

## KINETIC STUDIES OF THE ELECTROCHEMICAL REACTION BETWEEN LITHIUM AND PHTHALOCYANINE

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### Summary

The intercalation reaction of lithium in hydrogen phthalocyanine,  $\text{H}_2\text{C}_{32}\text{N}_8\text{H}_{16}$ , ( $\text{H}_2\text{Pc}$ ) has been studied in a propylene carbonate (PC) electrolyte containing  $\text{LiClO}_4$ . The theoretical specific capacity and energy of the  $\text{H}_2\text{Pc}/\text{Li}$  system are very high (870 A h/kg and 1190 W h/kg). The lithium diffusion coefficient in this material was determined from the first discharge depths and NMR measurements. Experimental results gave a  $D_{\text{Li}^+}$  value of around  $4 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ . Using NMR techniques, the variations of relaxation time,  $\tau_2$ , with temperature were studied for  $\text{H}_2\text{Pc}$  treated with n-butyllithium. The diffusion coefficient in this case is  $5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ .

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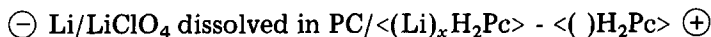
### 1. Introduction

During recent years considerable research has been devoted to electrochemical systems based on the intercalation of alkali metals in host structures with non-aqueous electrolytes. In the search for new positive electrodes, transition metal oxides or sulphides have been found to possess electrochemical properties of use in lithium secondary cells. The theoretical performance characteristics of the cells are, however, limited by the high atomic masses of the mineral elements used in their construction. Research has therefore been oriented towards lighter, carbon-based compounds [1, 2]. Recently, an electrochemical study of phthalocyanines was initiated by a Japanese laboratory [3]. These materials present very attractive electrochemical characteristics. According to Yamaji *et al.* they can host up to 17 Li/mole, giving very high specific capacity and energy values of 870 A h/kg and 1190 W h/kg, respectively, and a long life of around 100 charge-discharge cycles at usable voltages.

Hydrogen phthalocyanine consists of planar macrocycles formed by four "pyrrole" groups linked in the  $\alpha$  position by four nitrogen atoms, each group having a fused benzene ring. The compound exists in at least two polymorphic forms,  $\alpha$  and  $\beta$ . The  $\beta$  phase is the more stable and crystallizes in layers in a base-centered monoclinic structure [4]. Its lamellar structure may be expected to allow lithium ion intercalation between the molecular layers.

## 2. Experimental

We have studied the intercalation reaction of lithium in hydrogen phthalocyanine. Cells were constructed according to the following electrochemical chain:



- The negative electrode was a solid lithium disk, 20 mm in diameter and 3 mm thick, cut from a lithium plate ( $\alpha$  Product).
- The lithium perchlorate (Fluka) was vacuum dried for 48 h at 120 °C in a Bucchi T050 oven before use.
- The electrolyte was a 1M solution of  $\text{LiClO}_4$  dissolved in propylene carbonate (PC) previously redistilled and stored on anhydrous  $\text{Al}_2\text{O}_3$ . In our electrochemical cells, the electrolyte was retained on highly absorbent separator paper (Ecole Française de Papeterie de Grenoble).
- The positive electrode consisted of a thinly deposited layer of hydrogen phthalocyanine (Ventron) obtained by vacuum evaporation onto a 20 mm diameter stainless steel plate. During deposition, the temperature of the sample did not exceed 190 °C.

The deposits obtained were homogeneous. Thicknesses, determined from scanning electron microscopy photographs, were uniform and equal to 3.6  $\mu\text{m}$  per mg of  $\text{H}_2\text{Pc}$  deposited. X-ray analysis revealed the presence of the  $\beta$  phase.

The various components were assembled in button cell casings (Wonder Company), and assembly and crimping were carried out in a glove-box.

The working temperature was maintained at 25 °C.

The electrochemical intercalation reactions were undertaken using a Tacussel PRT 20-2X potentiostat in the galvanostatic mode. The potential was plotted on a Sefram X (t) recorder.

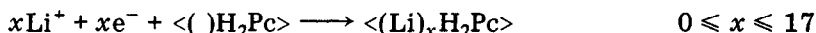
For the NMR analysis, the movement of the lithium was studied on chemically reduced phthalocyanine deposited in thin layers. The products were obtained by the reaction of n-butyllithium on known quantities of  $\text{H}_2\text{Pc}$  in hexane medium. They were hexane washed, dried at 100 °C, and then placed in special 5 mm dia. NMR tubes which were finally sealed. The NMR measurements were made using a Bruker WP 100 spectrometer.

### 3. Results

#### 3.1. Electrochemical study

##### 3.1.1. Influence of deposit thickness on first discharge depth

The first discharge of the system ( $\text{H}_2\text{Pc}/\text{LiClO}_4$  in PC/Li) was carried out at constant current ( $I = C/200$ ). The theoretical capacity of the cell is limited by the cathode, and we calculated it, assuming the intercalation of 17 lithiums per mole of host material, according to the topochemical reaction:



The results obtained are shown in Fig. 1. The initial e.m.f. was approximately 2.8 V. The voltage drops sharply to 1.8 V as soon as current starts to flow. The discharge depth values, which represent only 10 - 60% of the theoretical values, decrease as the deposit thickness increases.

##### 3.1.2. Blank tests

Since the discharge currents were very low, we carried out test discharges on cells free from active material other than the stainless steel current collector. The measured capacities were very low (0.01 mA h) and may be considered to be negligible with respect to those measured in the presence of active material.

#### 3.2. NMR analysis

Studies were undertaken in the temperature range 253 - 393 K. The lines,  $\Delta$ , which are given as a function of  $T$  in Fig. 2, are very broad at low temperatures. A large number of pulses ( $10^3$ ) were required to obtain a suitable signal. The accuracy of  $\Delta$  is only fair over this temperature range.

