Enhancement of Electrochemical Activity of $LiFePO_4$ (olivine) by Amphiphilic Ru-bipyridine Complex Anchored to a Carbon Nanotube

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Single walled carbon nanotubes (SWNTs) were dissolved in an acetonitrile + *tert*-butanol mixture, using the amphiphilic Ru-bipyridine complex NaRu(4-carboxylic acid-4′-carboxylate)(4,4′-dinonyl-2,2′bipyridine)$(NCS)_2$ as a surfactant. The assembly of the SWNT/Ru-bipyridine complex was adsorbed on the surface of $LiFePO_4$ (olivine), providing a material with approximately monolayer coverage by the Ru-bipyridine complex and ca. 0.04 wt % of SWNT. Electrodes fabricated from the surface-derivatized $LiFePO_4$ exhibited 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 Ru-bipyridine complex or by carbon nanotubes dispersed with the redox inactive pyrene butanoic acid. The SWNT backbone promotes the interfacial charge transfer between $LiFePO_4$ and the Ru-complex, whose redox potentials closely match each other. The nanotube-mediated redox wiring of virtually insulating electrode materials such as $LiFePO_4$ presents a novel strategy for application in high-energy lithium-ion batteries.

Introduction

The advent of olivine phosphates as novel cathode materials for lithium-ion batteries stems from the pioneering work of Goodenough and co-workers,[1] who had first reported on two generic structures, *viz.* $LiFePO_4$ and $LiMnPO_4$, as well as the mixed phases ($LiFe_xMn_{1-x}PO_4$ ($0 < x < 1$). Both materials are poor electronic conductors; the reported conductivities of $LiFePO_4$ and $LiMnPO_4$ are ($\sim 10^{-8}-10^{-9}$) S/cm and ($< 10^{-10}$ to 3×10^{-9}) S/cm, respectively.[2−4] The optical band gap of $LiFePO_4$ is between 3.8 eV and 4.0 eV, which accounts for the negligible concentration of intrinsic charge carriers.[5] Therefore, the electronic charge can only be transported via localized polarons at the transition metal, the mobility of which is a thermally activated (hopping) process. Nazar et al.[6] have noted that the polaron hopping is strongly correlated with the Li^+ transport. Enhancement of the electronic conductivity of $LiMPO_4$ (M = Mn, Fe) requires proper engineering of the material morphology[2,7−10] and surface modification, for which the carbon coating is the obvious strategy.[4,8,10−13] An alternative pathway is based on the doping of $LiFePO_4$ by supervalent cations, such as Zr^{4+} and Nb^{5+} at the Li^+ site;[14] however, this approach also raised

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some debate about the possible influence of carbon coating. Eventually, the conductive coating on $LiFePO_4$ olivine might not be a pure elemental carbon, but iron phosphides or phosphocarbides.[3]

In the conventional solid-state synthesis of $LiMPO_4$ (M = Mn, Fe), carbon is added to the precursor mixture composed of a stoichiometric amounts of the corresponding lithium salts (Li-salt), metal salts (M-salt), and phosphate salts (PO_4^{3-} salts).[4,11] During the synthesis, carbon simultaneously acts as a reductant, avoiding the formation of M^{3+} and also as a separator, blocking the growth of crystals.[11] The suppression of crystal growth by carbon manifests itself by the formation of particles in the 60−100 nm range. Li et al.[12] reported that $LiMnPO_4$ that was synthesized in this way delivered 140 mAh/g at 0.28 mA/cm^2. Unfortunately, this promising result was not reproduced by others,[4,10,13] and the cited paper[12] remains controversial.

The slow polaron mobility in $LiMPO_4$ is a fundamental problem, which, presumably, can be minimized by decreasing the particle size and by optimized decoration of particles with conductive carbon.[10] Recently, Graetzel and co-workers[15,16] developed a novel strategy for the charging/discharging of virtually insulating cathode materials such as $LiMPO_4$ (called molecular wiring[15] and redox targeting[16]). These methods are based on electron/hole transport from a redox active molecule interacting with the $LiMPO_4$ surface. Here, we report on a striking enhancement of the interfacial charge transfer, if the redox-active molecule is noncovalently bonded to a single walled carbon nanotube (SWNT) and the formed assembly is adsorbed on the $LiFePO_4$ surface.

