Activation of Phosphate Olivines LiMPO$_4$ (M = Fe, Mn) by Functionalized Carbon Nanotubes: Application for Cathode Materials of Li-Ion Battery

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ABSTRACT

The nanotube-mediated redox wiring is based on a synergic action of adsorbed redox-active molecule, which provides the interfacial charge transfer to the surface and the single-walled carbon nanotube (SWNT), which transports charge to longer distances in the cathode material. A Ru-bipyridine complex Z-907Na, turned to be particularly suitable for this purpose, because of its amphiphilic character enabling solubilization of SWNT. Electrodes fabricated from optimized composite materials containing LiFePO$_4$ (olivine) exhibit a greatly enhanced activity for electrochemical Li$^+$ extraction/insertion compared to electrodes from commercial carbon-coated LiFePO$_4$ or from LiFePO$_4$ derivatized either by adsorption of sole redox-mediator molecules or by pristine SWNT. Multi-walled carbon nanotubes (MWNT) functionalized by carboxylic groups, exhibit better affinity towards LiMPO$_4$ (M – Fe, Mn) as compared to that of pristine MWNT. The surface functionalization of MWNT enhances charge storage capacity and reversibility of a composite with LiMnPO$_4$ (olivine), but mediates also the electrolyte breakdown at potentials >4.2 V. Whereas the electrochemical activation of LiMnPO$_4$ (olivine) by functionalized MWNT is quite modest, excellent performance was found for LiFePO$_4$ (olivine) in composite materials containing only 2wt% of functionalized nanotubes.

Keywords: olivine cathode, Li-ion battery, carbon nanotubes, Ru-bipyridine complexes

1. OLIVINE CATHODES

Phosphate olivines LiMPO$_4$ (M = Fe, Mn; *Pmnb* space group) introduced by Goodenough et al. [1] are prospective cathode materials for Li-ion batteries, offering redox potentials of 3.5 or 4.1 V vs. Li/Li$^+$ and theoretical capacity of 170 mAh/g. Since this discovery, especially the LiFePO$_4$ (olivine) attracted considerable interest for application in Li-ion batteries with improved safety and reduced cost compared to the usual batteries with cobalt-oxide cathodes.

However, the poor electrical conductivity of olivines is a crucial issue to be addressed [2] either by doping [3] or by surface coating with elemental carbon [4,5]. The conductiv-

ity problem is considerably more significant for LiMnPO$_4$ (conductivity of≈10^{-14} S/cm compared to≈10^{-9} S/cm for LiFePO$_4$) [6] but optimization of the synthesis, that is the formation of carbon coating via ball-milling, provided reasonably active materials, too [7,8].

2. MOLECULAR WIRING

The molecular wiring, introduced by Graetzel et al. [9] consists in a cross-surface charge-transfer within a monolayer of redox active molecules, adsorbed on electrically insulating nanocrystals. The idea is applicable for promoting the activity of LiMPO$_4$ (M = Fe, Mn). In this case the hole, h$^+$ is located at the oxidized form of the redox mediator, and the following reaction is driven:

$$\text{LiMPO}_4 + h^+ \rightarrow \text{Li}^+ + \text{MPO}_4 \quad \text{M = Fe, Mn} \qquad (1)$$
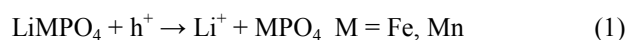
Two molecules turned to be most promising for molecular wiring of LiFePO$_4$ *viz.* [12-(2,5-di-*tert*-butyl-4-methoxy-phenoxy)-dodecyl]-phosphonic acid[10] and Na-Ru(-4,4'-dicarboxylic acid-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyri-dine)(NCS)$_2$, coded Z-907Na [11,12]. The first molecule exhibits excellent stability, but its redox potential of ca. 3.95 V vs. Li/Li$^+$ is too positive for reversible molecular wiring LiFePO$_4$. In other words, this molecule is active for anodic molecular wiring, that is the oxidized redox couple efficiently injects holes into LiFePO$_4$, and thus cause its subsequent chemical delithiation towards FePO$_4$. The second molecule has a redox potential of 3.5 V, but is still active for wiring of LiFePO$_4$ despite the redox-potentials driving force was very small [11,12]. In this case, both anodic and cathodic molecular wiring is possible in principle.

