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Molecular Batteries: Harnessing $\text{Fe}(\text{CN})_6^{3-}$ Electroactivity in Hybrid Polyaniline–Hexacyanoferrate Electrodes**

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Recent progress on hybrid organic–inorganic materials has concerned mainly the development of structural materials based on hybrid silicon–carbon networks.^[1–3] There is another category of materials that can also benefit from the synergy offered by the hybrid concept. In functional hybrid materials, for instance, the emphasis is not put on the improvement of mechanical properties but on harnessing useful chemical properties of the components. The combination of dissimilar compounds offers an opportunity to find complementary and synergic behavior in these materials.^[4]

This approach has guided our recent work on the design of functional hybrid materials based on conducting organic polymers (COPs) and electroactive inorganic species.^[4–15] The hybrid materials have the polymeric nature and good conductivity of COPs, and the added electroactivity of the inorganic species.^[4–6,10–12] This concept offers a way to harness the electroactivity of molecular species, putting them to work in a solid polymeric matrix, leading to hybrid materials that could be

useful as electrodes for plastic batteries. Among the hybrids with molecular anions, those based on polyoxometalates were first studied as models due to the structural and chemical connection of heteropolyanions with metal-oxide clusters.^[16,17] Thus, the synthesis, characterization, and electrochemical properties of polypyrrole/ $\text{PMo}_{12}\text{O}_{40}^{5-}$ and polyaniline/ $\text{PMo}_{12}\text{O}_{40}^{10-}$ hybrid materials were first reported. When heteropolyanions such as phosphomolybdate [$\text{PMo}_{12}\text{O}_{40}^{3-}$] are used as doping species, they are anchored into polyaniline (PAni) or polypyrrole (PPy) thanks to their large size and charge, which results in a cation-insertion mechanism during reduction of the hybrid.^[4,5,8,10] Thus, contrary to conventional p-doped COPs, these materials are lithium-insertion cathodes and can be used in source–sink reversible lithium cells. Nevertheless, these polyoxometalate anions present a very large electrochemical equivalent weight and a limited capacity to accept electrons reversibly. In contrast, hexacyanoferrate anions have a low molecular weight and can exchange reversibly in solution one electron per iron atom, resulting in a very favorable electrochemical equivalent weight.

We have previously reported the synthesis of PPy/HCF hybrid materials^[11] but found only moderate specific charge values possibly due to the formation of oxygenated groups (carbonyl, hydroxyl) in the polypyrrole chain.^[15]

Following the same strategy of using ferricyanide as an effective electroactive component, but trying to avoid the problems arising from the use of PPy as a COP in the hybrids, we have performed and report here the synthesis and characterization of PAni/HCF hybrids and have studied their electrochemical properties and performance as cathodes in reversible lithium cells. PAni is a conducting polymer whose behavior as a cathode in lithium batteries has been reported with many counterions,^[18–22] but to our knowledge, never in combination with electroactive inorganic anions to form hybrids. In the present communication we show the excellent behavior of PAni/HCF hybrids as cathodes in rechargeable lithium batteries, not only with respect to their cyclability but also to their high specific charge and efficiency.

The chemical synthesis of PAni/HCF was carried out at 0 °C (preferred) and at room temperature for comparison. In order to avoid the presence of any other anions in the reaction medium, which could compete with the hexacyanoferrate for the doping of polyaniline, $\text{H}_3\text{Fe}(\text{CN})_6$ prepared from $\text{K}_3\text{Fe}(\text{CN})_6$ was used as acid and oxidizing agent.

It is important to note that it is not necessary to carry out any crosslinking after the synthesis of PAni/HCF hybrids prepared under these conditions.^[23]

The Fourier transform infrared (FTIR) spectrum of a representative PAni/HCF polymer prepared chemically is shown in Figure 1. The presence of a band at 2050 cm^{-1} assigned to the –CN stretching confirms that HCF has been incorporated into the polymer. The low intensity of the HCF band is due to the high background corresponding to the tail of a charge-transfer band from the polymer. Samples prepared at different temperatures and times present essentially the same IR spectrum, the main difference between them being the yield obtained,

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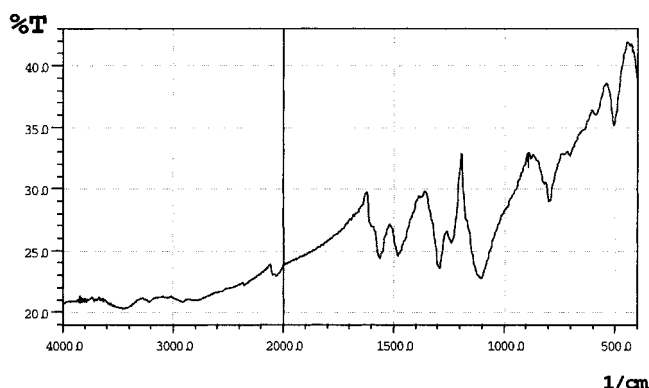


Fig. 1. FTIR spectrum of the PANi/HCF hybrid prepared chemically.

which increases with temperature and time of the reaction. FTIR spectra of electrochemically prepared PANi/HCF hybrids were essentially identical to the ones registered for the chemically prepared hybrids.

