

## BRIEF COMMUNICATION

# Solid State Electrochemical Intercalation of Lithium and Sodium Ions into Polyparaphenylene

M. Dubois and D. Billaud

*LCSM—URA CNRS No. 158, Université Henri Poincaré Nancy I, BP 239, 54506 Vandoeuvre-lès-Nancy, France*

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Polyparaphenylene powders are electrochemically intercalated with  $\text{Li}^+$  and  $\text{Na}^+$  ions in solid state cells operating with poly(ethyleneoxide) based electrolytes. The intercalation–deintercalation process proceeds in two reversible steps. The binders (PEO and PVDF) used in the composite polyparaphenylene electrode give rise to irreversible side reactions. © 1996 Academic Press, Inc.

### INTRODUCTION

Polyparaphenylene ( $\text{C}_6\text{H}_4$ )<sub>x</sub> is an electroactive polymer which can react either with electron accepting or donating species to give, in the intercalated state, compounds of high conductivity. The intercalation of alkali metals can be achieved by chemical or electrochemical ways (1, 3). The use of solid polymer electrolytes, like complexes composed of poly(ethyleneoxide) (PEO) and alkali metal salts, allows the intercalation of alkaline ions in solid state electrochemical cells. Since the alkali cation  $M^+$  moves through PEO free from any solvating molecule, only binary compounds can be obtained according to the reaction



Moreover, contrary to the chemical techniques, the electrochemical method allows the control of the doping and the study of the reversibility of the reactions.

In this paper, we particularly focused on the electrochemical behavior of composite electrodes, composed of polyparaphenylene powder and different binders, in solid state cells working with a PEO-based electrolyte.

### EXPERIMENTAL

Poly(paraphenylene) was synthesized according to the method of Kovacic and Oziomek (4) in the form of a brown insoluble powder. This material was washed out with hot

hydrochloric acid to remove the catalyst residues and was then heated at 400°C under vacuum for further purification.  $\text{LiClO}_4$  (Aldrich) and  $\text{NaCF}_3\text{SO}_3$  (Aldrich) were both dried at 150°C under vacuum prior to utilization.

Poly(ethyleneoxide) (PEO,  $5 \times 10^6$  g/mole, Aldrich) was heated under vacuum at 50°C to remove traces of moisture, and polyvinylidene fluoride (PVDF) (Aldrich) was used as received.

PPP, binder (PEO or PVDF), and alkaline salt were dissolved in organic solvents under magnetic stirring. (Propylene carbonate for PVDF and acetonitrile for PEO were used.) The slurry was cast onto a stainless steel current collector.

The electrode was then mounted in a button type cell using a PEO– $\text{LiClO}_4$  or  $\text{NaCF}_3\text{SO}_3$  film obtained by classical procedures (5). A freshly cut alkali metal (lithium or sodium) constituted the negative pole of the cell. Cells were assembled under high purity argon atmosphere, and then operated under an argon flow at 80°C to assure a high ionic conductivity of the electrolyte in an amorphous state (6).

Intercalation and deintercalation were investigated using a computer-controlled potentiostat-galvanostat Mac Pile (Biologic).

### RESULTS AND DISCUSSION

Figure 1 shows the two first cyclic voltammograms of the system  $\text{Li}/\text{P}(\text{EO})_8\text{LiClO}_4/\text{PPP}-\text{PEO}(60/40)$  recorded with potential steps of 20 mV every 0.5 h between 2.5 and 0.05 V. The scan starts from the equilibrium value attained at the end of the previous relaxation. Such a low voltage sweep rate is necessary for a good observation of the intensity peaks. Both first and second cycles show, in the reduction process, a poorly defined peak at around 0.45 V and a hump at 0.18 V. These peaks can be associated respectively with those appearing at 0.70 and 0.38 V in the oxidation process.

