Poly(5-amino-1,4-naphthoquinone), a Novel Lithium-Inserting Electroactive Polymer with High Specific Charge

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The monomer 5-amino-1,4-naphthoquinone can be polymerized electrochemically or chemically to form a redox polymer in which the quinone/hydroquinone redox couple can be electrochemically oxidized and reduced in aqueous and organic electrolytes. The polymer exchanges cations for the charge-compensating process. In LiClO$_4$/acetonitrile electrolyte lithium ions can be inserted and expelled reversibly. Cyclic voltammograms and galvanostatic experiments show that the charge storage capacity of this polymer is very close to its theoretical value of 290 Ah/kg. The redox potential is about 2.6 V more positive than that of the Li/Li$^+$ couple. If the electrode potential is kept within the window from −1.25 to −0.20 V vs. Ag/AgCl the stability of poly(5-amino-1,4-naphthoquinone) (PANQ) is reasonable, and an acceptable cycle life can be reached. However, at lower potentials irreversible electrochemical reactions proceed, and the cycle life of PANQ is shortened. Hence, PANQ is an interesting electrode material for lithium metal or lithium-ion batteries. From potential-jump experiments on porous composite PANQ electrodes an overall diffusion coefficient at least $1 \cdot 10^{-7}$ cm^2/s was estimated for the lithium deinsertion. Assuming a thin-layer cell with a LiC$_6$ negative and a PANQ positive electrode (using common dimensions for the current collectors and battery housing, and accounting for the electrolyte necessary to fill the pores in the electrode and separator), we estimated that a battery having a specific energy of up to 125 Wh/kg at very low charge/discharge rates could be realized. For the 1 h discharge rate about 100 Wh/kg should be possible.
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A novel conducting polymer, poly(5-amino-1,4-naphthoquinone) (PANQ)
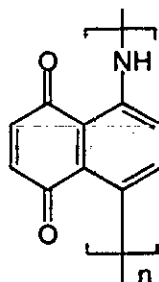
has recently been prepared as a film by electrochemical polymerization of 5-amino-1,4-naphthoquinone (ANQ), and as a powder by a chemical polymerization process.[1] The polymer structure was determined by different spectroscopies [infrared, ultraviolet visible, X-ray photoelectron spectroscopy (IR, UV/vis, XPS)] and confirmed by frontier orbital calculations.[1,2] The film redox process has been studied in situ by several spectroelectrochemical methods including probe beam deflection (PBD) and multiple internal reflection Fourier transform infrared spectroscopy (MIRFTIRS).[3]

The lithiated form of the polymer, PANQ-Li$_2$, has a rather high theoretical specific charge of 290 Ah/kg. This value has been calculated assuming the transfer of two electrons per monomeric unit and including Li$^+$ as counterions. The additional charge storage capacity of the polyaniline backbone polymer which carries the redox-active centers of the quinone groups is not included in this calculation. In thin films the charge stored in the quinone moieties can be recovered almost completely, and the polymer can be cycled reversibly. The quinone system is electroactive both in acetonitrile and in aqueous solutions up to pH 11.[2,3]

It is interesting to note that PANQ is promising not only because of its rather high specific charge, but also because the polymer provides intrinsic overcharge protection due to the polyaniline backbone polymer chain which can be oxidized and reduced at higher potentials. We did not evaluate this additional capacity in this investigation

because it is associated with anion-exchanging properties which do not fit into the ion-transfer concept of the batteries we are seeking.

In this work we evaluate the potential use of PANQ as a positive electroactive material in lithium-ion batteries with aprotic electrolytes. Composite electrodes about 500 μm thick were made from polymer powder (prepared by chemical polymerization) and carbon black (as a conducting additive). Galvanostatic experiments were used to investigate the stability during cycling, while potential-jump measurements provided information about the dynamic properties of the composite electrodes.