Molecular wiring of LiMnPO$_4$ is considerably more difficult than the wiring of LiFePO$_4$. However, two complexes, viz. Ru-bis(4,4'-diethoxycarbonyl-2-2'-bipyridine)(4,4'-dicarboxylic acid-2,2'-bipyridine), coded Z-974 and Ru-bis(4,4'-dicarboxylic acid-2,2'-bipyridine)(4,4'-dinonyl-2,2'bipyridine), coded Z-975 (Figure 1) turned out to be active even for LiMnPO$_4$ [13]. Both complexes, Z-974 and Z-975 expectedly activated the oxidation of LiFePO$_4$[12], because the electrochemical potentials were by ca. 0.7 to 1

V larger than those required for the wiring of LiFePO$_4$ [12]. The possibility of molecular wiring of LiMnPO$_4$ is a novel issue which was demonstrated for the first time in 2009 [13]. We should note that Z-975 is a simple homologue of Z-907Na in which one di-carboxy-bipyridine was replaced by two thiocyanate ligands (cf. also Figures 1 and 2). These two Ru(II)-bipy complexes demonstrate a possibility of fine tuning of the redox potentials (within a window as large as 1 V) by molecular engineering of the ligand(s).
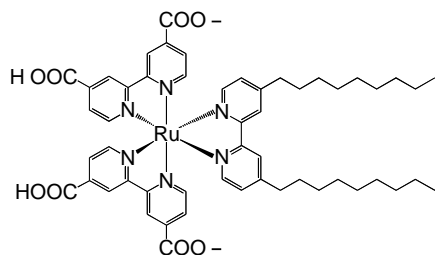

Figure 1. Formula of Z-975, redox potential 4.25 V vs. Li/Li$^+$. This molecule is active for wiring of both LiFePO$_4$ and LiMnPO$_4$.

3. NANOTUBE WIRING: SWNT

The problems associated with molecular wiring (Section 2) that is low charge capacity and poor cyclability are minimized, if the redox mediator is interconnected to a single walled carbon nanotube, SWNT [11,12,14,15]. An example of this supramolecular assembly is a complex of Z-907Na with SWNT shown in Figure 2.
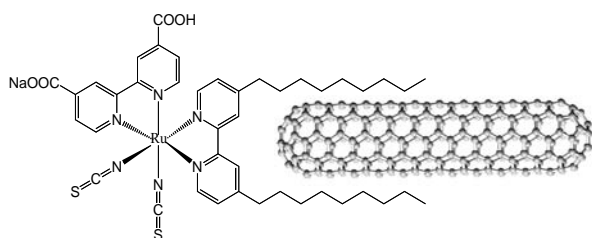

Figure 2: Scheme of the interaction of SWNT with Z-907Na (redox potential 3.5 V vs. Li/Li$^+$). This assembly is active for wiring of LiFePO$_4$.

This assembly offers unique electrochemical activation of LiFePO$_4$ called 'nanotube wiring' [11,12]. It keeps the amount of conductive additives in the active electrode material at its natural minimum ($\approx$0.04 wt% of carbon in LiFePO$_4$). This is important for optimization of Li-ion batteries. The reason is that the electrode materials based on olivines require *ca.* 10-20 wt% of graphitic carbon to be added. However, graphite does not contribute to the fara-

daic reaction in the cathode, but presents ballast, decreasing the charge (energy) density of the electrode in the same proportion.

4. NANOTUBE WIRING: MWNT

The next step in developing of practical olivine electrodes was replacement of the expensive and complicated materials with Ru-complexes and SWNT (Sections 2 and 3). The most promising material turned out to be multi-walled carbon nanotube (MWNT) oxidatively functionalized by carboxylic groups. Compared to SWNT, the multi-walled carbon nanotubes are cheaper, mechanically more robust, and their electrical conductivity is less affected by chemical functionalization.

MWNT for this application were prepared from ethylene gas by chemical vapor deposition, and Fe nanoparticles supported on alumina served as catalyst [16]. Oxidative functionalization was carried out by 65% HNO$_3$ for 3 hrs at 120°C. The carbon-free olivines, LiFePO$_4$ and LiMnPO$_4$ had the BET surface areas as of 9 m^2/g (for LiFePO$_4$) and 35 m^2/g (for LiMnPO$_4$). The latter material was prepared *via* the "polyol" route, and consisted of platelets oriented in the *a-c* plane of the olivine lattice [7].