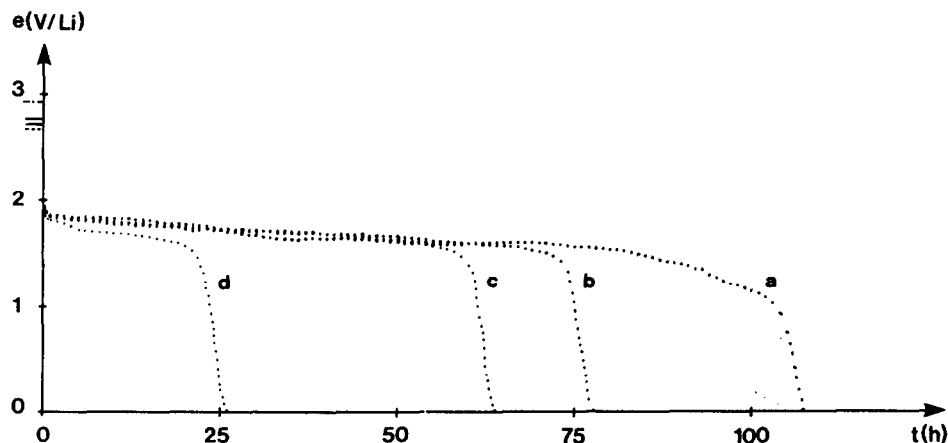


Fig. 1. Discharge depth vs. deposit thickness,  $I = C/200$ .  $l$  ( $\mu\text{m}$ ): a, 21.6; b, 25.6; c, 27.0; d, 39.6.  $C$  (mA h): a, 5.32; b, 6.30; c, 6.65; d, 9.75.

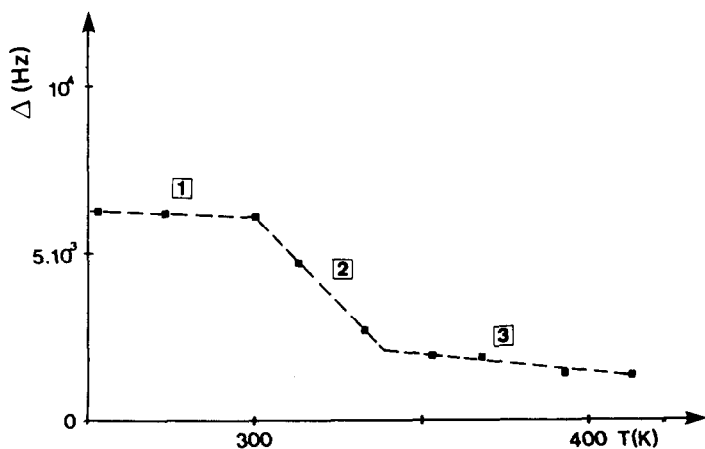


Fig. 2. Line width vs.  $T$ .

The line width decreases as the temperature is increased and an adequate signal was obtained after only about 10 pulses.

## 4. Discussion

### 4.1. Electrochemical results

We assume that the reduction reaction kinetics of hydrogen phthalocyanine are limited only by the diffusion of the cation in the solid phase. We also assume that this reaction controls the overall kinetics of the cell. X-ray analyses conducted on the reduced product seem to indicate that the system always remains as a single phase. This result is supported by differential scanning microcalorimetry tests.

Under these conditions, the first discharge depth at constant current can be calculated as a function of the thickness of the cathode material (for one-dimensional diffusion) for various values of the diffusion coefficient of lithium in  $H_2Pc$  [5] (Fig. 3).

According to our experimental results, the diffusion coefficient,  $D_{Li^+}$ , is approximately equal to  $4 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ . This low value confirms the necessity for slow discharges.

### 4.2. NMR results

The value of the diffusion coefficient is given by the relation  $D = \bar{l}^2/\bar{\tau}_2$  [6], where  $\bar{l}$  represents the mean elementary jump distance in the lattice and  $\bar{\tau}_2 = (2\pi\Delta^\circ)^{-1}$ .

The values of  $D_{Li^+}$  and the jump activation energy are  $5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  and 3.77 kcal/mole, respectively.

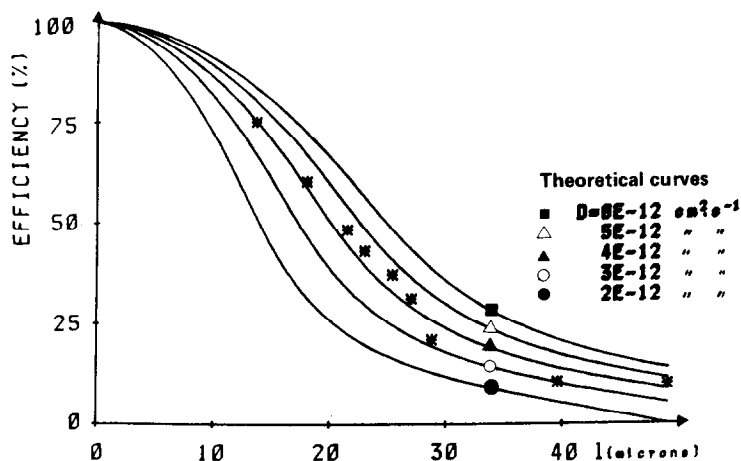


Fig. 3. Coulombic efficiency vs. cathode thickness. \* Experimental data.

## 5. Conclusion

Our results show that the kinetics of the intercalation reaction of lithium in  $H_2Pc$  are about 100 times slower than in the host materials generally used. A cycling test could not be considered for this material due to the low discharge rate required.

## Acknowledgements

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## References

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