Experimental

Electrode preparation.—Poly(5-amino-1,4-naphthoquinone) (PANQ) powder was prepared by chemical polymerization of 5-amino-1,4-naphthoquinone (synthesized as described in Ref. 1). The monomer was dissolved in anhydrous acetonitrile with added Cu(BF$_4$)$_2$ as an oxidant. The mixture was stirred under argon for 24 h. The black precipitate was then filtered, thoroughly rinsed with acetonitrile, and finally dried under vacuum for 48 h.

The electrode mass was an intimate mixture of 250 mg PANQ, 250 mg carbon black (Vulcan XC 72), and 13.3 mg Oppanol® (BASF) as a binder. About 25 mg of this mass were pressed into hollow titanium current collectors forming electrodes with a geometric area of 1.13 cm^2 and a thickness of 480 μm.

Electrochemical cell.—Spring-loaded three-electrode cells described elsewhere[4] were used containing a porous LiMn$_2$O$_4$/carbon counter electrode (3:1 w/w) and a Ag/AgCl reference electrode in LiClO$_4$/acetonitrile. In some cases the potential of the PANQ electrode has been recalculated to the lithium scale assuming that 0 V vs. Ag/AgCl ≈ +3.2 V vs. Li/Li$^+$. Prior to the experiment the working and counter electrodes were vacuum dried for 14 h at 60 and 100°C, respectively. Hermetically sealed cells were then assembled in an argon-filled glove box. Two pieces of 1 mm glass fleece were used to separate the electrodes. An electrolyte solution of a 0.75 M LiClO$_4$ in acetonitrile (Fluka) was used and dried over lithiated molecular sieves for at least several days to reach a H$_2$O content of less than 50 ppm.

Electrochemical experiments.—All experiments were performed at laboratory temperature. Cyclic voltammetry and constant-current experiments were performed using standard electrochemical equip-

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ment. For potential-jump experiments the Amel System 5000 was used, and the measurements were performed as follows. After a delay to ensure equilibration, the potential was jumped within the potential limits indicated in the captions of Fig. 5 and 6. (In the experiment illustrated by Fig. 6 the electrode was preconditioned with linear potential sweeps like those of Fig. 1.) Before triggering the next potential jump the potential was maintained constant until the electrochemical reaction was complete. The lithium insertion/deinsertion cycles were repeated three times. We used the linear portion of a Cottrell plot (as indicated in Fig. 4) to estimate the global diffusion coefficient of Li^+ ions in the composite electrode.

Results and Discussion

Cyclic voltammetry.—The first cycle of a typical cyclic voltammetric experiment performed with a porous PANQ electrode is shown in Fig. 1. The voltammetric curve begins at the open-circuit potential, which was typically about +0.3 V vs. Ag/AgCl. The potential was first scanned in the negative direction as indicated by the arrow in the figure. At the lower and higher potential limits of −1.25 and −0.20 V vs. Ag/AgCl, respectively, delays of 3 h were inserted to ensure that the current dropped to zero before changing the scan direction.

Two well-separated electron transfer processes were always detected. At a sweep rate of 25 μV/s the mean potentials, E_0, of these redox processes were $E_0^1 = -0.460$ V and $E_0^2 = -0.835$ V vs. Ag/AgCl. The observed behavior can be explained in terms of a two-step reduction or oxidation in which the lithiated semiquinone (radical) is rather stable. At the end of the Li^+ insertion process (−1.25 V vs. Ag/AgCl) a total specific charge of 256 Ah/kg (calculated with respect to the PANQ weight) was measured in the experiment shown in Fig. 1. The main part of this charge was consumed during the potential sweep and only about 10 Ah/kg was consumed during the 3 h delay at the lower potential limit. For the lithium de-insertion a specific charge of 208 Ah/kg was measured, corresponding to a charge efficiency of about 80% in the first cycle. For the redox process at $E_0^1 = -0.460$ V the specific charge between +0.30 and −0.69 V vs. Ag/AgCl was 144 Ah/kg, i.e., about half of the total charge.