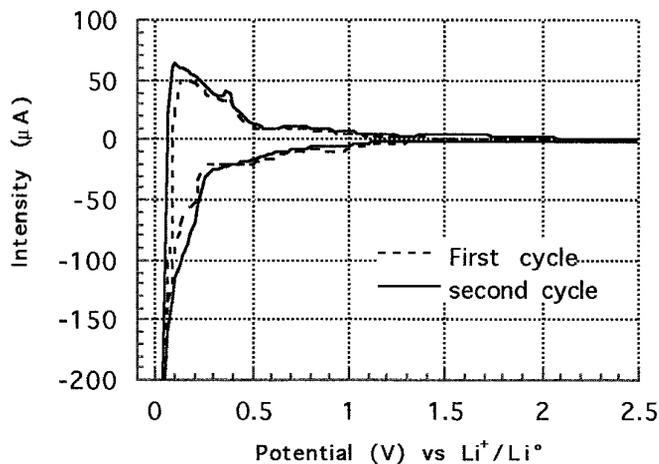


FIG. 1. Voltammograms of first and second cycle in Li/P(EO)<sub>8</sub>LiClO<sub>4</sub>/PPP-PEO (60-40) system with 20 mV/0.5 h scan rate.

The region between 0.6 and 1.4 V, in the reduction process, has been magnified in Fig. 2. It shows a peak near 0.9 V in the first cycle which disappears nearly totally in the second run: this additional transformation is related to an irreversible reduction involving the complex PEO-LiClO<sub>4</sub> and resulting in the formation of Li<sub>2</sub>CO<sub>3</sub> as previously discussed (7).

Figure 3 displays the two first cyclic voltammograms of the system Li/P(EO)<sub>8</sub>LiClO<sub>4</sub>/PPP-PVDF-CB (80/10/10). The working electrode is a composite material composed of PPP, an insulating binder (PVDF), and carbon black (CB) acting as electronic conductor. Using PVDF instead of PEO does not modify the shapes of the voltammograms at low potentials. The two reversible peaks visible in Fig. 1

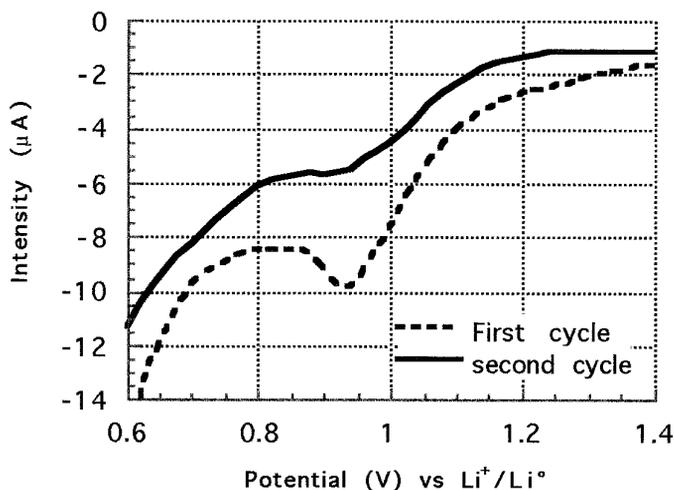


FIG. 2. Voltammograms between 1.6 and 1.4 V of first and second reduction process in the Li/P(EO)<sub>8</sub>LiClO<sub>4</sub>/PPP-PEO (60/40) system with a 20 mV/0.5 h.

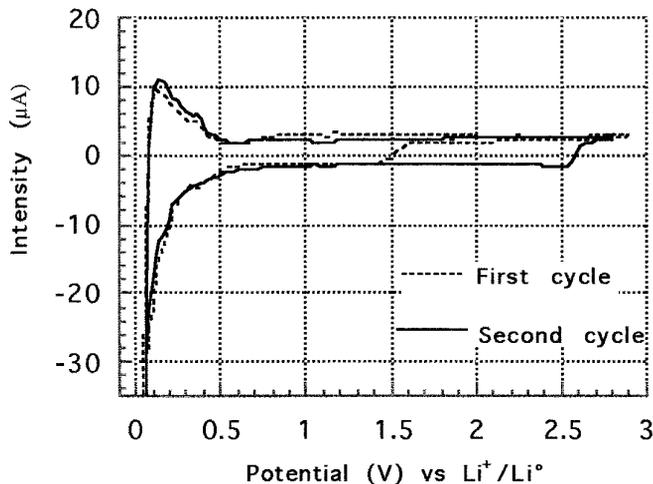


FIG. 3. Voltammograms of first and second cycle in Li/P(EO)<sub>8</sub>LiClO<sub>4</sub>/PPP-PVDF-BC (80-10-10) system with a 20 mV/0.5 h scan rate.

are also present here. However, a negative current is observed from 2.5 V in the reduction process of the first cycle. This cathodic current has not only occurred in the first cycle but also in the following runs and it begins at only 1.6 V. This side current can be attributed to an irreversible reduction of PVDF already pointed out in Ref. (8). The potential values of the reversible transformations are presented in Table 1 as well as the corresponding free enthalpies  $\Delta G = -FE$  of these reactions.