Experimental Section

$LiFePO_4$ was synthesized by a variant of solid-state reaction[17] as follows. The stoichiometric amounts $FeC_2O_4{\cdot}2H_2O$ and LiH_2PO_4 were mixed and ground in a planetary ball-milling machine for 4 h. Then the powder was calcined in a tube furnace with flowing Ar−H_2 (92/8 v/v) at 600 °C for 24 h. After cooling down to room temperature, the sample was ground in agate mortar. X-ray diffraction (XRD) confirmed the phase purity. The Brunauer−Emmett−Teller (BET) surface area of the powder was ca. 5 m^2/g, with an average particle size of ca. 400 nm. SWNTs were grown by catalytic dual-beam laser ablation method. The main ablation laser was Nd:YAG operating at 1064 nm, with a frequency of 20 Hz and ~800 mJ per pulse, accompanied by a continuous CO_2 laser (power of ~100 W at 10.6 μm). Both lasers were focused to a diameter of 6 mm, scanning at the target. The target was prepared by dry pressing a composition of 1% nickel, 1% cobalt, and 98% graphite. The working atmosphere was argon at 660 mbar and 500 sccm flow, and the temperature was 1200 °C. (The acronym sccm represents standard cubic centimeters per minute.) Such a setup produced ca. 300 mg SWNT per day. The average diameter of tubes was determined by Raman and visible−near-infrared (Vis-NIR) spectroscopy to be ca. 1.3−1.4 nm. The Ru-bipyridine complex, NaRu(4-carboxylic acid-4′-carboxylate)(4,4′-dinonyl-2,2′bipyridine)$(NCS)_2$, coded as Z-907Na was synthesized as described elsewhere.[18] Other chemicals were from commercial sources and were used as received.

The SWNTs were dispersed with solutions of surfactants (either pyrene butanoic acid in dimethylformamide (DMF) or Z-907Na in acetonitrile + *t*-butanol (1:1) (AN/*t*-BuOH) by sonication. The optimized synthetic protocol using Z-907Na was as follows: 9 mg of SWNT was sonicated for 2 h with 10 mL of 6×10^{-4} mol/L Z-907Na in acetonitrile + *t*-butanol (1:1). The resulting black−brown solution was centrifuged at 5000 rpm for 1 h, while ca. 4 mg of undissolved carbon remained as sediment. This working solution (abbreviated as Z-907Na/SWNT) was stable for at least months at ambient temperature without precipitation. The olivine $LiFePO_4$ (200 mg) powder was mixed with several portions (0.5 − 0.7 mL) of this working solution. At the initial stages, the supernatant turned to colorless within several seconds after mixing. After each addition of the Z-907Na/SWNT solution, the slurry was centrifuged, the supernatant separated, and a next portion of the solution was added. This procedure was repeated until the supernatant did not decolorize. The total amount of applied solution was 1.5 mL. Finally, the powder was washed with AN/*t*-BuOH and dried at room temperature; the product is further coded Z907/SWNT/$LiFePO_4$. The same synthetic protocol was also adopted also for surface derivatization of $LiFePO_4$ with pyrene butanoic acid/SWNT. Electrodes were prepared by mixing the powder of surface-derivatized $LiFePO_4$ with 5 wt % of poly(vinylidene fluoride) (PVDF) dissolved in *N*-methyl-2-pyrolidone. The resulting homogeneous slurry was then doctor-bladed onto fluorine-doped conducting glass (FTO) and dried at 100 °C overnight. The typical film mass was 1.5−2 mg/cm^2. Blank electrodes from pure $LiFePO_4$ were prepared in the same way for reference experiments. A second reference material was a carbon-coated $LiFePO_4$ (Nanomyte BE-20, from NEI Corporation, USA).

The morphology of the materials was investigated with a Hitachi S-4700 scanning electron microscopy (SEM) system. Vis-NIR spectra were measured using a Varian Cary 5 spectrometer in 2-mm glass optical cells. The measurement was conducted in transmission mode with an integrating sphere. Electrochemical experiments used an Autolab PGSTAT 30 potentiostat. The reference and counter-electrodes were made from lithium metal. The electrolyte solution was 1 mol/L $LiPF_6$ in ethylene carbonate + dimethylcarbonate (EC/DMC; 1/1, v/v). Experiments on battery cycling were conducted galvanostatically using an Arbin BT 2000 electrochemical measurement system. For this purpose, the electrodes were prepared from the Z907/SWNT/$LiFePO_4$ composite bonded with 5% PVDF as described previously, except for the fact that the film was deposited an aluminum current collector instead of FTO, and the film mass was in the range of 5−9 mg/cm^2. Reference battery cycling experiments were also performed with the Z907/SWNT/$LiFePO_4$ mixed with 5% graphite (KS4) and 5% PVDF. After drying at 160 °C under vacuum, the electrodes were compressed into 23-mm-diameter disks. The cells were assembled in Swagelock fittings using lithium metal foil as the counterelectrode with a microporous polymer separator (Celgard 2400).

