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Covalent vs. non-covalent redox functionalization of C–$LiFePO_4$ based electrodes

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HIGHLIGHTS

- ► We functionalize fast redox molecular relay on carbon additive and C–$LiFePO_4$.
- ► We correlate FTIR, XPS, elemental analysis, dc conductivity and electrochemistry.
- ► Conductivity is more impacted by covalent molecular grafting than by non-covalent.
- ► Simultaneous anion and cation based electrochemical processes occur.
- ► π–π stacking redox grafting does not show adverse effect on Li insertion in C–$LiFePO_4$.

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ABSTRACT

During high rate utilization of porous Li battery, Li^+ refuelling from the electrolyte limits the discharge kinetics of positive electrodes. In the case of thick electrodes a strategy to buffer the resulting sharp drop of Li^+ concentration gradient would be to functionalize the electrode with anionic based redox molecules (RMR) that would be therefore able to relay intercalation process. The occurrence of these RMR in the electrode should not however, induce adverse effect on Li intercalation processes. In this respect, this work studies the effect of functionalizing LFPC based electrodes by either covalent or non-covalent chemistry, on Li intercalation kinetics. To do so, model molecules containing a nitro group were introduced at the surface of both carbon conducting additives and active material (C–$LiFePO_4$). It is shown that presumably due to formation of sp^3 defects, covalent anchoring using diazonium chemistry inhibits the intercalation kinetics in C–$FePO_4$. On the contrary, if molecules such as pyrene derivatives are immobilized by pi-staking interactions, Li intercalation is not impeded. Therefore non-covalent functionalization of pyrene based RMR appears as a promising route to relay Li intercalation reaction during high power demand. The framework for future development of this strategy is discussed.

1. Introduction

Lithium (Li)-ion batteries are known to deliver relatively high energy densities (150–200 Wh kg^{-1}) in comparison to other electrochemical energy storage systems. This property is associated with redox reactions that take place within the volume of active grains by simultaneous ions and electrons uptake/removal. When low electronic and ionic conductivities materials are involved, high rate can be reached by reducing transport length as in nanograins [1–3] or nanostructured materials [4]. Recent calculations also point out that statistical crystal defects significantly impede Li^+ diffusion constant. Kinetics therefore depends on the lithium diffusion length with microscopic crystals being much favoured than nanoparticles [5]. When fast electronic and ionic motion may occur within the active material, power performance (1–3 kW kg^{-1}) are usually frustrated by slow ionic "refuelling" from the electrolyte [6,7] because the amplitude of intercalation reactions is large in respect to the amount of ions available in the porosity of the electrodes. As the discharge rate increases, bulk Li^+ intercalation processes become surface limited in these parts of the electrode where Li^+ depletion occurs. Therefore for power applications, electrodes are made thin to reduce ionic diffusion path lengths. This results however, in low energy batteries (Wh cm^{-2}). One possible alternative to decreasing the electrode thickness would be to use additional redox molecular relay (RMR) which charge compensation occurs with anions rather than Li^+ ions. This strategy

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should therefore not only allow buffering power properties of thick electrodes but also provides means against over discharge/charge issues, considering RMR can be chosen with a redox potential lower (higher) than the active material on discharge (charge). To prevent any dissolution of RMR in the electrolyte of Li-ion batteries, RMR can be functionalized at the active material and/or conducting agent surfaces. However, one should verify that functionalization does not hinder Li^+ intercalation kinetics. This is the main goal of the present study.

So far, molecular functionalization of Li battery components has been proposed to stabilize the SEI (solid electrolyte interface) at the surface of carbon [8], to maintain contact between silicon particles and graphite flakes or carbon nanotubes [9], and to increase cycle life by limiting electrolyte decomposition at the surface of positive active material [10]. Moreover, in the field of electrochemical capacitors, molecular functionalization of carbon has been used to provide a novel type of electrical double layer [11] and to increase energy densities [12–18]. All these works refer however, to covalent functionalization. On the contrary, interest of non-covalent interactions such as $\pi-\pi$ staking has only be proven very recently in the field of energy storage [19].

Covalent modification of carbon surface is mostly performed by electrochemical or spontaneous reduction of diazonium salts [20–22]. It occurs along with N_2 departure at a potential threshold close to 0 V vs. SCE ($\sim$3 V vs. Li^+/Li^0), leaving an aryl radical that covalently bonds to the surface of the substrate. Among diazonium salts, the para-nitrobenzene derivative is often used as a model molecule because the nitro group can easily be detected from conventional spectroscopies.

This study deals with the functionalization aspects of the carbon additive and the active material of a composite electrode by model RMR chosen as para-nitrobenzene or 1-NitroPyrene. This paper aims at determining first, what can be expected in term of capacity gain from the RMR strategy where the carbon additive and/or on the active material of a composite electrode are functionalized, and second, how covalent or non-covalent functionalization chemistries impact Li intercalation processes.

2. Experimental

2.1. Materials

Carbon coated $LiFePO_4$ powder (referred to as LFPC), with 150 nm particle size, was supplied by UMICORE Cobalt & Specialty Materials, Belgium. Purity (Li = 4.4 wt%, Fe = 34.4 wt%, P = 17.6 wt %) and carbon content (2.8 wt%) were confirmed by XRD and elemental analysis (Service Central d'Analyse–CNRS, Vernaison, France) respectively.