Figure 4 shows the first and second cyclic voltammograms obtained for the system Na/P(EO)<sub>12</sub>NaCF<sub>3</sub>SO<sub>3</sub>/PPP-PEO (60/40) after potential steps of 20 mV · 0.5 h<sup>-1</sup>. The potential values of the two reversible transformations are displayed in Table 1: the hump observed around 0.8 V is attributed to the irreversible reduction of the PEO-NaCF<sub>3</sub>SO<sub>3</sub> complex as mentioned above for the PPP/Li system. The electrochemical reversible capacities  $y$  related to the stoichiometry  $(M_yC_6H_4)_x$  and calculated from the cyclic voltammograms appeared to be  $y = 0.35$  and  $y = 0.40$ , respectively, for Na and Li system.

TABLE 1  
Potentials Corresponding to the Maxima of Intensity, Equilibrium Potentials, and Corresponding Free Energies  $\Delta G$  for the PPP-Li and PPP-Na Systems

|    | Potential (V) vs $M^+/M^0$ |           |                       | $-\Delta G$<br>(kJ/mol · M) |
|----|----------------------------|-----------|-----------------------|-----------------------------|
|    | Reduction                  | Oxidation | Equilibrium potential |                             |
| Li | 0.45                       | 0.71      | 0.57                  | 55.5                        |
|    | 0.18                       | 0.38      | 0.28                  | 27.0                        |
| Na | 0.56                       | 0.90      | 0.73                  | 70.4                        |
|    | 0.16                       | 0.30      | 0.25                  | 22.2                        |

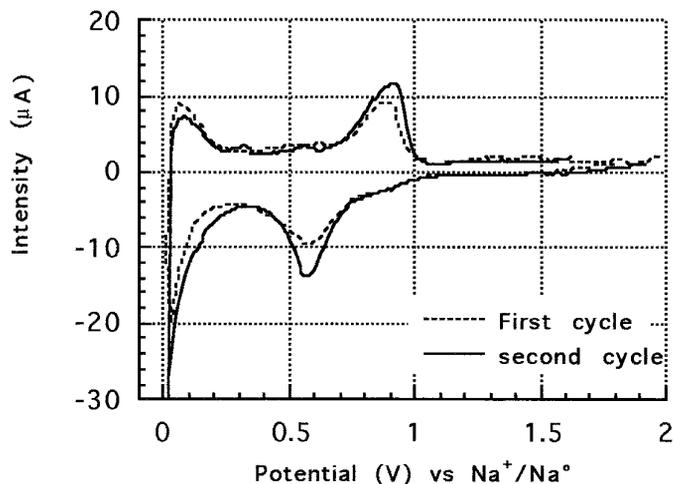


FIG. 4. Voltammograms of first and second cycle in the Na/P(EO)<sub>12</sub> NaCF<sub>3</sub>SO<sub>3</sub>/PPP-PEO (60–40) system with a 10 mV/0.5 h scan rate.

These capacities appear slightly lower than those previously reported for Li<sup>+</sup> and Na<sup>+</sup> intercalation into PPP in liquid electrolytes such as lithium tetraphenylborate/THF, sodium tetraphenylborate/THF (2, 10), or NaPF<sub>6</sub>/DME (10). In our cases, the capacities are between 0.40 and 0.45. They are, however, lower than the theoretical ones ( $y = 0.5$ ) obtained by direct reaction of gaseous alkali metal with PPP (9). This indicates that the electrochemical intercalation does not lead to the formation of saturated materials.

### CONCLUSION

By analogy with previous data related to the intercalation of alkaline ions into PPP in liquid electrolytes, the

two reversible transformations observed for the Li and Na-PPP systems can be attributed to the formation of discrete intercalation “stages.” Structural studies, now in progress, and comparison with compounds prepared by direct reaction of gaseous sodium and PPP will further support this aspect (9). Evidence of oxide reactions like the irreversible reductions involving the electrode binders (PEO or PVDF) has been seen. The influence of the formation of such side products on the reversibility and on the values of the electrochemical capacities have to be studied carefully before utilization of the compounds as the negative electrode in solid state alkali metal secondary generators.

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