Elemental analyses of the chemically prepared samples (included in the Experimental section) show that the PANi/HCF ratio is 6–8 for the hybrids prepared at 0 °C, while for the samples prepared at room temperature this ratio increases to 8–9. There are no main differences between the samples synthesized for different reaction times except for the yield, which is higher in the hybrids prepared for longer reaction times (5 days).

The chemically prepared hybrids have been characterized electrochemically using cyclic voltammetry (CV) both in aqueous and in organic media (Figs. 2a,b). Along with the couple of usual redox waves characteristic of PANi, the CVs of the hybrid present an additional redox wave that must be due to the electroactive $\text{Fe}(\text{CN})_6^{3-/4-}$ anion. A second possibility is that it could be due to the over-oxidation of PANi, as has been previously described by Evans.^[24] In that case though, the wave could be expected to be weaker. The strong feature observed together with the large specific capacity of these materials in reversible lithium cells (see below) supports the HCF assignment.

One of the most important features of the reversible lithium cells tested is their good cyclability, which indicates the good reversible redox chemistry of these hybrid materials. The cells maintain their maximum specific charge for more than 100 cycles with no significant decrease in its value. Furthermore, specific charge values as high as 137 Ah/kg have been obtained at moderate discharge rates of C/15. These values are very close to the maximum theoretical specific charge expected for these hybrid materials (for instance, 142 Ah/kg calculated for the exchange of four electrons per formula weight $[(\text{Ani})_6\text{Fe}(\text{CN})_6]_n$). Figure 3 shows a representative cycle (10th cycle) obtained at a C/15 discharge rate between 3.9 and 2.7 V. The mean discharge voltage of 3.2(3) V and the specific charge of 137 Ah/kg yield a specific energy of 438 Wh/kg for the active cathode material, which also presents low polarizability cycling.

Figure 4 is a plot of the specific charge versus the number of cycles obtained during the discharging process in a lithium

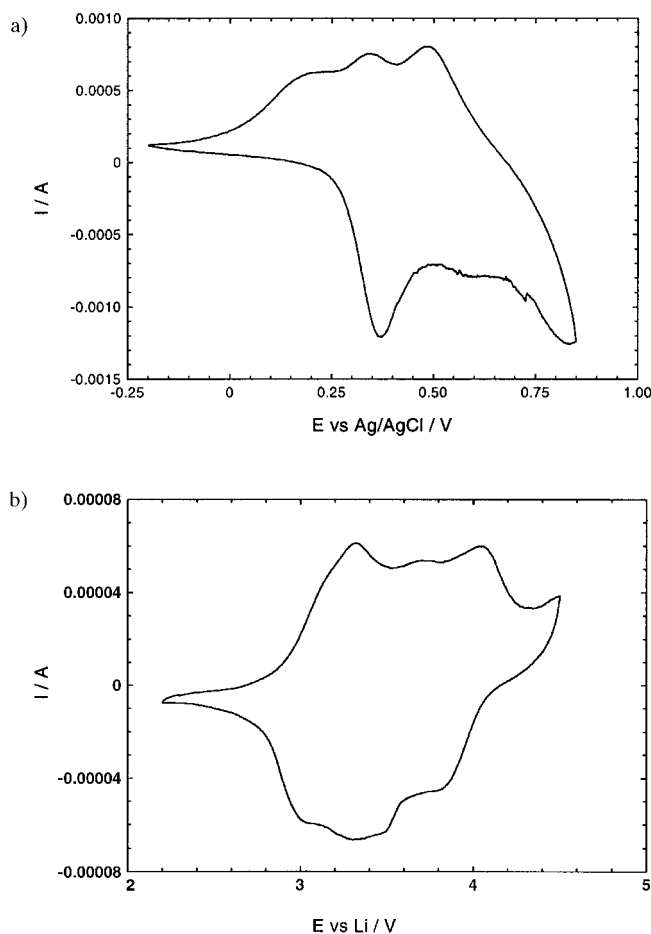


Fig. 2. a) Cyclic voltammogram of the PANi/HCF hybrid prepared chemically. Electrolyte: HClO_4 1 M, scan rate 0.4 mV/s. b) Cyclic voltammogram of the PANi/HCF hybrid prepared chemically. Electrolyte: EC/DMC 1:1, LiPF_6 1 M, scan rate 0.2 mV/s.

