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Conducting Polymers

A Soft Chemistry Approach to Coating of $LiFePO_4$ with a Conducting Polymer**

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Lithium ion batteries play an important role in reducing atmospheric pollution by enabling the use of clean energy sources like solar, hydro, and wind for transportation. Numerous approaches have been or are being developed for lithium batteries. Particularly interesting for the cathode is the olivine $LiFePO_4$[1] because of its environmentally friendly and inexpensive constituents, iron and phosphate. However, the use of $LiFePO_4$ as a cathode requires that its poor electronic conductivity has to be overcome.[1–2] Several schemes, such as doping of the structure with foreign metal ions, have been put forth to circumvent this drawback;[3] however, the most common approach remains coating with carbon. Coatings are usually formed by mixing an organic precursor with preformed $LiFePO_4$ before a heat treatment at high temperature (500–700 °C) in an inert or reducing atmosphere.[4] The decomposition of the organic constituent leads, in addition to the formation of carbon, to the formation of volatile organic compounds (VOCs), CO, and CO_2, which pose environmental problems.[5] It is, however, more critical for battery applications that irregular coating of $LiFePO_4$ can lead to poor connectivity of the particles and hence performance loss.[6] It would therefore be an important improvement to the current $LiFePO_4$ system, if low temperature methods could be found to coat $LiFePO_4$ uniformly without the formation of VOCs, CO, or CO_2.

Previously it has been shown that conducting polymers, including redox polymers,[7] can have a positive effect on the performance of $LiFePO_4$[8] and other cathode materials such as $Li_{1.03}Mn_{1.97}O_4$[9] and $LiCoO_2$.[10] Several means have been used to make polymer/$LiFePO_4$ composites, including electropolymerization from a suspension of $LiFePO_4$ particles,[8d] polymerization using a chemical oxidant in the presence of the particle[8b] or, more recently, formation of a colloidal suspension of the polymer immediately before the introduction of the $LiFePO_4$ particles.[11]

Herein, we present a methodology that significantly improves the fabrication and use of conducting polymer/$LiFePO_4$ composites. Firstly, the method relies on the intrinsic oxidation power of $Li_{(1-x)}FePO_4$ rather than on an external oxidant as the driving force of the polymerization process. Thus the risk of residual oxidant or oxidant by-products leaching from the polymer into the battery electrolyte, which would wreak havoc on the anode electrode process, is eliminated. Secondly, polymerization propagation requires the reinsertion of lithium into the partially delithiated lithium iron phosphate, as well as the transport of Li^+ ions and electrons through the deposited polymer coating. In turn, these are also the functionality characteristics of an effective conducting coating for $LiFePO_4$. As such, the propagation reaction intrinsically favors the functionality of the final product. Moreover, compared to the classical carbon coating technology, this approach is devoid of high temperature processing and VOCs, CO, and CO_2 formation. Thirdly, an environmentally benign process based on H_2O_2 is used to form $Li_{(1-x)}FePO_4$ from the standard olivine $LiFePO_4$. Finally, the conducting polymer/$LiFePO_4$ composite made by our method can be used directly in a "no-carbon-added" cathode.

The first processing step is delithiation of $LiFePO_4$. Several oxidants, such as nitronium[1,12] and Br_2,[13] are known to delithiate $LiFePO_4$. However, these reagents cannot generally be considered environmentally benign. Instead, inexpensive hydrogen peroxide is used herein because its degradation product is water. Importantly, it has previously been shown that $LiFePO_4$ is stable in water.[14] The first reaction step therefore is:

$$LiFePO_4 + x/2\,H_2O_2 + x\,H^+ \rightarrow Li_{(1-x)}FePO_4 + x\,Li^+ + x\,H_2O \qquad (1)$$

Once the solid $Li_{(1-x)}FePO_4$ is removed from the reaction mixture by filtration, the extracted lithium can be recovered by simple evaporation, thus minimizing the waste.