Covalent functionalization of carbon substrates was performed by direct contact of amorphous carbon black Super P, referred to as Csp, or, graphitised carbon black C-NERGY™ Super C65 from TIMCAL, referred to as C65, with dissolved para-nitrobenzene diazonium tetrafluoroborate ($C_6H_4N_3O_2BF_4$, CAS 456-27-9, referred to as PNBDiaz) in ultra pure water (pH = 5–6). In the case of LFPC a similar procedure was followed except PNBDiaz was dissolved in anhydrous acetonitrile (HPLC grade). We shall recall for the sake of clarity that reaction of PNBDiaz at a carbon surface yields the grafting of the para-nitrobenzene moiety ($C_6H_4NO_2$, referred to as PNB) [22]. Non-covalent anchoring was conducted by immersion of C65 in a methanol solution of 1-nitropyrene ($C_{16}H_9NO_2$, CAS 5522-43-0, referred to as NPyr). Taking L as the theoretical amount corresponding to a dense monolayer coverage of PNB at the surface, the amount of PNBDiaz was varied from $n = 0.05L$ to $n = 10L$ for Csp, while it was set to 0.1L and 2L for C65, and 2L for LFPC. Non-covalent functionalization of NPyr was performed for $n = 4L$ in the case of C65. Theoretical dense monolayer coverage was estimated based on Van Der Waals bond distances from the gyration surface area of a grafted phenyl unit in the case of PNB (close to 25 Å^2), from the geometrical surface of a pyrene unit (195 Å^2) for NPyr, and from specific surface areas deduced from BET analysis for LFPC (23 $m^2\ g^{-1}$), Csp (66 $m^2\ g^{-1}$) and C65 (63 $m^2\ g^{-1}$). The contact time was 24 h and 120 h in case of covalent and non-covalent grafting respectively. The mass powder to solvent volume ratio was held constant (250 mg/16 ml). Grafted Csp, C65 and LFPC samples are referred to as Csp-NO_2-nL, C65-NO_2-nL, C65-PyrNO_2-nL and LFPC-NO_2-nL respectively. All filtered samples were washed three times by a few minutes immersion in 250 ml of ethanol to remove un-grafted species.

2.2. Physical characterizations

Elemental analyses were performed by ICP at Service Central d'Analyse–CNRS, Vernaison, France.

BET surface area analyses were performed with a micromeritics ASAP 2010 apparatus using nitrogen gas.

Fourier transform infrared spectroscopy (FTIR) spectra were collected with a Brucker Vertex 70 in absorbance mode using KBr pellets and a DTGS detector at a resolution of 4 cm^{-1}. KBr was used as a reference and for each samples, 0.2 mg of powder was mixed with 300 mg of KBr.

X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Axis Ultra spectrometer using an Al Kα monochromatic beam working at 1486.6 eV. Data were collected at room temperature and the operating pressure in the analysis chamber was kept below 8 10^{-9} Torr. Powders were deposited onto a carbon tape and all spectra were recorded in the CEA (constant analyser energy) mode with an analyser pass energy of 20 eV. Data treatment was performed with CasaXPS software. To determine the atomic concentrations (in %), pseudo-voight function constrained by full width at half-maximum (FWHM) ranges typical of each element have been used and all spectra are calibrated taking 284.5 eV (graphite like carbon) as a reference binding energy.

2.3. Electrochemical cell preparation and standard cycling protocol

Electrodes constituted of 70 wt% of C, 25 wt% LFPC and 5% of PTFE are referred to as "carbon rich electrodes" where those obtained from 10 wt% of C, 85 wt% LFPC and 5% of PTFE are referred to as "practical electrodes". These mixtures were hand mixed and resulting self supported films were pressed at 5 Tons on a 0.8 cm^2 Al current collector. For both types of electrodes, loadings were close to 15 $mg_{electrode}\ cm^{-2}$ which is a reasonable value for extrapolating electrode performance in a real device [23]. Electrolyte (LP30) obtained from Novolyte as a highly purity grade is 1 M $LiPF_6$ in 1:1 EC-DMC and was used as received. Karl Fischer titration indicates LP30 contains approx. 10 ppm of H_2O. Electrochemical tests were evaluated at 22 °C and monitored by voltammetric potentiostat (VMP-Biologic SA, Claix, France) in galvanostatic mode using EC-Lab software (Biologic SA, version 10.18). All voltages given in the text are reported vs. Li^+/Li^0. Carbon rich electrodes were used in Section 3.3.1 to evaluate the RMR electrochemical behaviour. According to a standard protocol, cycling was performed at a 1 C rate (1Li/1 h, approx. 0.64 mA cm^{-2} or 42.5 mA $g^{-1}_{electrode}$) both on discharge and on charge, in a 3 V or 1.5 V–4.2 V potential range. A 1 min open circuit voltage (OCV) was allowed upon each half cycle. In Section 3.3.2, practical electrodes were used to study the power capability of LFPC based functionalized electrodes. Power tests were performed by successive discharge current pulses of decreasing values after three cycles at a C/5 rate. OCV relaxations