Results and Discussion

Figure 1 shows the optical spectra of acetonitrile + *t*-butanol (1:1) solutions of Z-907Na either pure (curve B) or containing dispersed carbon nanotubes (curve A; this

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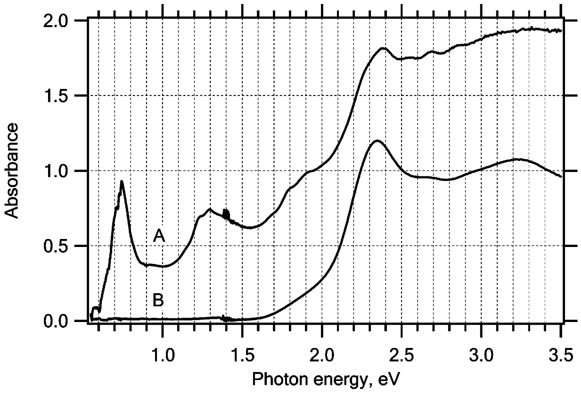
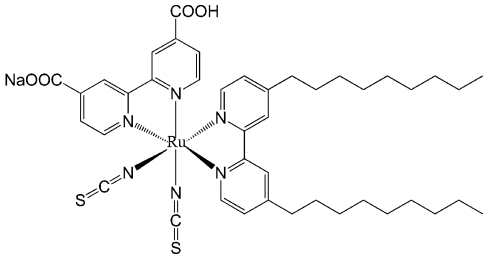


Figure 1. Optical visible−near-infrared (Vis-NIR) spectrum of the working solution of single wall carbon nanotubes (SWNTs) dispersed by Ru-complex, Z-907Na/SWNT (curve A) and pure Ru-complex Z-907Na (curve B). The concentration of Ru-complex was 6×10^{-4} mol/L in both cases, and the optical cell thickness was 2 mm.

Scheme 1. Formula of Z-907Na



solution is further coded Z-907Na/SWNT). Spectrum A (Figure 1) exhibits the characteristic features of carbon nanotubes.[19] Semiconducting SWNT are characterized by optical transitions between van Hove singularities at ca. 0.7 and 1.3 eV for the first and second pair of singularities, respectively. Metallic tubes manifest themselves by a transition at 1.8−1.9 eV, which corresponds to the first pair of van Hove singularities. The main peak of Z-907Na occurs at 2.35 eV and is blue-shifted by ca. 50 meV in the SWNT-containing solution (see Figure 1). Obviously, the Z-907Na complex acts as an efficient surfactant for SWNT, because of the presence of the two hydrophobic aliphatic C_9 chains (Scheme 1), which interact with the carbon tube surface. The solution is stable against precipitation for at least months at ambient temperature.

Many other molecules that solubilize SWNTs have been reported, the most popular being sodium dodecyl sulfate (SDS).[20] However, to the best of our knowledge, the solubilization of SWNT by Ru-bipyridine complexes is demonstrated here for the first time. We should note that the described effect is just opposite to that observed for $[Ru(phenantroline)_3]^{2+}$: The latter complex causes coagulation of the carbon nanotubes in a dimethylformamide (DMF) medium, instead of promoting their dissolution.[21] The interpretation is straightforward: simple ionic species, such as $Ru(diimine)_3^{2+}$ or $RuCl_3$, increase the ionic strength of solution, and, hence, nanotubes that are separated by less than the Debye length flocculate.[21]

The morphology of our composite Z-907Na/SWNT/$LiFePO_4$ is shown in a scanning electron microscopy (SEM) image in Figure 2. Obviously, the submicrometer-sized olivine particles are cross-linked with carbon nanotubes, which are anchored to the $LiFePO_4$ surface. The SWNTs in the composite seem to be, at least partly, aligned into bundles. Although the dissolution of nanotubes with surfactants such as Z-907Na is, obviously, promoted by an exfoliation of bundles, they may partly recombine during subsequent interaction of the surfactant (Z-907Na) with the $LiFePO_4$ surface. However, we did not observe any flocculation of nanotubes in the composite. Hence, the adsorption of Z-907Na on the $LiFePO_4$ surface does not break all the Z-907Na/SWNT interactions, which would release the tubes into a separate phase of surfactant-free bundles. Hence, the Z-907Na/SWNT/$LiFePO_4$ keeps the morphology of a homogeneous composite, in which the $LiFePO_4$ crystals are interconnected with the Z-907/SWNTs "wires". This is beneficial for their electrochemical activation, vide infra.