The second step is the polymerization of 3,4-ethylenedioxythiophene (EDOT) by reinsertion of lithium into $Li_{(1-x)}FePO_4$. EDOT was chosen because the polymerization potential is close to the redox potential of $LiFePO_4$/$FePO_4$ and it is known to from stable films with high electronic conductivity.[15] The lithium source used in Equation (2) is lithium bistrifluoromethanesulfonamide (LiTFSI) since it is a stable salt under ambient conditions[16] and has negligible redox currents below 4.2 V in $LiFePO_4$ lithium batteries.[17] In addition, it has been shown that using TFSI as the counter ion for the oxidized state of PEDOT gives polymers with high conductivity.[18] The polymerization reaction of EDOT by the

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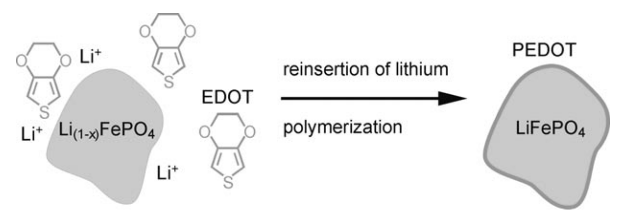

Figure 1. The polymerization reaction. The reinsertion of lithium into $Li_{(1-x)}FePO_4$ leads to the oxidation of EDOT, which is deposited on the solid surface as the conducting polymer PEDOT.

reinsertion of lithium operates without any other source of oxidant or initiator (Figure 1).

The reinsertion of lithium into the structure of $Li_{(1-x)}FePO_4$ follows Equation (2). An excess of LiTFSI is used to maximize the reinsertion of lithium into $Li_{(1-x)}FePO_4$.

$$Li_{(1-x)}FePO_4 + LiTFSI + EDOT \rightarrow PEDOT\text{-}LiFePO_4 \qquad (2)$$

The X-Ray diffractograms (Figure 2) show the industrial grade olivine $LiFePO_4$ without carbon coating before and after the oxidation process. The oxidized material, with the average composition $Li_{(1-0.3)}FePO_4$, as determined by atomic emission/absorption spectroscopy, is composed of 0.7 olivine $LiFePO_4$ and 0.3 heterosite $FePO_4$ (Figure 2, labeled with *). This phase separation is well documented.[19] The final X-Ray diffractogram (Figure 2 c) obtained after the polymerization reaction confirms the reinsertion of the lithium into the olivine structure. The PEDOT coating is not detected by this technique because of its predominantly amorphous nature.

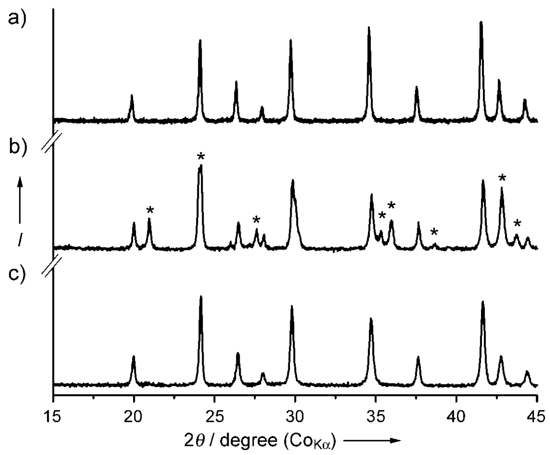

Figure 2. XRD patterns of a) $LiFePO_4$, b) $Li_{(1-0.3)}FePO_4$, and c) PEDOT–$LiFePO_4$.

The TEM micrograph (Figure 3) shows that the thickness of the polymer coating can be as thin as two nanometers for isolated particles. In areas, in which agglomerated particles overlap, the polymer is less uniform and thicker (see Figure S2 in the Supporting Information).

Confirmation of the presence of the PEDOT on the surface of $LiFePO_4$ was achieved by comparison of the IR spectra of $LiFePO_4$, $Li_{(1-x)}FePO_4$, and PEDOT-$LiFePO_4$ (Figure 4). Olivine $LiFePO_4$ have three main bands at 979, 1061, and 1136 cm^{-1} caused by the stretching mode of $(PO_4)^{3-}$. Two other bands at 633 and 647 cm^{-1} stem from the bending modes (ν_2 and ν_4) of P–O–P.[5a] The two new bands at 684 and 1237 cm^{-1} found in the spectrum of $Li_{(1-x)}FePO_4$ indicate the formation of heterosite $FePO_4$.[20] After the polymerization reaction, the formation of PEDOT is confirmed by the C=C ring and C–O–R vibrations at 1181 cm^{-1} and the C–S vibration at 929 cm^{-1}.[21] The polymer *p*-doping is indicated by the bands at 1514 and 1320 cm^{-1}.[22] Thus, the PEDOT formed is similar to the material polymerized by solution oxidants, which exhibit high electronic and ionic conductivities.[23] This result was further evidenced by the conductivity measurement of pressed powders, in which the PEDOT-covered samples showed conductivities in the 0.1 $S\,cm^{-1}$ range, while uncoated samples were below the limit of detection ($< 10^{-6}\ S\,cm^{-1}$).