Nanotubes were dispersed in water under sonication. To this solution a powder material (LiMnPO$_4$ or LiFePO$_4$) was added (in a proportion of 1-10 wt% of nanotubes in the mixture) and evaporated to dryness. Thus made material, was mixed with 5 wt% of polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidon, and the slurry was doctor-bladed onto F-doped conducting glass. The film's mass was between ca. 0.2-1 mg/cm^2.
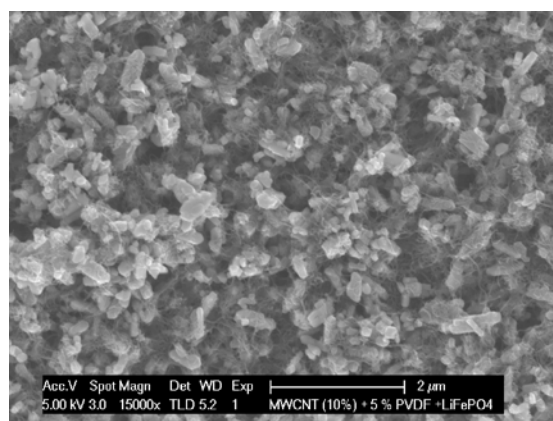

Figure 3. Scanning electron microscopy images of thin film electrodes from LiFePO$_4$ in a composite with 10 wt% of functionalized nanotubes, MWNT.
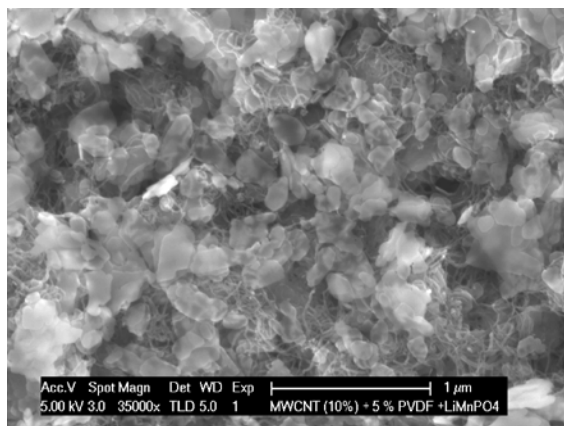
Figure 4. Scanning electron microscopy images of thin film electrodes from LiMnPO$_4$ in a composite with 10 wt% of functionalized nanotubes, MWNT.

Figures 3 and 4 show the morphological features of our olivine/MWNT composites (10 wt% MWNT). The nanotubes are easily recognized between the individual crystals of LiFePO$_4$ (Fig. 3) as well as between LiMnPO$_4$ crystals (Fig. 4).

The electrochemical performance of LiFePO$_4$ based electrode is demonstrated on Figure 5. The improvement caused by surface oxidation of nanotubes is dramatic. The composite LiFePO$_4$/MWNT exhibits a capacity of 149 mAh/g (cyclic voltammetry at the scan rate of 0.1 mV/s) and nearly perfect charge/discharge reversibility of 99-100%. On the other hand, the LiFePO$_4$ in a composite with blank (non-functionalized) MWNT attains only 32 mAh/g at the same conditions (cf. Fig. 5). Comparative tests were carried out in which the concentration of MWNT varied. Perfect charge reversibility and nearly the same charge capacity was maintained for materials containing 2-10 wt% of MWNT, but there was a sudden drop of charge capacity for MWNT concentrations between 1 and 2 wt%. This seems to be the effective charge-percolation threshold in our composite.

Figure 6 shows analogous data for the system with LiMnPO$_4$. The beneficial effect of surface oxidation of MWNT is again demonstrated by comparing the composites containing blank MWNT and oxidized MWNT. Here we show the data for nanotube/LiMnPO$_4$ electrodes of roughly comparable film masses around 0.85 mg/cm^2. The peak current for anodic process in olivine, that is oxidation of LiMnPO$_4$ to MnPO$_4$ is roughly identical for both electrodes, but the material with blank MWNT shows very small cathodic charge for the reverse reaction. Hence the oxidative treatment of nanotubes improves the reversibility of LiMnPO$_4$ charge/discharge. However, the surface oxida-

tion of nanotubes also activates the electrolyte decomposition. This is demonstrated by anodic branch of our voltammograms between 4.2 to 4.5 V. The surface oxides (carboxyls) mediate these parasitic breakdown reactions, although the mechanism of this activation is unknown.
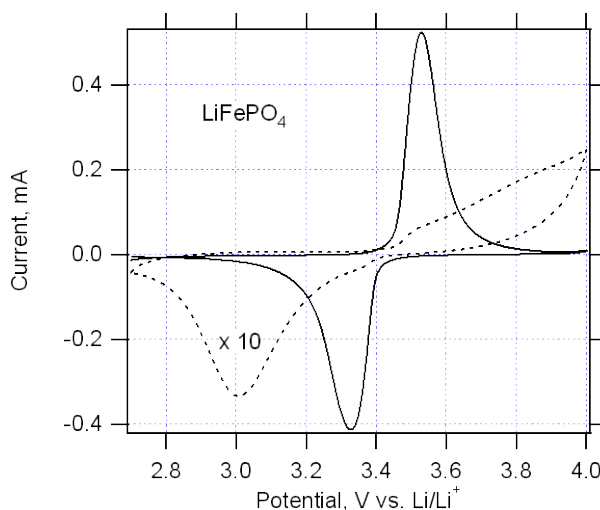

