

Chemical grafted carbon-coated LiFePO₄ olivine using diazonium chemistry

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Lithium iron phosphate LiFePO₄ with olivine structure has become of great interest as a potential storage cathode for the next generation lithium-ion batteries, particularly for hybrid electric vehicle applications, because of its high energy density, low cost, safety and environmental compatibility^[1]. The Li⁺ ion can be extracted/inserted from/into LiFePO₄ at the electrode potential of 3.5 V versus Li/Li⁺, and the theoretical discharge capacity is 170 mA.h⁻¹. The stability of LiFePO₄ is ensured with strong P-O covalency of the polyanion (PO₄)³⁻^[2]. On the other hand, the major drawback of LiFePO₄ is the decrease of capacity with increasing charge/discharge current density, associated with its fundamentally low electronic and ionic conductivity. Since the first work of Padhi et al.^[1], many studies have attempted to overcome this obstacle with particle-size reduction, surface coating, doping and conducting agents^{[3] [4] [5] [6] [7]}.

In order to improve the electrochemical properties of LiFePO₄/C powder, a new grafting method for carbon coated cathode material was adopted in this study inspired from the previous studies of carbon modification^[8]. The reduction of diazonium cations has been widely investigated during the past decades in order to functionalize surfaces^[8-9]. Toupin and Bélanger^[10] have undertaken detailed studies of the spontaneous reaction between Vulcan carbon black and aryl diazonium salts in aqueous solution. This method allows the attachment of various substituted aryl groups with a strongly C-C bond in order to change the surface properties. The reduction of *in situ* generated diazonium cations in organic media leads to the functionalization of the carbon coating of LiFePO₄/C.

This presentation will focus on the study of LiFePO₄/C cathodes for Li-ion batteries. More specifically, the aim of this work is to functionalize the carbon coating of LiFePO₄/C particles using diazonium chemistry. Up to now, the work focused on grafting aromatic amine molecules in order to increase the electrode capacity and to enhance the surface reactivity between electrolyte and active material. Several organic groups were successfully grafted on carbon coating by reduction of *in situ* generated diazonium ions. An increase of specific capacity has been observed during cycling in coin-cell and more specifically at high rate.

The grafting reaction onto the carbon coating leads to a partial oxidation of LiFePO₄/C related to the amount of precursors used for the reaction. X-ray diffraction patterns show the presence of LiFePO₄/C and FePO₄ phases. ICP analyses were performed in order to determine accurately the lithium content of the grafted samples. The ratios of LiFePO₄ and FePO₄ deduced from ICP analyses are consistent with those obtained with XRD measurements.

Using EDX, the presence of grafted molecules on the carbon coating of LiFePO₄/C was confirmed.

Galvanostatic measurements at various current rates were carried out to further compare the electrochemical performances of LiFePO₄/C blank and grafted samples. At current rates of 0.1 and 5C, the grafted LiFePO₄/C electrode displays an improvement of 7 and 28 % of the discharge capacity, respectively, compared to the blank LiFePO₄/C sample. The specific capacity of the grafted LiFePO₄/C sample is enhanced even at high current rates and the discharged capacity reach up to 109 mA.h.g⁻¹ at 5 C retaining almost 64 % of the theoretical capacity. From these results, the rate capability enhancement of the grafted samples can be explained by the presence of specific grafted groups onto the surface of the LiFePO₄/C particles that can "improve" the interfacial properties at the electrode particles/electrolyte interface. Future work will focus on the characterization of the surface of the grafted LiFePO₄/C.

References

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