Galvanostatic cycling.—Typical galvanostatic charge/discharge (i.e., lithium deinsertion/insertion) curves of PANQ are shown in Fig. 2. The voltage profile is sloping, but ill-developed plateaus corresponding to the peaks observed in the cyclic voltammogram (Fig. 1) can be detected. The specific charge with respect to the PANQ weight is shown in Fig. 3 as a function of the cycle number. At the beginning of cycling nearly 300 Ah/kg was obtained, which corresponds nicely to the theoretical value calculated for the polymer. The higher specific charge obtained from the galvanostatic experiment, as compared to the result of cyclic voltammetry, is due to
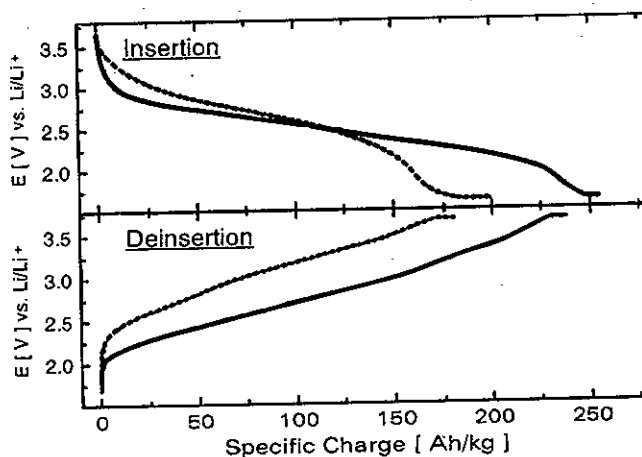

Figure 2. Second (——) and fifteenth (- - - - -) galvanostatic cycle of a porous PANQ electrode cycled at 20 μA/mg of polymer (≈240 μA/cm²).

the broader potential window used in the galvanostatic measurement. However, Fig. 2 and 3 show that the specific charge decreases rather rapidly during cycling and stabilizes at about 200 Ah/kg. The reason for this decrease is not yet known. However, at negative potentials we observed some irreversible reduction processes which appear to be related to the capacity loss. Moreover, it is known from a large number of experiments with conducting polymers that during the Li^+ insertion process a considerable amount of solvent is incorporated into the polymer. The mechanical stress due to solvent intake (manifested in the swelling of the polymer) may impair the electrical contact between the polymer and the current collector.

Dynamics of the Li^+ insertion process.—For the performance of a prospective battery the deinsertion/insertion dynamics of lithium in PANQ based electrode will be decisive. A fast deinsertion and insertion would lead to a larger specific power and short charging time of the cells. Potential-jump experiments can be used for a quick evaluation of the kinetic parameters.[5] As both the kinetics and the specific charge of the sample may change during cycling, the potential-jump experiments were repeated three times for each cell under investigation.

The overall deinsertion/insertion process of Li^+ ions from/into PANQ electrodes consists of at least three major physical processes: (i) the diffusion of lithium ions in the liquid electrolyte solution present in the pores of the composite electrode (i.e., between the PANQ and carbon grains), (ii) the electrochemical redox process in the
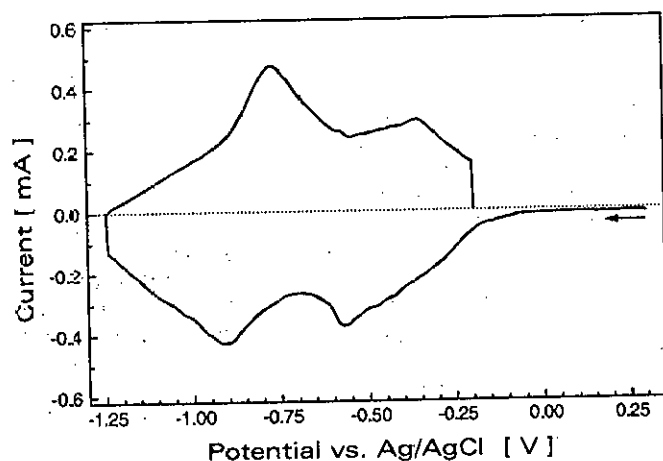