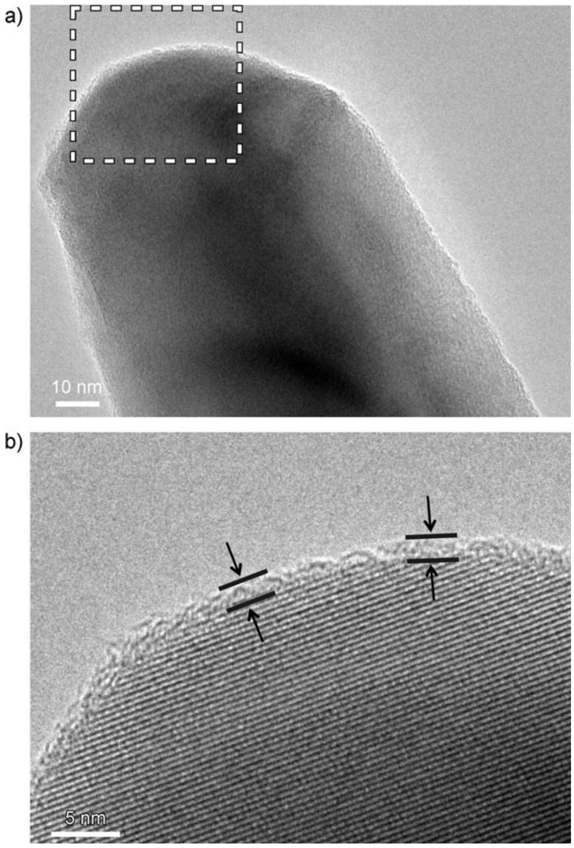

Figure 3. TEM of a) PEDOT–$LiFePO_4$. b) Enlargement of boxed area.

The weight percentage of PEDOT in the $LiFePO_4$ polymer composite was determined by a thermogravimetric analysis. The differential weight loss of $Li_{(1-0.3)}FePO_4$ and PEDOT-$LiFePO_4$ was 7.1 % (see Figure S1 in the Supporting Information).

Electrochemical testing (Figure 5) using coin-type batteries and a constant rate of discharge of ten hours (C/10) showed capacities of 163 $mAh\,g^{-1}$, which are similar to the theoretical capacity of $LiFePO_4$ (170 $mAh\,g^{-1}$). At higher rates of discharge, more specifically at 10 C (at constant current for a discharge in 6 min) the capacity is 123 $mAh\,g^{-1}$

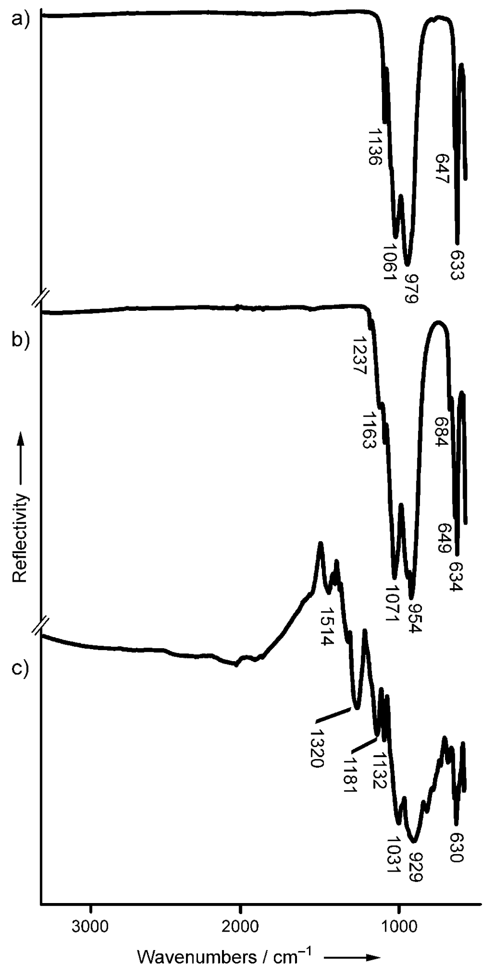

Figure 4. FTIR of a) $LiFePO_4$, b) $Li_{(1-0.3)}FePO_4$, and c) PEDOT–$LiFePO_4$.

