

Promoting the activity of LiFePO₄ (olivine) cathode of Li-ion battery by supramolecular complexes with single walled carbon nanotubes

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ABSTRACT

The amphiphilic Ru-bipyridine complex, Z-907Na acts as a surfactant for solubilization of single walled carbon nanotubes (SWNTs) in acetonitrile+*t*-butanol. The supramolecular assembly Z-907Na/SWNT was characterized by optical and Raman spectro/electrochemistry. Its redox potential of 3.5 V vs. Li/Li⁺ is matching almost exactly the formal potential of LiFePO₄/FePO₄ couple. The Z-907Na/SWNT assembly is adsorbed on the surface of LiFePO₄ (olivine) via the free carboxylic groups at the bipyridine ligand. This provides a composite material with roughly monolayer coverage by Z-907Na. Electrodes fabricated from Z-907Na/SWNT/LiFePO₄ composite exhibited greatly enhanced activity for electrochemical Li⁺ extraction/insertion compared to the performance of electrodes made from pure LiFePO₄.

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

1 MOLECULAR WIRING

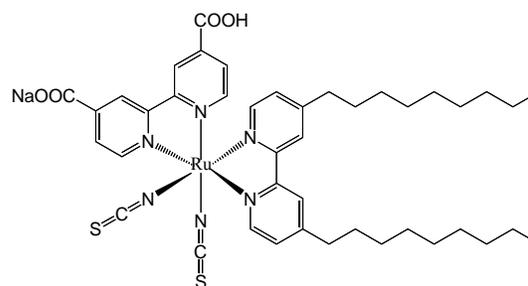
In 1997, Goodenough et al. [1] have introduced the orthorhombic olivine LiFePO₄ (*Pmnb* space group) as a prospective cathode material for Li-ion batteries, offering a redox potential of 3.5 V vs. Li/Li⁺ and theoretical capacity of 170 mAh/g. Since this pioneering discovery, the LiFePO₄ (olivine) attracted 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 LiFePO₄ needs to be addressed [2] either by doping [3] or by carbon additives [4]. Also the strain generated during the charge/discharge may control the performance of olivine cathode [5]. The classical core-shell model with interfacial solid solution of Li_xFePO₄ has been replaced by a model of two-phase conversion of LiFePO₄/FePO₄ with Li⁺ ions moving parallel to the b-axis of the olivine lattice [6,7].

The conductivity of cathode materials for Li-batteries is usually enhanced by addition of graphitic carbon in a pro-

portion of *ca.* 10 wt%. This decreases the faradaic capacity of the composite electrode in the same proportion, because carbon does not contribute to the charge/discharge capacity of the cathode, and especially the volumetric energy density is significantly lower

Graetzel et al. [8,9] have developed a novel strategy to avoid carbon additives in virtually insulating electrode materials. It is called molecular wiring, and is based on hole/electron transport from a current collector *via* a redox active molecule adsorbed on the surface.



Scheme 1: The formula of Z-907Na

Among the suitable redox systems for molecular wiring of LiFePO₄, two molecules turned to be most promising, *viz.* [12-(2,5-di-*tert*-butyl-4-methoxy-phenoxy)-dodecyl]-phosphonic acid, coded DW [10] and NaRu(-4,4'-dicarboxylic acid-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyridine)(NCS)₂, coded Z-907Na [11,12] (see Scheme 1). 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 LiFePO₄ (olivine). In other words, DW is active for anodic molecular wiring that is the oxidized DW⁺ efficiently inject holes into LiFePO₄, and thus cause its subsequent chemical delithiation towards FePO₄:



In principle, the charge transfer process (Eq. 1) can be reversed, if there is correct matching of the redox potential of the relay molecule and the Fermi levels of LiFePO₄/FePO₄ [8]. A complete charge/discharge process can be wired *via* adsorbed molecules provided the redox potential

of the used molecule is close to ≈ 3.45 V vs. Li/Li^+ , which is the potential of LiFePO_4 charging/discharging [8]. Secondly, a fine tuning of the interfacial redox electrochemistry is required via shifting the Fermi level of the $\text{LiFePO}_4/\text{FePO}_4$ system. This is possible by changing the Li^+ activity in electrolyte solution, a_{Li^+} . The Nernst potential of olivine is:

$$E = E_0 + (RT/F) \ln a_{\text{Li}^+} \quad (2)$$

with $E_0 = 3.45$ V vs. Li/Li^+ . In saturated solution of LiPF_6 , E becomes slightly more positive, and allows that electron injection into FePO_4 occurs from the reduced relay molecule with a concomitant lithiation of FePO_4 .