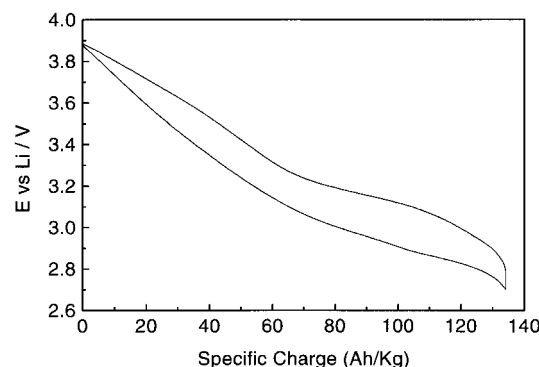


Fig. 3. Charge–discharge cycle of a reversible lithium cell with PANi/HCF as active cathode material, 1 M LiPF_6 in EC/DMC 1:1 as electrolyte, and lithium metal as anode (10th cycle shown). Discharge rate C/15.

battery using the PANi/HCF cathode. Two different discharge regimes used during the first 40 cycles are shown: C/15 and C/5. First of all, it should be noted that the charge values during the initial cycles increase as cycling progresses. This is not completely unusual in COP electrodes. This behavior, which we have previously found in PPy/HCF hybrids,^[15] must be as-

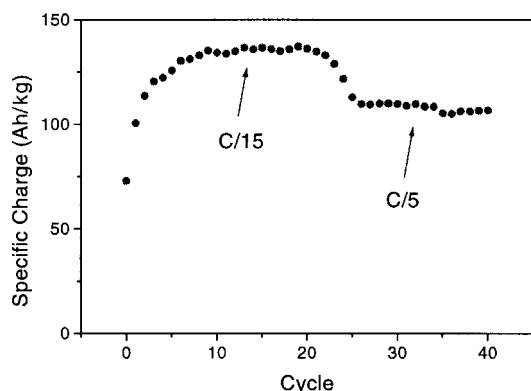


Fig 4. Plot of capacity vs. cycle number for the first 40 discharge cycles of a reversible lithium cell using PANi/HCF as active cathode material, 1 M LiPF₆ in EC/DMC 1:1 as electrolyte, and lithium metal as anode. Constant currents were calculated to discharge the active material in 15 h (C/15) and in 5 h (C/5) as indicated.

sociated with the progressive opening of the polymer matrix upon cycling, which favors a more complete impregnation of the cathode by the electrolyte and improves the efficiency of the redox processes. Also, a very important feature from the data in Figure 4 is the high stability of the values of specific charge upon repeated cycling both at C/15 and C/5 regimes. As should be expected, a faster discharge leads to lower effective specific charge.^[25] Nevertheless the drop is not too drastic and allows values of 100 A h/kg (at C/5) and 137 A h/kg at C/15, which we consider very promising for these first results on our novel PANi/HCF electrode materials.

Experimental

Chemical Synthesis: 25 mL of 2.1 M HClO₄ solution was added to 5.679 g of K₃[Fe(CN)₆] dissolved in 25 mL of water. The white precipitate obtained was filtered off and the yellow solution was added drop-wise to 25 mL of 0.2 M aniline solution kept at 0 °C or at room temperature depending on the particular samples. This mixture was stirred for 3, 4, or 5 days and kept between 0 and 4 °C, or at room temperature. The black-green powder obtained was washed with water and then with ethanol and dried under vacuum for at least 12 h. Conductivity measurements carried out on pellets of these chemically prepared hybrids using the Van der Pauw method give values ranging from 2 × 10⁻² to 10 × 10⁻² S/cm, with no significant differences between samples prepared at 0 °C and at room temperature.

Electrochemical Synthesis: The electrochemical synthesis of the PANi/HCF hybrid was carried out by multiple cyclic voltammetry using Pt foil as working electrode, Ag/AgCl reference electrode, and Pt coil as counter-electrode. Thus

50 mL of electrolyte was prepared dissolving 3.785 g of K₃[Fe(CN)₆] and 0.8 mL of aniline in water. The hybrid material was obtained as a thin film on the working electrode by means of repeated cyclic voltammetry (25 cycles) between 0.85 and -0.2 V (vs. Ag/AgCl) at a scan rate of 50 mV/s.

Battery Analyses: Using the chemically prepared PANi/HCF hybrids as active materials, film cathodes were prepared using PVDF as a binder (25 wt.-%) and Super P Carbon (15 wt.-%). These cathodes were tested in lithium batteries between 2.7 and 3.9 V (vs. Li anodes), at different discharge regimes (C/15, C/5, C/1). The electrolyte was 1 M LiPF₆ in EC/DMC 1:1 from Merck.

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