

KINETIC STUDIES OF THE ELECTROCHEMICAL REACTION BETWEEN LITHIUM AND PHTHALOCYANINE II. REDUCTION REACTION MECHANISM

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Summary

The reduction reaction mechanism of metal-free phthalocyanine (H_2Pc) in the presence of alkali cations was studied. The chemical lithiation was obtained by reaction with n-butyl lithium. The chromatographic analysis of the chemical products revealed both octane and butane. The presence of butane as a co-product could be due to the hydrogen substitution reaction with n-butyl lithium.

The electrochemical behaviour was studied with evaporated H_2Pc thin cathodes on stainless steel with a polyethylene oxide- $LiClO_4$ electrolyte. When current flow, the phthalocyanine can partially migrate into the electrolyte. This phenomenon, detected using a microporous nickel foil inserted into the electrolyte, was prevented by coating the H_2Pc deposit with a thin layer of a polycation. Thus the reversible capacity given by the topochemical reaction could then be studied rationally.

The present work suggests that the cathodic reduction involves both lithium intercalation and phthalocyanine anion dissolution into the polymer electrolyte.

1. Introduction

The characteristics of lithium batteries, such as cell voltage, discharge capacity and rechargeability, are dependent on the cathode active material. Many materials have been examined [1] and much effort has been devoted to the research and development of existing, rechargeable cathode materials for secondary non-aqueous or solid lithium cells [2]. Most of these compounds, like the dichalcogenides, dioxides and disulphides of transition metals of the IV, V and VI groups, are inorganic.

However, it has been reported that, theoretically, organic compounds have many of the characteristics desirable for lithium battery cathodes [3, 4]. Amongst them polyacetylene has certainly been one of the most investigated [5].

The utilization of hydrogen phthalocyanine as a positive electrode in Li cells was first studied at the Nippon Telegraph Labs [6]. According to this study it has some attractive electrochemical characteristics which should lead to high cell voltages and energy densities. Furthermore, its lamellar structure [7] allows this compound to react reversibly with lithium cations. In a previous paper [8], the reduction mechanism was supposed to be only that of lithium intercalation between the layered phthalocyanine molecules. The values of D_{Li} obtained from electrochemical and nuclear magnetic resonance (NMR) measurements are close to 5×10^{-10} and $4 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, respectively. In the present work, we try to explain the discrepancies between the NMR and electrochemical values.

2. Experimental

Hydrogen phthalocyanine (Fluka), previously dried for 48 h at 140 °C under vacuum, was mixed with an excess of n-butyl lithium solution 1.6 M in hexane (Fluka). The mixture was then put in a sealed container and stirred for 15 days. All operations were done in a dry glove box where the moisture content was less than 2 p.p.m.

Chromatography was used for chemical analysis.

The electrochemical behaviour was studied by cyclic voltammetry on the following electrochemical chain:



The counter and reference electrodes (CE, RE) were made of solid lithium in the form of a disc (diameter 11 mm) and a ring (ϕ_{in} 11 mm and ϕ_{ex} 16 mm), respectively. They were cut from a 3 mm thick lithium plate (Alpha product).

The working electrode (WE) was prepared by the vacuum coating of a 5.6 mm diameter stainless steel tip with metal-free phthalocyanine.

In order to prevent H_2Pc dissolution during cathodic sweeps, the working electrode was coated with a thin layer of poly(*N,N*-dimethyl-3,5-dimethylene-piperidinium perchlorate) prepared from the commercial chloride (Aldrich) by ion exchange with Dowex 1 \times 8 50 - 100 mesh (Fluka).

The electrolyte was a 300 μm thick film of P(EO) (5×10^6 mol. wt.)- LiClO_4 complex with an O/Li ratio of 8. The operating temperature was maintained at 80 °C. At this temperature the polymer electrolyte is mainly amorphous, its conductivity is about $8 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$. The P(EO)- LiClO_4 electrolyte was prepared, dried and kept in an anhydrous argon atmosphere.

The H_2Pc dissolution into the electrolyte was characterized, using a microporous (photo-etched) nickel foil which was set between the counter- and working electrodes.

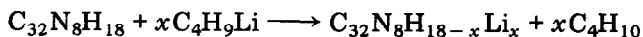
The various components were assembled in a three-electrode cell, described by Fouletier [9].

3. Results and discussion

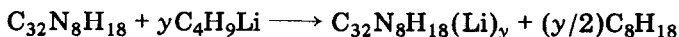
3.1. Chemical lithiation

Hydrogen phthalocyanine consists of multiple delocalized electrons and includes 18 hydrogen atoms which confer an acidic character to this compound. These atoms could partially be exchanged in an acid-base reaction with n-BuLi. Thus the butyl lithium reaction with hydrogen phthalocyanine can follow two different paths:

(a) acid-base reaction: proton transfer



(b) redox reaction: electron transfer



Depending on whether the reaction is acid-base or redox, either butane or octane, respectively, are obtained.