Figure 1. Cyclic voltammogram of a porous PANQ electrode at 25 μV/s (first cycle). At −1.25 and −0.20 V vs. Ag/AgCl, respectively, delays of 3 h were inserted. During these delays the current dropped to zero.
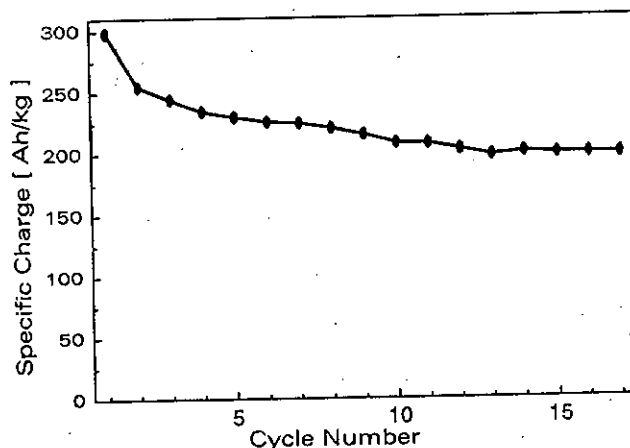

Figure 3. Typical relation between the specific charge of PANQ (Li^+ insertion) and the cycle number during galvanostatic cycling at 20 μA/mg (≈240 μA/cm²). The potential limits were as shown in Fig. 2.

polymer grains or at the surface of it, and (*iii*) the diffusion of lithium in the bulk of the polymer. The integrated current response obtained by a potential-jump experiment with a composite PANQ electrode (Fig. 4) does not behave exactly as if the deinsertion/insertion of lithium followed the normal Fick's diffusion law (a straight line is predicted for semi-infinite diffusion). However, the current response at the beginning of the experiment is fairly close to this behavior. Thus, an apparent diffusion coefficient which roughly describes the overall insertion process can be evaluated even though the composite electrode is heterogeneous and contains at least two phases (the electrolyte and the PANQ particles) in which the real lithium diffusion rates are very different. A comprehensive analysis of the potential jump experiments will be part of our forthcoming publication where a more detailed model simulating the dynamics of the Li^+ insertion process in metal oxide, graphite, and PANQ-based electrodes will be introduced.[6] Here the apparent diffusion coefficients evaluated using Fick's law are discussed.

Figure 5 shows that the Li^+ deinsertion is significantly slower than the Li^+ insertion. The same figure also shows that the apparent lithium diffusion coefficient decreases slightly during the first three cycles performed in the rather broad potential window from −1.50 to +0.05 V vs. Ag/AgCl. However, the apparent lithium diffusion coefficient increases slightly with the cycle number if the potential is stepped only between −0.835 V (mean redox potential E_0^2) and −0.460 V vs. Ag/AgCl (mean redox potential E_0^1), and the difference between the value for insertion and deinsertion is not as large

Figure 6. The apparent diffusion coefficient of Li^+-ions for the insertion/deinsertion from a porous PANQ electrode as a function of cycle number. The potential of the PANQ electrode was repeatedly jumped between −0.835 and −0.460 V vs. Ag/AgCl.

(Fig. 6). The swelling of the polymer and, thus, the diffusion behavior of the Li^+ ion depends on the degree of ion insertion (which at equilibrium is a function of the electrode potential). We believe that the different values obtained in the experiments of Fig. 5 and 6 can be explained in terms of potential-dependent (i.e., lithium-content-dependent) volume changes of the polymer.

