 100 cycles (85 days). The results are very close to the ones obtained from the untreated electrodes cycled in hazardous organic electrolytes (155 mAh/g, not shown here). In this sense, the plasma-membrane highlights an exceptional



Figure 3: Photographs recorded at different times (from 0 to 25 s) after placing the plasma-treated and untreated IC electrodes over an aqueous electrolyte.

the optimal behaviour of the final battery. Therefore, to validate the transfer of small water-soluble ions from the electrolyte to the composite electrode, experiments were also conducted using an electrode with Indigo-Carmine (IC) instead of LiFePO₄. IC is a well-known organic blue dye that easily dissolve in water. The comparison of the plasma-treated and untreated surface reveals different behaviours when both surfaces remain in contact with the aqueous electrolyte (Figure 3). The treated electrode exhibit a hydrophobic character when exposed to water. Compared to untreated electrodes, the transport of molecules from the IC electrode into water is slower. Moreover, the modification made by plasma enhance the mechanical cohesion of the electrode, avoiding a complete dissolution of the electrode in the liquid. In this sense, one can conclude that the plasma-layer that acts as a porous membrane allowing the diffusion of electro-active species from the composite material to the electrolyte. At this stage, the galvanostatic analysis is realized to study the electrochemical performance of the modified electrodes. Figure 4 depict the charge/discharge curves obtained after the plasma-polymerization process from the HMDSO/He mixture. All curves indicate that the devices modified by the discharge can cycle in aqueous electrolytes. Therefore, the plasma membrane does not impede the diffusion of the charge carriers under the electric field. One must also consider that pristine electrodes cannot be cycled in aqueous electrolyte because of an immediate dissolution caused by their poor mechanical cohesion of the hydrophilic composite material. Galvanostatic behaviours slightly change when different thicknesses for the plasma layer are compared. In fact, different polarizations are

interfacial compatibility with aqueous electrolytes as well as a good ionic conductivity. Comparing the results obtained from different organosilicon precursors, no major modification has been observed during the galvanostatic analysis. This highlights that the battery stability, thereby electrode stability over a very large number of cycles is not affected by the small modifications of the chemical composition. Therefore, one can suggest that only the density/porosity of the plasma-membrane will strongly change the characteristic of the electro-chemical device.



Figure 4: Galvanostatic charge–discharge profiles at the 5th cycle at 0.1C-rates (1 C = 170 mA g^{-1}) for the treated electrode having different membrane thickness.

4. Conclusion

Over the range of experimental conditions studied here, we have shown that the fragmentation of the organosilicon molecules in helium atmospheric pressure dielectric barrier discharge (DBD) strongly alters the surfaces of composite electrochemical devices. After plasma treatment, all the samples can withstand the mechanical stress associated with the electrochemical cycling of the active materials. Similar galvanostatic charge-discharge profiles can be observed with thin layers from different organosilicon precursors. An increase of the resistance is observed with thicker coatings. Hence, it can be concluded that the porosity of the plasma-membrane plays a crucial role for the diffusion of charge carriers during the cycling process. The results highlighted in this work will contribute to the understanding of the fundamental mechanisms of diffusion through thin, porous membranes synthesized by plasma at atmospheric pressure. However, the scientific discoveries resulted from this work could be highly beneficial to other industrial sectors.

5.References

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