The chromatographic analysis of the reaction products revealed the presence of both butane and octane (Fig. 1). This indicates that both reactions occur simultaneously.

Yamaki and Yamaji [6] reported the reversible incorporation of 17 equivalents of lithium into H_2Pc , in an electrochemical cell. Since we find butane as a reaction co-product which is indicative of a proton transfer, we are led to conclude that the likely mechanism is more complex than a simple topochemical intercalation. From Yamaki and Yamaji's considerations, a ten lithium rechargeable reaction was explained, however the H_2Pc layer structure was supposedly maintained even after the addition of seven more lithiums.

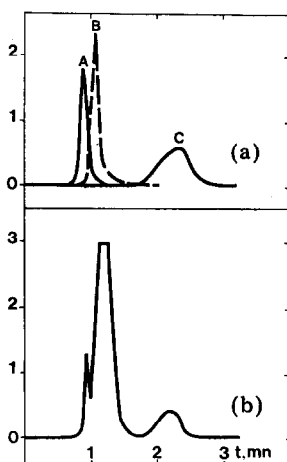


Fig. 1. Chromatographic spectra at room temperature: (a) blank test — curve A, 0.5 cm^3 of butane; B, 1 μl of hexane; C, 1 μl of octane; (b) solution of H_2Pc in butyl lithium after 15 days.

The present results explain the small useful capacities, as compared with the theoretical ones, which were reported by Yamaki and Yamaji. We thus believe that these reported theoretical values were overestimated.

3.2. Electrochemical study

3.2.1. Voltammetric investigation

The complex reduction mechanism of H_2Pc is evidenced by the pattern of the linear sweep voltammograms (Fig. 2). Two cathodic peaks (A, B) and two anodic peaks (A', B') are observed in the voltage range 0 - 3 V/Li. As it can be seen, the cathodic (A) and anodic (A') peaks are very symmetrical and very obvious, whereas the others are irreversible. In a previous paper [8], by using galvanostatic discharge results, we assumed that the cathodic peaks were due only to lithium cation intercalation between phthalocyanine layers. The two voltage domains at 1.6 and 0.75 V/Li, observed on the first galvanostatic discharge (at $I = C/200$) of cells with H_2Pc as the positive electrode, were assigned to be a multiphase intercalation mechanism.

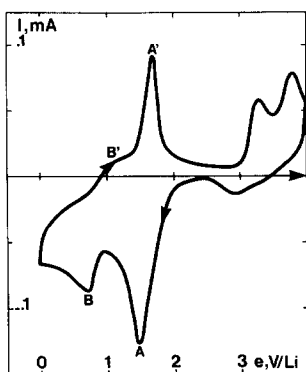


Fig. 2. Cyclic voltammogram on H_2Pc film electrode in PEO_8LiClO_4 electrolyte. $T = 80^\circ C$, sweep rate = 1 mV/s.

The present measurements, however, allow a more rational interpretation of these peaks to be made. Furthermore, it is worthwhile to point out a set of two irreversible anodic peaks, when the sweep potential is carried to the voltage range 3 - 4 V/Li. We have interpreted this phenomenon as the oxidation of phthalocyanine itself.

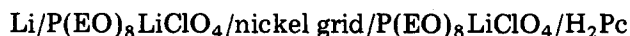
The irreversibly anodically oxidized species go into the $P(EO)-LiClO_4$ electrolyte either as solvated cations or other soluble entities. Recently, by using a rotating disc electrode, Melendres and Xu [10] observed a similar phenomenon on iron phthalocyanine ($FePc$) film electrodes in aqueous solutions.

3.2.2. Characterization of H_2Pc migration

Even though phthalocyanine is very stable in the presence of poly-(ethylene oxide), a greenish coloration of the polymer electrolyte film was

observed only when the cell were discharged. The reaction observed between 1 and 2.6 V/Li is highly reversible, while below 1 V/Li the reaction seems to be irreversible and no significant reoxidation peak was observed.

Thus, this cathodic reduction process could result in the production of soluble species, which are not or only partially reoxidizable. In order to determine if the film deposit is dissolving and if the reduced species migrate, a special cell was constructed according to the following electrochemical chain:



Evidence for H_2Pc in the electrolyte will be obtained by voltammetry between the nickel (WE) and lithium electrodes (RE and CE). After phthalocyanine reduction, the Ni electrode $E(I)$ characteristic approaches that of H_2Pc and typical H_2Pc reduction and oxidation peaks are then observed on this electrode (Fig. 3).