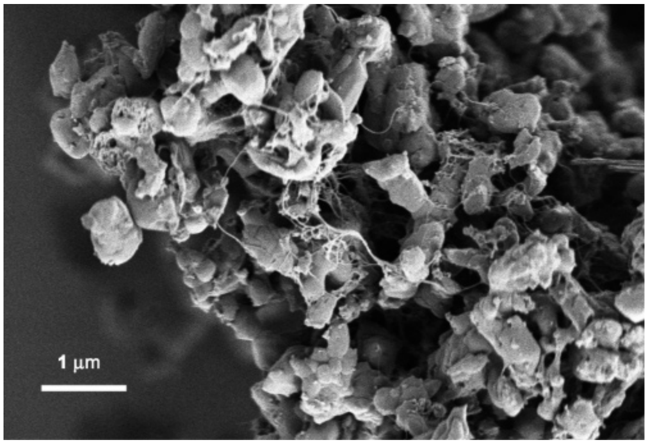


Figure 2. Scanning electron microscopy (SEM) image of the Z-907Na/SWNT/$LiFePO_4$ composite.

Figure 3 (left-hand chart) shows the cyclic voltammogram of a thin-film electrode from pure, carbon-free $LiFePO_4$ (bonded with 5 wt % PVDF), which was treated by dip-coating into the 6×10^{-4} mol/L solution of Z-907Na for 3 h, rinsing with AN/*t*-BuOH, and drying under vacuum at room temperature. The right-hand chart plots analogous data for a pure $LiFePO_4$ electrode, which was treated with the Z-907Na/SWNT solution in the same way. We see a plateau anodic current, which indicates the so-called "molecular wiring" of $LiFePO_4$.[15,16] The Z-907 complex (as in Scheme 1, but with both carboxyls protonated) can transport electronic charge via surface percolation in an adsorbed monolayer, even on insulating surfaces such as Al_2O_3.[22] Here, the NCS groups act as mediators for the surface-confined hole percolation, and the bipyridine ligands transport electrons. The hole diffusion coefficient within the adsorbed Z-907 was on the order of 10^{-9} cm^2/s above the charge percolation threshold, ca. 50% of surface coverage.[22]

Our data confirm that the hole-transport wiring is possible with the Z-907Na complex. The anodic current, which can be wired to the $LiFePO_4$ electrode, exceeds 0.2 mA/cm^2 at a scan rate of 0.1 V/s. The formal redox potential of Z-907Na adsorbed on an inert TiO_2 surface was ca. 3.5 V vs Li/Li$^+$,[22,23]

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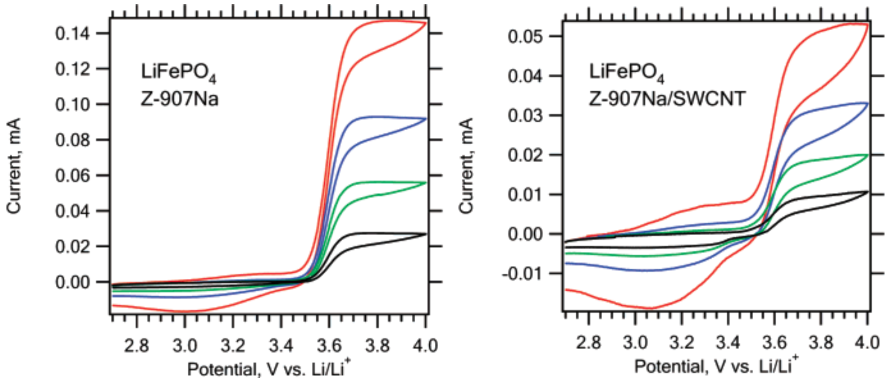

Figure 3. Cyclic voltammograms of pure $LiFePO_4$ electrode (with 5% PVDF; total film mass of 1.54 mg/cm^2) treated by dip coating into 6×10^{-4} mol/L solution of Z-907Na (left-hand chart) or Z-907Na/SWNT (right-hand chart). Scan rates are 50, 20, 10, and 5 mV/s for the curves, from top to bottom. Electrolyte solution: 1 mol/L $LiPF_6$ in EC/DMC.