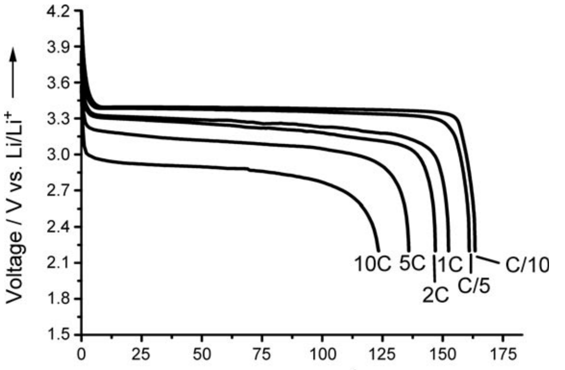

Figure 5. Discharge curves of PEDOT/$LiFePO_4$/PVDF 5.9:86.6:7.5 in wt.%. (Charge conditions are 2.2–4.2 V, versus Li+/Li). The term 1C represents a constant current discharge for 1 hour and C/10 represents a constant current for a discharge in 10 h.

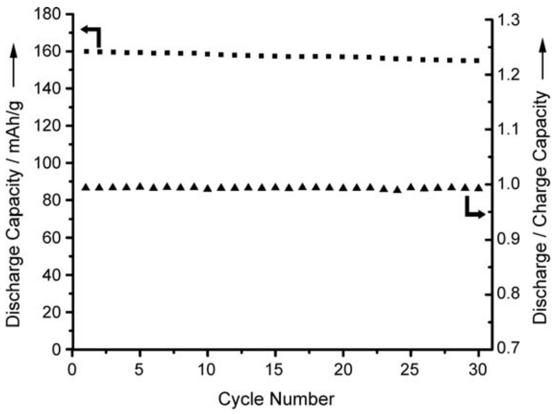

Figure 6. Discharge capacity (squares) and coulombic efficiency (triangles) at the C/2 rate of the PEDOT–$LiFePO_4$ composite at 60 °C. (PEDOT/$LiFePO_4$/PVDF 10:84:6 in wt.%)

that is, approximately 70% of the theoretical capacity. Importantly, $LiFePO_4$ treated in the same manner as the composite, but without the addition of EDOT, exhibit little practical capacity, thus illustrating the importance of the polymer layer (see Figure S5 in the Supporting Information). The PEDOT–$LiFePO_4$ electrochemical tests were performed on "no-carbon-added" electrodes. This is significant since carbon is used in the standard cathode fabrication as an additive that ensures electronic conductivity throughout the electrode. It is however not electrochemically active and therefore diminishes the practical storage capacity of the electrode.[4b] In addition, it also increases the tortuous electrolyte conduction path in the electrode.[24] The ability to replace carbon by a polymeric conductor that conducts both ions and electrons is for these reasons is highly advantageous. Cycling data at the C/2 rate for 30 cycles at 60 °C confirms the stability of the coating in the highly alkaline lithium-ion battery environment (Figure 6).

Using environmentally benign reactants and solvents, we have shown that olivine $LiFePO_4$ can be oxidized to form a product that is appropriate for polymerization of the conducting polymer PEDOT. Importantly, the waste products from this oxidation reaction are only water and lithium acetate. The latter can therefore be recuperated at minimal cost. We have further shown that our polymer coating can eliminate the pyrolysis reaction used to form carbon coating on $LiFePO_4$ without significant electrochemical performance loss. More importantly, we have shown that substituting the standard carbon coating by the conductive polymer leads to a material that can be assembled directly into functional "no-carbon-added" electrodes. Combined, the method reported here offers a compelling case for the replacement of the industrial standard of carbon coating $LiFePO_4$ with our soft chemistry polymerization reaction.

Experimental Section

Formation of $Li_{(1-0.3)}FePO_4$: Glacial acetic acid (2 mL, Alfa Aesar) and hydrogen peroxide (5 mL, ACS Grade, 29.0–32.0%, EMD Chemicals) was added to water (100 mL). Carbon-free $LiFePO_4$ (10.2 g, Phostech Lithium, Saint-Bruno de Montarville, Canada, prepared according to US Patent 7,807,121 B2) in aqueous suspension (250 mL) was added to the solution. The suspension was vigorously stirred for 15 min, filtered, and rinsed with water. The $Li_{(1-x)}FePO_4$ was dried at 60 °C overnight in vacuum. The supernatant was combined with the washing water and analyzed using a Varian spectrAA 220 FS to determine the level of deinsertion of lithium and the iron concentration. When compared to a LiFePO$_4$ sample treated in the same manner, but without the oxidant, no additional iron was found.