The above mentioned complex, Z-907Na is suitable for wiring of LiFePO_4 , because the redox potential of both systems are similar [11,13]. In 1 M Li^+ -containing electrolyte solution, solely the anodic wiring of LiFePO_4 (delithiation) takes place (Eq. 1) [11]. However, by increasing the a_{Li^+} (cf. Eq. 2) the reversible charge/discharge via Z-907Na is possible in saturated solution of LiPF_6 [12].

2 NANOTUBE WIRING

The molecular wiring (Section 1) allows that the carbon additives are avoided in the olivine cathode, but it requires quite special conditions to be fulfilled, both at the side of the olivine surface and the redox molecule. Hence, this method does not seem to be suitable for practical batteries, which must be robust enough, and work at various temperatures and Li^+ concentrations (Eq. 2) as well as the monolayer of adsorbed wiring molecules must be perfect, because the molecular wiring stops, if the surface coverage is below the charge-percolation threshold [13].

However, efficient wiring is possible, if Z-907Na is anchored to single-walled carbon nanotube [11]. This effect called "nanotube wiring"[11] allows that currents by an order of magnitude larger are wired to the olivine surface. The composite Z907Na/SWNT/ LiFePO_4 exhibited fast and reversible charging/discharging, despite the total amount of elemental carbon in the Z907Na/SWNT/ LiFePO_4 was ca. 0.04 wt% only [11].

2.1 Syntheses and properties: Z-907Na/SWNT

The CoMoCat carbon nanotubes were purchased from SouthWest Nanotechnologies, Inc. The laser-grown nanotubes (further abbreviated LA) were purchased SINEUROPP Nanotech GmbH, Germany. SWNTs were sonicated with 3-6 mM solution of Z-907Na in acetonitrile+*tert*-butanol (1/1, w/w). The resulting solution was centrifuged at 5000 rpm to remove undissolved particles. The atomic ratio C/Ru (C is elemental carbon from SWNT) in the solution was between 70 to 100; this solution was stable for months at room temperature. Figure 1 shows the optical spectra of our solutions. The Vis-spectrum of pure Z-907Na is dominated by the metal-to-ligand charge-transfer transition at ca. 2.25 eV

(MLCT; from the $t_{2g}d$ orbitals localized at Ru(II) to the π orbitals at bipyridine).

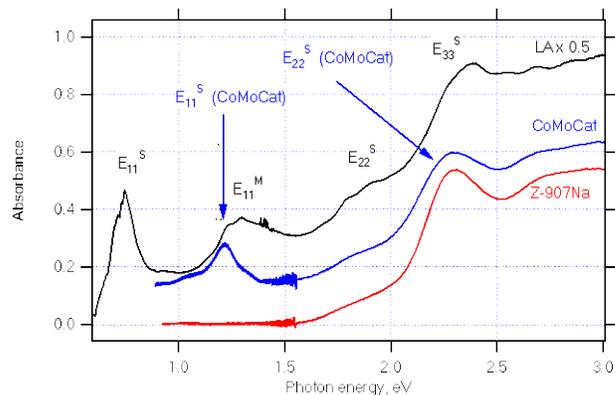


Figure 1: Optical Vis-NIR spectrum of the solution of Z-907Na/SWNT and pure Ru-complex Z-907Na (3mM) in acetonitrile+*tert*-butanol. LA nanotubes were dispersed in 6 mM solution and CoMoCat nanotubes in 3mM solution of Z-907Na. The optical cell thickness was 2 mm.

The spectra of Z-907Na/SWNT exhibit the superposition of this MLCT with optical transitions in SWNT. The latter are at ca 1.2 eV for the CoMoCat, and are assignable to the optical transitions between the first pair of Van Hove singularities in semiconducting tubes, E_{11}^S of rather small diameters. They comprise the (6,5), (7,5), (8,3) and (8,4) tubes with diameters between 0.757 to 0.840 nm [12,14,15]. The laser-grown tubes (LA, diameters 1.3 – 1.4 nm) showed a broad E_{11}^S band centered at 0.75 eV. The interaction of Z-907Na with SWNT manifests itself by a blue shift of E_{11}^S . For the LA tubes, the E_{11}^S equal: 0.68 eV (bundled pure SWNTs), 0.71 eV (assembly in thin film) and 0.75 eV (assembly in solution, Fig. 1) [12,14,15].