Layout of a thin-layer lithium-ion/redox-polymer battery.—Obviously, the electrochemical data measured for PANQ imply that this
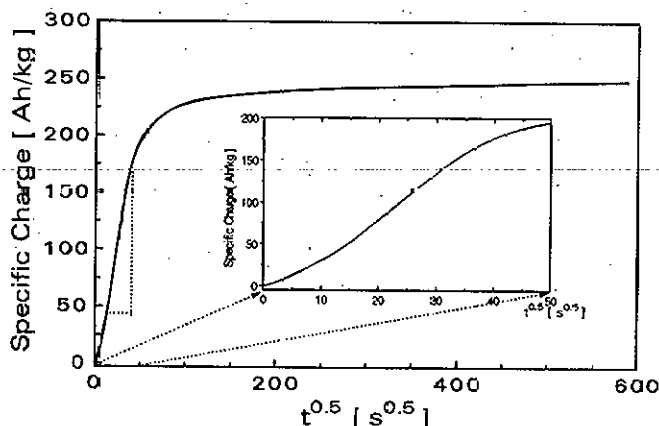

Figure 4. Typical Cottrell plot for lithium deinsertion from a porous PANQ electrode. The potential was jumped from −1.50 to +0.05 V vs. Ag/AgCl. The inset shows the initial section of the curve in more detail.
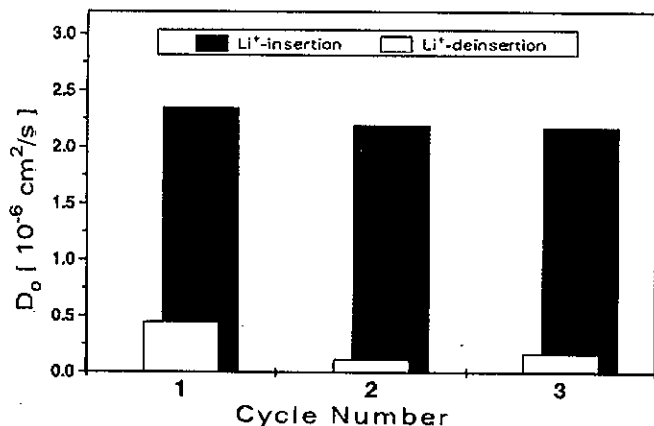

$$LiC_6 + P_{1/x} \longleftrightarrow 6C + LiP_{1/x}$$

LiC₆/Cu Electrolyte P₁/ₓ/Al

	µm	mg/cm²	mAh/cm²
LiC_6 (Composite 220 Ah/kg)	149	24.7	5.5
P (Composite 140 Ah/kg)	335	39.5	5.5
Separators	50	5.1	
Al - Sheet	25	6.8	
Cu - Sheet	18	16.1	
Total	577	92.2	5.5

➡ 1.6 g/cm³   95 mAh/cm³

2.6 V
➡ 60 mAh/g   ➡ 156 mWh/g

With Containment   125 Wh/kg (C/∞)

Specific Energy   100 Wh/kg (C/1)

Figure 5. The apparent diffusion coefficient of Li^+-ions for the insertion/deinsertion from a porous PANQ electrode as a function of cycle number. The potential was repeatedly jumped between −1.50 and +0.05 V vs. Ag/AgCl.
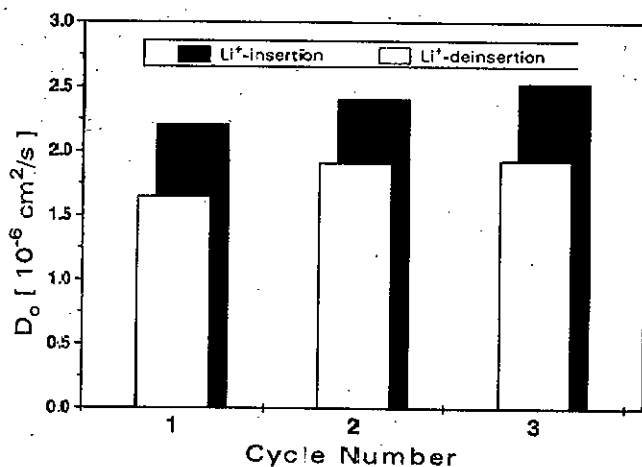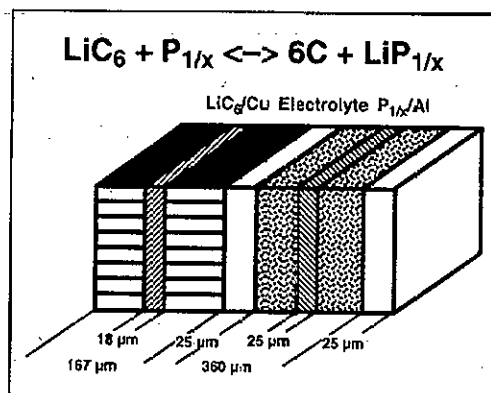
Figure 7. Possible layout of a thin layer lithium-ion/redox-polymer cell (P = polymer, e.g., PANQ).