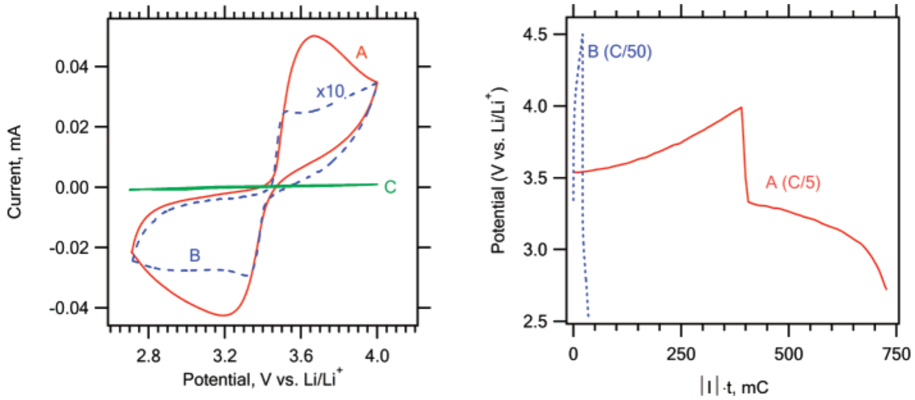

Figure 4. Left-hand chart: Cyclic voltammograms (scan rates of 0.1 mV/s); electrolyte solution 1 mol/L $LiPF_6$ in EC/DMC. (A) Electrode from the Z-907Na/SWNT/$LiFePO_4$ composite (2.04 mg/cm^2); (B) (dashed line) electrode from carbon-coated $LiFePO_4$ (Nanomyte BE-20, 2.28 mg/cm^2); and (C) Electrode from $LiFePO_4$ surface-derivatized with pyrene butanoic acid/SWNT (1.83 mg/cm^2). The current scale is multiplied by a factor of 10 for curve B. Right-hand chart: Galvanostatic chronopotentiometric cycle; electrolyte solution 1 mol/L $LiPF_6$ in EC/DMC. (A) Electrode from the Z-907Na/SWNT/$LiFePO_4$ composite (2.04 mg/cm^2), charging rate C/5. (B) (dashed line) Electrode from carbon-coated $LiFePO_4$ (Nanomyte BE-20, 2.28 mg/cm^2), charging rate C/50.

which is just sufficient for the anodic wiring of $LiFePO_4$ (whose redox potential is 3.45 V vs Li/Li$^+$) but not for cathodic wiring. Our data on Figure 3 also confirm that the −COOH/−COONa are suitable anchoring groups for the surface of $LiFePO_4$. The total anodic charge was between 2 mC and 4 mC (0.4−0.7 mAh/g) for the electrode in Figure 3 (left-hand chart) at the given scan rates. This charge was not much larger at slower scanning, and, moreover, the electrode was unstable during repeated cycling at slower scan rates. Obviously, the molecular wiring via adsorbed Z-907Na is sensitive to imperfections in the surface layer, which hamper the hole percolation.

Figure 3 (right-hand chart) shows a variant of the previous experiment, where the $LiFePO_4$/PVDF thin film was treated by dip-coating into the Z-907Na/SWNT solution. Surprisingly, the anodic current is now considerably smaller, which may be due to poor accessibility of the pores in the pre-deposited fluoropolymer-bonded $LiFePO_4$ layer for SWNT. As the carbon nanotubes are typically 1−10 μm long, they cannot easily interpenetrate the compact solid film. Hence, the Z-907Na/SWNT assemblies reside prevailingly on top of the $LiFePO_4$/PVDF layer. We may assume that either some free complex Z-907Na may still be present in our working solution (Z-907Na/SWNT) or may be partly released from the SWNT upon interaction with the $LiFePO_4$ surface (cf. the discussion of Figure 2 above). This causes poor surface coverage and attenuated molecular wiring in this case.