Formation of PEDOT-LiFePO$_4$: LiTFSI (3.10 g, 3M™ Fluorad) was dissolved in methanol (25 mL) in a Petri dish. Hereafter 3,4-ethylenedioxythiophene (0.51 g, Aldrich) and Li$_{(1-0.3)}$FePO$_4$ (4.68 g) was added to the solution. The Petri dish was placed in an oven at 60 °C for 2 h. A blue color appeared upon solvent evaporation. The mixture was transferred to a filter and rinsed with methanol and acetonitrile. The PEDOT–LiFePO$_4$ was dried at 60 °C overnight in vacuum. The reinsertion of Li into Li$_{(1-x)}$FePO$_4$ was confirmed by atomic absorption/emission: Li:Fe 1.02 ± 0.02 (95 % confidence interval).

Characterization: The crystal structures were determined using a SIEMENS (D5000) CoK$_\alpha$ diffractometer equipped with a position sensitive detector. TEM images were recorded with Jeol JEM-2100F TEM operating at 200 kV. The FTIR analysis was carried out with a Nicolet 6700 FTIR Smart Endurance using the Single-Reflection Diamond ATR tool. The electrochemical properties of PEDOT–LiFePO$_4$ were determined with CR2032-type coin cells using metallic lithium as the anode. The cathode was made by coating PEDOT–LiFePO$_4$ and a solution of PVDF (Kynar KF Polymer W#1100) in *N*-methylpyrrolidone (Aldrich) onto carbon-coated Al foil (Exopack #2651). The product ratio was PEDOT/LiFePO$_4$/PVDF (8:84.5:7.5 in wt. %). The thickness of the active materials varied between 13 μm to 30 μm. The cells were assembled in an argon atmosphere glove box ($H_2O < 1$ ppm, $O_2 < 1$ ppm). The electrolyte was LiPF$_6$ (1 M) in a 1:1 ethylene carbonate and dimethyl carbonate mixture (Novolyte Technologies). Celgard 2500 was used as the separator. Electrochemical testing was completed using constant current cycling, between 2.2 and 4.2 V using a Bio-Logic VMP3 potentiostat. For room-temperature testing a charging rate of C/10 was used, while 60 °C testing required 5 cycles of break in at the C/10 rate (data not shown) before stability cycling at the C/2 rate.

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[1] A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, *J. Electrochem. Soc.* **1997**, *144*, 1188.

[2] P. P. Prosini, M. Lisi, D. Zane, M. Pasquali, *Solid State Ionics* **2002**, *148*, 45.

[3] S.-Y. Chung, J. T. Bloking, Y.-M. Chiang, *Nat. Mater.* **2002**, *1*, 123.

[4] a) M. Konarova, I. Taniguchi, *Powder Technol.* **2009**, *191*, 111; b) Z. Chen, J. R. Dahn, *J. Electrochem. Soc.* **2002**, *149*, A1184; c) N. Ravet, J. B. Goodenough, S. Besner, M. Simoneau, P. Hovington, M. Armand, *The Electrochemical Society and The Electrochemical Society of Japan, Meeting Abstracts*, **1999**, *99–2*, Honolulu, HI, Oct 17–22.

[5] a) A. Ait Salah, A. Mauger, K. Zaghib, J. B. Goodenough, N. Ravet, M. Gauthier, F. Gendron, C. M. Julien, *J. Electrochem. Soc.* **2006**, *153*, A1692; b) S.-T. Myung, S. Komaba, N. Hirosaki, H. Yashiro, N. Kumagai, *Electrochim. Acta* **2004**, *49*, 4213.

[6] a) Y. Wang, Y. Wang, E. Hosono, K. Wang, H. Zhou, *Angew. Chem.* **2008**, *120*, 7571; *Angew. Chem. Int. Ed.* **2008**, *47*, 7461; b) Y. Hu, M. M. Doeff, R. Kostecki, R. Finones, *J. Electrochem. Soc.* **2004**, *151*, A1279.