material is interesting for positive electrodes of lithium metal or lithium-ion batteries. We investigated a possible layout of such a battery in order to substantiate this conclusion. Figure 7 presents the most important data for a hypothetical thin-layer cell with a polymer like PANQ as a positive material and LiC_6 as a negative electroactive material. The inserted table gives the dimensions and weights of the components, from which we can estimate an upper limit for the specific energy which may be obtainable in practice with such a thin-layer arrangement.

The thickness of the entire electrode package is assumed to be 500-600 μm. The current collector at the positive electrode is a 25 μm thick Al foil, as in comparable commercial cells, that at the negative electrode is a 18 μm thick copper foil.[7] The composite electrodes (consisting of active materials, conducting fillers, binder, and 50% pores filled with the electrolyte) should then yield the specific charges indicated in Fig. 7 (220 Ah/kg for the negative electrode and 140 Ah/kg for the positive electrode). For the negative electrode this can, for instance, be reached with graphite as an electroactive material having a specific charge of about 350 Ah/kg and containing 5 wt % of a binder. The value of 220 Ah/kg follows if we keep in mind that the density of bulk graphite is 2.25 g/cm^3, the density of the electrolyte is about 1.1 g/cm^3, and the porosity of the composite electrode would be 50 vol %.[8] For the positive electrode material a specific charge of 290 Ah/kg for the lithiated polymer ($\rho \approx 1.2$ g/cm^3), 10 wt % carbon as a conducting filler, and a porosity of about 50 vol % (electrolyte-filled pores) were assumed. The expected average cell voltage is about 2.6 V (Fig. 2) for the LiC_6/PANQ couple, which leads to a possible specific energy of about 156 Wh/kg. The electrolyte, separators, and current collectors are included in this figure. It will drop to about 125 Wh/kg, however, if we allow some 20% of the weight for the housing, etc. Of course, this value could only be reached at a very slow charge/discharge rate. But a 1 h discharge rate should still deliver about 100 Wh/kg, which is comparable to the specific energy demonstrated with "4 V" lithium-ion cells based on metal oxides and available on the market.[7]

Using the global apparent diffusion coefficient of $D \cong 1 \cdot 10^7$ cm^2/s (the lowest value from the potential-jump experiments) and the relation $\delta x = (2Dt)^{1/2}$ we calculate that the Li^+ ions can diffuse about 270 μm in 1 h, which means that a 1 h discharge rate should be possible with our cell arrangement assuming 168 μm thick composite polymer electrodes (one side). A 1 h discharge rate demands a current density of about 3 mA/cm^2 (one side) with the cell concept proposed.

Conclusions

The experimental charge storage capacity of a PANQ polymer is 220-290 Ah/kg in nonaqueous electrolytes. The mean redox potential is about 2.6 V more positive than that of the Li/Li^+ couple. Therefore, PANQ is an interesting positive electrode material for lithium metal or lithium-ion batteries. Assuming a thin-layer cell with a LiC_6 negative and a PANQ positive electrode, using common dimensions for the current collectors and battery housing, and accounting for the electrolyte necessary to fill the pores in the electrode and separator, we estimated that with a 1 h discharge rate a specific energy of the battery of about 100 Wh/kg can be realized. Further investigations are needed, however, to elucidate the reasons for the capacity loss occurring during prolonged cycling.

Acknowledgment

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