The assembly Z-907Na/SWNT was further characterized by in-situ Raman spectroelectrochemistry at various potentials [15]. Two laser excitation energies were used: 2.18 eV (Kr^+ -laser) and 2.41 eV (Ar^+ laser). Figure 1 confirms that these lasers resonate both with the MLCT as well as with E_{22}^S (CoMoCat) E_{33}^S (LA). Application of electrochemical potential causes attenuation of the nanotube-related Raman lines at both cathodic/anodic charging, but the Raman lines, assigned to Z-907Na, selectively bleach for anodic charging only. The attenuation of tube-related features is caused by erasing of resonance-enhancement due to quenching of optical transitions E_{22}^S (CoMoCat) and E_{33}^S (LA). This effect is generally amphoteric, both for pure SWNT and for the assembly Z-907Na/SWNT. In contrast to the tube-related transitions, the MLCT band is quenched selectively as a result of the oxidation of Ru(II) to Ru(III). This reaction generates a significantly red-shifted LMCT band (at ca. 1.6 eV). Hence, the hole injection into the supramolecular assembly causes abrupt attenuation of Raman scattering of the Raman lines assigned to Z-907Na, but there is no mirror effect of electron injection, because the MLCT in Z-907Na remains intact by cathodic charging.

2.2 Synthesis of Z-907Na/SWNT/LiFePO₄

The undoped and carbon-free LiFePO₄ (olivine, LFP) powder with a BET surface area of 9 m²/g was obtained from Süd-Chemie, AG. The powder was mixed with several portions of the working solution of Z-907Na/SWNT (Section 2.1) until complete adsorption occurred. The powder was washed with pure solvent and dried. Electrodes were prepared by mixing the derivatized powder with 5 wt% of polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidone. The resulting homogeneous slurry was then doctor-bladed onto F-doped conducting glass (FTO), cut into smaller pieces and dried at 100°C overnight. The film mass was *ca.* 1.5 – 2 mg/cm². Figure 2 shows its morphology imaged by scanning electron microscopy (SEM). According to ATR-FTIR spectra, there were no apparent differences in the IR active vibrations of the assembly and those of the parent components.

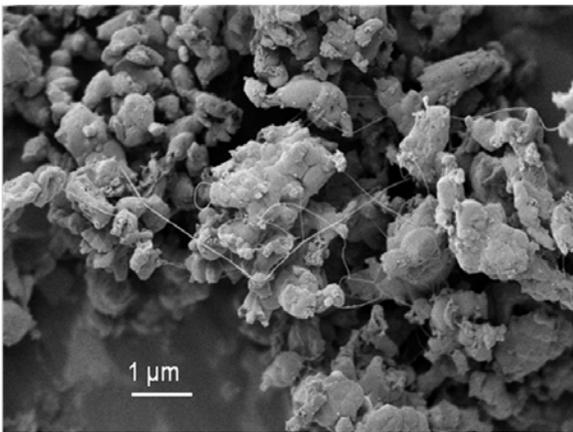


Figure 2: SEM image of the Z-907Na/SWNT/LiFePO₄ composite electrode.

2.3 Electrochemistry of Li-insertion

Electrochemical experiments were carried out under Ar-atmosphere in 1 mol/L LiPF₆ in ethylene carbonate + propylene carbonate + dimethylcarbonate (EC/PC/DMC; 1/1/3; w). The reference and counter electrodes were from Li-metal, hence all potentials are quoted against the Li/Li⁺ reference electrode in this medium.

Figure 3 compares the cyclic voltammograms of a pure (unmodified) LiFePO₄ (LFP) with the voltammogram of the same material upon surface-modification with Z-907Na/SWNT. It is apparent that the nanotube wiring enhances the charge/discharge currents by 2 orders of magnitude. The LA tubes are more efficient for promoting the cathodic reaction (lithiation of FePO₄) than the CoMoCat tubes [11,12].