However, this situation changes dramatically, if the electrode is fabricated from the separately pre-synthesized Z-907Na/SWNT/$LiFePO_4$ composite powder. Figure 4 (left-hand chart) shows the cyclic voltammogram of an electrode made from the Z-907Na/SWNT/$LiFePO_4$ composite, which was subsequently bonded with 5% PVDF and finally doctor-bladed on an FTO current collector (see Experimental Section). Also shown is the voltammogram of an electrode, which was fabricated in the same way, but instead of using Z-907Na as a surfactant, the SWNTs were solubilized by pyrene butanoic acid. Obviously, this electrode shows practically no activity, indicating that the sole carbon nanotubes do not promote the charging/discharging of $LiFePO_4$. Also, the electrode from a reference commercial carbon-coated $LiFePO_4$ (Nanomyte BE-20, NEI) shows much less activity, compared to our Z-907Na/SWNT electrode under the same conditions. We should note, however, that the Nanomyte electrode shown in Figure 4 is far from its standard optimum composition: The electrode was fabricated from a pure as-received BE-20 powder bonded with 5% PVDF, but without any deliberate addition of extra graphite. (If 5−10% graphite is added, the BE-20 material shows good

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rate performance with the first cycle charge capacity of 150 mAh/g at 7.5 mA/g; data not shown).

A comparative experiment was carried out with $LiMnPO_4$ which was treated with Z-907Na/SWNT analogously to $LiFePO_4$. However, the $LiMnPO_4$ wired by Z-907Na/SWNT exhibited negligible electrochemical activity (data not shown). This expectedly provides evidence that the redox wiring of $LiMnPO_4$ is impossible, because of the mismatch of the redox potentials of both components, and the presence of nanotubes has no effect for the activation of $LiMnPO_4$. Consequently, our “nanotube wiring” effect is based on a synergic action of adsorbed redox-active molecule, which provides the interfacial charge transfer to the olivine surface and the SWNT, which transports charge to longer distances in the composite. The charging/discharging of $LiFePO_4$ via the surface attached Z-907Na/SWNT assemblies was reasonably reversible, providing, at a scan rate of 0.1 mV/s, the specific capacity of ca. 41 mAh/g for anodic process and 40 mAh/g for cathodic process (see the cyclic voltammogram on Figure 4). The electrode was also quite stable, showing no obvious capacity fading in repeated voltammetric scans.

The exceptional properties of our Z-907Na/SWNT/$LiFePO_4$ electrode are further demonstrated by galvanostatic chronopotentiometric plot in Figure 4 (right-hand chart). Despite the large polarization observed on the curves, the electrode delivered at the charge rate C/5 and cutoff potentials 4 and 2.7 V vs Li/Li^+ the anodic charge of 390 mC (51 mAh/g) and the cathodic charge of 337 mC (44 mAh/g). A comparative test with a reference carbon-coated $LiFePO_4$ (Nanomyte BE-20, NEI; no extra graphite added, see previous discussion) cannot be conducted, because of negligible activity of this electrode at the C/5 rate. Even at slower charging (by a factor of 10), this carbon-coated electrode exhibits much worse performance (see curve B in Figure 4, right-hand chart).

The applied amount of the working solution Z-907Na/SWNT (1.5 mL; 6×10^{-4} mol/L Z-907Na) gives the upper limit of the adsorbed Z-907Na to be 0.9 μmol, and the amount of adsorbed carbon (in the form of SWNT) to be 6.3 μmol per 200 mg of $LiFePO_4$ (see Experimental Section). Therefore, the concentration of elemental carbon from SWNT was <0.04 wt % in the final solid electrode material. From the BET surface area of our $LiFePO_4$ (5 m^2/g), we can calculate that the surface coverage of Z-907Na is equivalent to approximately 1 molecule per 2 nm^2. This is not far from the monolayer coverage, if we take into account the usual dimensions of Ru-bipyridine molecules.[24]