Figure 5. Cyclic voltammograms of LiFePO$_4$ thin film electrodes. Full curve: LiFePO$_4$ in a composite with 10 wt% of functionalized MWNT (film mass 0.33 mg/cm^2). Dashed curve: LiFePO$_4$ in a composite with 10 wt% of blank (non-functionalized) MWNT (film mass 0.38 mg/cm^2); this curve is zoomed by a factor of 10 in the current scale. Scan rate 0.5 mV/s.
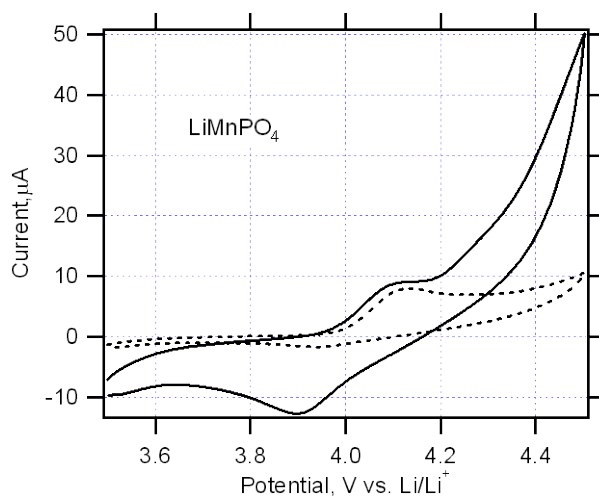

Figure 6. Cyclic voltammograms of LiMnPO$_4$ thin film electrodes in a composite with 10 wt% of MWNT (film mass 0.83 mg/cm^2). Dashed curve: LiMnPO$_4$ in a composite with 10 wt% of blank (non-functionalized) MWNT film mass 0.87 mg/cm^2). Scan rate 0.5 mV/s.

The conclusions from cyclic voltammetry were further supported by discharge/charge cycles which were tested using galvanostatic chronopotentiometry. While the system with $LiMnPO_4$ exhibits poor performance with considerable irreversibility, the electrodes with $LiFePO_4$ were good. This system allows that 88 % of its theoretical capacity (170 mAh/g) can be reversibly cycled at C/2. This electrode can still deliver 38 % of its theoretical capacity at 50C, that is within 72 s. It is interesting to note that the charge capacity observed at C/2, C, 5C, 10C etc. is roughly similar to the voltammetric charge capacity at scan rates (in mV/s) of 0.5, 1, 5, 10 etc. Obviously, both experiments require comparable times for completing the discharge/charge. However, the electrode $LiMnPO_4$/MWNT loses ca. half of its initial capacity during fifteen subsequent discharge/charge cycles at C/5. This illustrates the conclusions from cyclic voltammetry that the process is irreversible due to anodic electrolyte breakdown enhanced by MWNT-ox. On the other hand, the cycle life of $LiFePO_4$/MWNT-ox is excellent: we did not observe any breakdown during hundreds of cycles which were repeatedly carried out for the same electrode.

5. CONCLUSIONS

Molecular and SWNT-wiring is a feasible method of activation of $LiMPO_4$ olivines for electrochemical Li-storage. The activation is achieved by a monolayer of redox active molecules and/or assemblies of redox molecules with nanotubes. However, the system is too complicated for practical use in Li-ion batteries. From this point of view, the application of oxidatively functionalized MWNT is the most promising strategy.

The composite of $LiMnPO_4$ (olivine) with functionalized MWNT shows enhanced electrochemical charge/discharge performance, which, however, is not comparable to that of the state-of-art carbon-coated $LiMnPO_4$ (olivine). The surface functionalization also promotes the electrolyte breakdown at potentials >4.2 V.

In contrast to $LiMnPO_4$, excellent electrochemical activation of $LiFePO_4$ by functionalized nanotubes was found. The charging was reversible near 100 % and was unperturbed during repeated discharge/charge cycling at C/2 to 10C. This confirms that there was no significant nanotube-mediated electrolyte breakdown at the operating voltage of $LiFePO_4$ (olivine) cathode in Li-ion batteries. The percolation threshold for nanotube networking of our $LiFePO_4$ was between 1 to 2 wt% of MWNT-ox in the composite.

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