To rationalize these differences, the voltammograms were studied of Z-907Na/SWNT in thin films deposited on FTO [14]. Surprisingly, the redox reaction Ru(II)/Ru(III) gives rise to a doublet of voltammetric peaks (labeled C₁ and C₂) with formal potentials, E_f of 3.59 and 3.81 V vs. Li/Li⁺, respectively, instead of just single voltammogram, which would be expected in analogy to earlier experiments on Z-907Na adsorbed on the Al₂O₃ or TiO₂ [13].

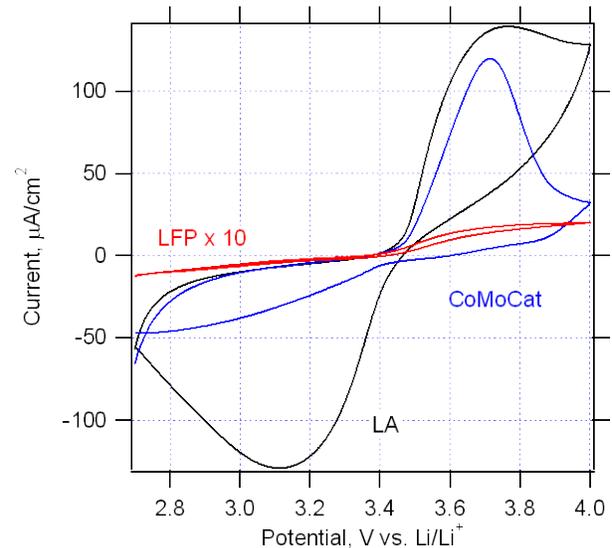


Figure 3: Cyclic voltammetry of the LFP electrode wired with Z-907Na/SWNT (CoMoCat and LA nanotubes). The voltammogram of pure (unmodified) LiFePO₄ (LFP) is also shown; this curve is zoomed in the current scale by a factor of 10. The electrolyte solution is 1 M LiPF₆ in EC+PC+DMC (1/1/3, w); the scan rate is 0.5 mV/s.

The C₁/C₂ peaks are superimposed on the background of capacitive double-layer charging of SWNT which manifests itself by a featureless cyclic voltammogram. The current for capacitive double-layer charging of SWNT, I_C , at the given scan rate, ν scales according to:

$$I_C = m_C \cdot C_C \nu \quad (3)$$

where m_C is the mass of the SWNT film and C_C its specific capacitance; $C_C \approx 40$ F/g. The C₁/C₂ peaks characterize surface confined redox couples, which formally obey Eq. 3, too. The integral area of C₁/C₂ roughly correspond to the oxidation/reduction of all the Z-907Na present in the assembly. Similar voltammogram was found also for the Z-907Na adsorbed on ordinary carbon black. On the other hand, the Z-907Na adsorbed on Al₂O₃ or dissolved in the electrolyte solution show a single diffusion-controlled voltammogram with solely one redox couple at *ca.* 3.6 V vs. Li/Li⁺. In this case, the forward peak current density, J_p

scales with the square root of the scan rate, $v^{1/2}$ according to the Randles-Sevcik equation:

$$J_p = 0.4463nFv^{1/2} D_+^{1/2} v^{1/2} \quad (4)$$

where n is number of electrons and the other symbols have their usual meaning. The diffusion coefficients (from Eq. 4) equal $7.8 \cdot 10^{-10} \text{ cm}^2/\text{s}$ (for Z-907Na adsorbed on Al_2O_3) or $1.5 \cdot 10^{-6} \text{ cm}^2/\text{s}$ (for Z-907Na in solution).

The differences in redox behavior of Z-907Na on carbon or oxidic surfaces are tentatively interpreted as a result of two different anchoring modes (Figure 4). The Z-907Na can interact with surface oxidic functionalities on carbons via the 4,4'-carboxyls on the bipyridine ligand. This interaction is analogous to that occurring on oxidic surfaces (Al_2O_3 or TiO_2). It is termed 'hydrophilic', and it gives rise to the C_1 peaks. For the heteroleptic amphiphilic complex like Z-907Na, there is a specific interaction called 'hydrophobic', which gives rise to the C_2 peaks. This interaction is assumed to consist in the interaction of the carboxyl-free bipyridine with the unperturbed graphene areas on the carbon surface (Figure 4).