[7] D. Wang, S. E. Ela, S. M. Zakeeruddin, P. Pechy, I. Exnar, Q. Wang, M. Grätzel, *Electrochem. Commun.* **2009**, *11*, 1350.

[8] a) K.-S. Park, S. B. Schougaard, J. B. Goodenough, *Adv. Mater.* **2007**, *19*, 848; b) G. X. Wang, L. Yang, Y. Chen, J. Z. Wang, S. Bewlay, H. K. Liu, *Electrochim. Acta* **2005**, *50*, 4649; c) Y.-H. Huang, K.-S. Park, J. B. Goodenough, *J. Electrochem. Soc.* **2006**, *153*, A2282; d) I. Boyano, J. A. Blazquez, I. de Meatza, M. Bengoechea, O. Miguel, H. Grande, Y. Huang, J. B. Goodenough, *J. Power Sources* **2010**, *195*, 5351.

[9] C. Arbizzani, M. Mastragostino, M. Rossi, *Electrochem. Commun.* **2002**, *4*, 545.

[10] L.-J. Her, J.-L. Hong, C.-C. Chang, *J. Power Sources* **2006**, *157*, 457.

[11] A. Vadivel Murugan, T. Muraliganth, A. Manthiram, *Electrochem. Commun.* **2008**, *10*, 903.

[12] C. Delacourt, J. Rodríguez-Carvajal, B. Schmitt, J.-M. Tarascon, C. Masquelier, *Solid State Sciences* **2005**, *7*, 1506..

[13] A. S. Andersson, B. Kalska, L. Häggström, J. O. Thomas, *Solid State Ionics* **2000**, *130*, 41.

[14] a) W. Porcher, P. Moreau, B. Lestriez, S. Jouanneau, D. Guyomard, *Electrochem. Solid-State Lett.* **2008**, *11*, A4; b) K. Zaghib, M. Dontigny, P. Charest, J. F. Labrecque, A. Guerfi, M. Kopec, A. Mauger, F. Gendron, C. M. Julien, *J. Power Sources* **2008**, *185*, 698.

[15] a) H. Yamato, M. Ohwa, W. Wernet, *J. Electroanal. Chem.* **1995**, *397*, 163; b) G. Heywang, F. Jonas, *Adv. Mater.* **1992**, *4*, 116.

[16] L. J. Krause, W. Lamanna, J. Summerfield, M. Engle, G. Korba, R. Loch, R. Atanasoski, *J. Power Sources* **1997**, *68*, 320.

[17] F. Sauvage, L. Laffont, J. M. Tarascon, E. Baudrin, *J. Power Sources* **2008**, *175*, 495.

[18] P. M. Dziewoński, M. Grzeszczuk, *Electrochim. Acta* **2010**, *55*, 3336.

[19] a) C. Delacourt, P. Poizot, J.-M. Tarascon, C. Masquelier, *Nat. Mater.* **2005**, *4*, 254; b) C. Delmas, M. Maccario, L. Croguennec, F. Le Cras, F. Weill, *Nat. Mater.* **2008**, *7*, 665.

[20] a) A. Ait Salah, P. Jozwiak, K. Zaghib, J. Garbarczyk, F. Gendron, A. Mauger, C. M. Julien, *Spectrochim. Acta Part A* **2006**, *65*, 1007; b) C. M. Burba, R. Frech, *J. Electrochem. Soc.* **2004**, *151*, A1032.

[21] C. Kvarnström, H. Neugebauer, S. Blomquist, H. J. Ahonen, J. Kankare, A. Ivaska, *Electrochim. Acta* **1999**, *44*, 2739.

[22] a) C. Kvarnström, H. Neugebauer, A. Ivaska, N. S. Sariciftci, *J. Mol. Struct.* **2000**, *521*, 271; b) P. Damlin, C. Kvarnström, A. Ivaska, *J. Electroanal. Chem.* **2004**, *570*, 113.

[23] a) M. J. Ariza, T. F. Otero, *Colloids Surf. A* **2005**, *270–271*, 226; b) C. Deslouis, T. El Moustafid, M. M. Musiani, B. Tribollet, *Electrochim. Acta* **1996**, *41*, 1343; c) T. Shimidzu, A. Ohtani, K. Honda, *J. Electroanal. Chem.* **1988**, *251*, 323.

[24] I. V. Thorat, D. E. Stephenson, N. A. Zacharias, K. Zaghib, J. N. Harb, D. R. Wheeler, *J. Power Sources* **2009**, *188*, 592.