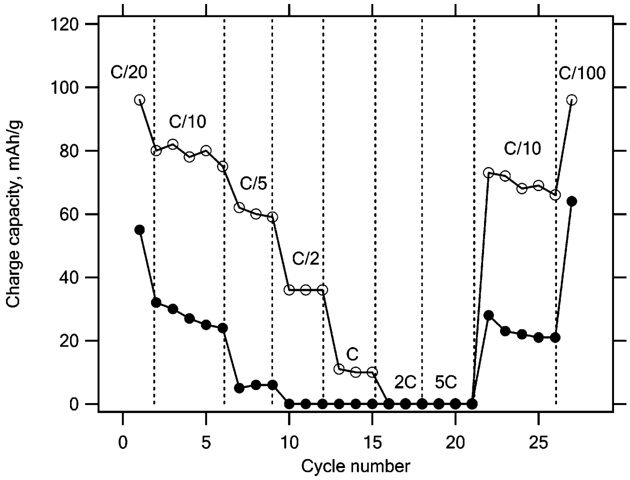

Figure 5. Galvanostatic charge/discharge cycling of a Swagelock-type cell with a lithium-metal anode. The charging rate was changed during the cycling from C/20 to 5C to C/100, as indicated on the graph. Full points: electrode from Z-907Na/SWNT/$LiFePO_4$ (8.6 mg/cm^2) bonded with 5% PVDF. Open points: electrode from Z-907Na/SWNT/$LiFePO_4$ (5.6 mg/cm^2) bonded with 5% PVDF and 5% graphite (KS4).

Figure 5 shows the cycle performance of our Z-907Na/SWNT/$LiFePO_4$ composite at the standard conditions of battery testing. The capacity at C/5 is smaller due to ~4-times-larger material loading and film thickness (cf. Figure 5 and Figure 4, left-hand chart), but charge capacities of ~60 mAh/g are still achievable for a pure Z-907Na/SWNT/$LiFePO_4$ composite at slower charging. The charge capacities expectedly improve as a result of deliberate addition of extra graphite (open points in Figure 5). However, we should stress that our pure material, which is virtually free from any conductive carbon additive (~0.04 wt %; see previous discussion) exhibits significant performance in a real lithium battery. Further optimization of this composite material should address the slow Li^+ diffusion in $LiFePO_4$, which is another issue to be solved, presumably by transforming this approach to nanosized $LiFePO_4$.

The unprecedented activity of the $LiFePO_4$/Z-907Na/SWNT composite is obviously due to the presence of carbon nanotubes, which dramatically enhance the cross-surface-mediated charge transport by the Z-907Na complex by electrically bridging the olivine nanoparticles. This beneficial action of carbon nanotubes even promotes the cathodic process. The latter is almost absent in sole molecular wiring, because of a low driving force of the redox process in Z-907Na for the reduction of $Li_{1-x}FePO_4$ back to the starting stoichiometric composition (see Figure 3).

Conclusions

The amphiphilic Ru-bipyridine complex, NaRu(4-carboxylic acid-4′-carboxylate)(4,4′-dinonyl-2,2′bipyridine)$(NCS)_2$, coded as Z-907Na, can be used as a surfactant for solubilization of single walled carbon nanotubes (SWNTs) in acetonitrile−*t*-butanol (1:1). The Z907Na complex represents an anchored redox functionality of 3.5 V vs Li/Li^+, which matches the formal potential of $LiFePO_4$/$FePO_4$ couple (redox potential 3.45 V vs Li/Li^+) almost exactly.

The supramolecular assembly of SWNT/Ru-bipyridine complex can be adsorbed on the surface of $LiFePO_4$ (olivine) via the free carboxylic groups of Z-907Na. This provides a material with approximately monolayer coverage by the Ru-bipyridine complex. The total amount of elemental carbon in the SWNT form is ~0.04 wt %, which is significantly smaller than the amount of elemental carbon in the conventional composite materials for lithium-ion batteries.

Electrodes fabricated from the Z907/SWNT/$LiFePO_4$ composite exhibited greatly enhanced activity for electrochemical

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(24) Nazeeruddin, M. K.; Pechy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613.

Li^+ extraction/insertion, compared to electrodes from commercial carbon-coated $LiFePO_4$ or from $LiFePO_4$ derivatized either by adsorption of sole Ru-bipyridine complex or by carbon nanotubes dispersed with the redox inactive pyrene butanoic acid. The SWNT backbone promotes the interfacial charge transfer between $LiFePO_4$ and the Ru-complex, whose redox potentials closely match each other.

The "nanotube wiring" effect is based on a synergic action of adsorbed redox-active molecule, which provides the interfacial charge transfer to the olivine surface and the SWNT, which transports charge to longer distances in the composite. The nanotube-mediated redox wiring of virtually insulating electrode materials such as $LiFePO_4$ presents a novel strategy for application in high-energy lithium-ion batteries.

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