The C_1/C_2 peaks exhibit different relative intensities for the supramolecular assembly Z-907Na/SWNT prepared either from the CoMoCat tubes or from the LA tubes. These differences explain, at least qualitatively, why the latter system is more active for promoting the cathodic nanotube wiring (reductive lithiation of FePO_4) and *vice versa*.

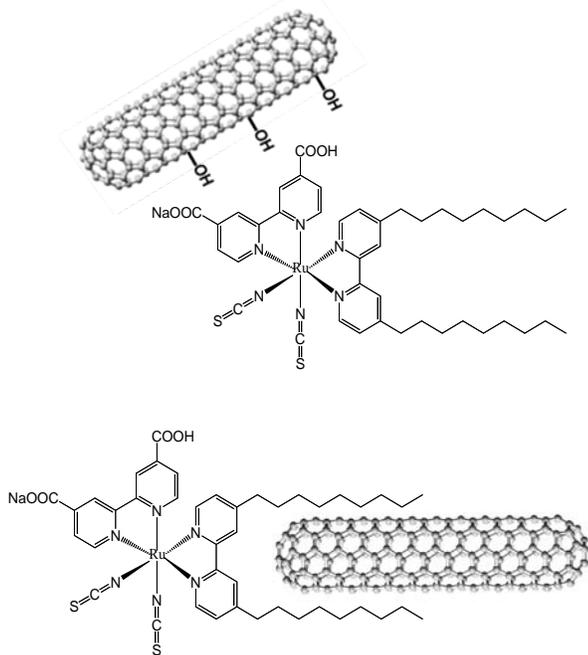


Figure 4: Scheme of two anchoring modes of Z-907Na to SWNT: Hydrophilic (top) and hydrophobic (bottom).

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REFERENCES

- [1] A.K.Padhi, K.S.Nanjundasawamy and J.B.Goodenough, *J.Electrochem.Soc.*, **144**, 1188, 1997.
- [2] B.Ellis, L.K.Perry, D.H.Ryan and L.F.Nazar, *J.Am.Chem.Soc.*, **128**, 2006.
- [3] S.Y.Chung, J.T.Bloking and Y.M.Chiang, *Nature Mat.*, **1**, 123, 2002.
- [4] P.S.Herle, B.Ellis, N.Coombs and L.F.Nazar, *Nature Mat.*, **3**, 147, 2004.
- [5] N.Meetlong, H.Y.J.S.Huang, S.A.Speakman, W.C.Carter and Y.M.Chiang, *Adv.Funct.Mater.*, **17**, 1115, 2007.
- [6] G.Chen, X.Song and T.J.Richardson, *Electrochem.Solid State Lett.*, **9**, A295, 2006.
- [7] L.Laffont, C.Delacourt, P.Gibot, M.Y.Wu, P.Koyman, C.Masquelier, et al., *Chem.Mater.*, **18**, 5520, 2006.
- [8] Q.Wang, N.Evans, S.M.Zakeeruddin, I.Exnar and M.Grätzel, *J.Am.Chem.Soc.*, **128**, 3163, 2007.
- [9] Q.Wang, S.M.Zakeeruddin, D.Wang, I.Exnar and M.Grätzel, *Angew.Chem.*, **118**, 8377, 2006.
- [10] L.Kavan, I.Exnar and M.Grätzel, *Chem.Mater.*, **20**, 3163, 2008.
- [11] L.Kavan, I.Exnar, J.Cech and M.Grätzel, *Chem.Mater.*, **19**, 4716, 2007.
- [12] L.Kavan, I.Exnar, S.M.Zakeeruddin and M.Grätzel, *J.Phys.Chem.C.*, **112**, 8708, 2008.
- [13] Q.Wang, S.M.Zakeeruddin, M.K.Nazeeruddin, R.Humphry-Baker and M.Grätzel, *J.Am.Chem.Soc.*, **128**, 4446, 2006.
- [14] L.Kavan, S.M.Zakeeruddin, I.Exnar and M.Grätzel, *J.Electrochem.Soc.* **156**, K44-K50, 2009.
- [15] L.Kavan, O.Frank, M.Kalbac and L.Dunsch, *J.Phys.Chem.C.* **113**, 2611, 2009.