3.2.3. Suppression of anion migration

Moreover, the reduced species are presumably H_2Pc carbanions. In order to prevent the migration of this species, an ultra-thin layer of a polycation (poly(*N,N*-dimethyl-3,5-dimethylene-piperidinium perchlorate)) was laid on top of the H_2Pc electrode. A different behaviour of the H_2Pc electrode is then reflected by the cyclic voltammery curves in Fig. 4.

During the first sweeps, no significant peaks were observed. The system seems to be stable and the H_2Pc electrode is insulated from the electrolyte by the polycation membrane. Thus the lithium cations cannot pass through this layer because of the electrostatic repulsive forces. The first sweeps can be interpreted as due to the reduction of H_2Pc . This leads to the formation of carbanions which are electrostatically bonded by the polyelectrolyte. Therefore, when the interface electroneutrality is achieved, the lithium may

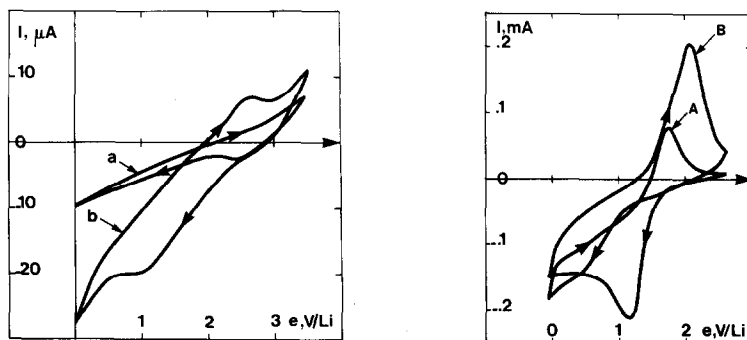


Fig. 3. Cyclic voltammogram on nickel grid in $\text{PEO}_8\text{LiClO}_4$ electrolyte: curve a, before H_2Pc reduction; b, after H_2Pc reduction. $T = 80^\circ\text{C}$, $\nu = 1 \text{ mV/s}$.

Fig. 4. Cyclic voltammogram on H_2Pc film electrode coated with poly(*N,N*-dimethyl-3,5-dimethylene-piperidinium perchlorate) in $\text{PEO}_8\text{LiClO}_4$. $T = 80^\circ\text{C}$, $\nu = 10 \text{ mV/s}$. Curve A, 5th sweep; B, 10th sweep.

diffuse into the host material. After these first cycles, a well-defined and reversible peak is observed in the potential range 1 - 2.6 V/Li, whereas no peak appeared below 1 V/Li.

The variation of anodic and cathodic peak separation with the sweep rate shows that the kinetics of this reaction are governed by diffusion. This is confirmed by the linear variation of peak current intensities with respect to the square root of the sweep rates (Fig. 5). We also carried out a test on cells using only a thin layer of poly(*N,N*-dimethyl-3,5-dimethylene-piperidinium perchlorate) on a stainless steel tip working electrode. The cyclic voltammetry was performed under the same conditions as the above-mentioned H₂Pc cell test. No peak was observed in the voltage range of 0 - 4 V/Li.

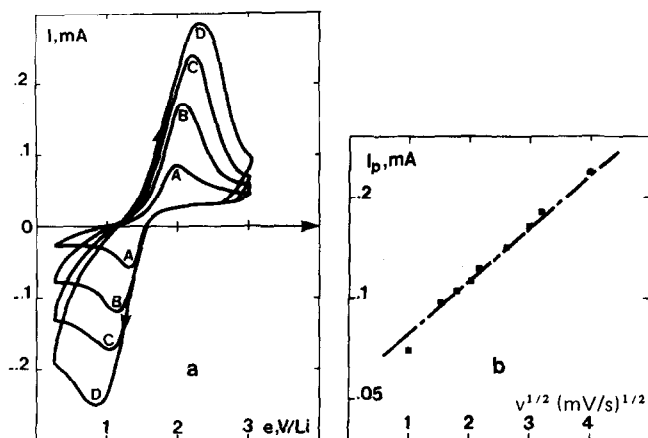


Fig. 5. (a) Evolution of voltammogram with potential sweep rate. Curve A, $v = 1$ mV/s; B, 4 mV/s; C, 9 mV/s; D, 16 mV/s. (b) Peak current intensities as a function of the square root of the potential sweep rates. Working electrode = H₂Pc film coated with polycation. $T = 80^\circ\text{C}$.

4. Conclusions

This work shows the complexity of the cathodic reduction mechanism of phthalocyanine. During chemical lithiation by *n*-butyl lithium, we found that phthalocyanine could exchange both protons and electrons.

In our electrochemical cells, the cathodic reduction process results in the production of soluble species at potentials below 1 V/Li. This hypothesis is well confirmed by the greenish coloration of the polymer electrolyte film observed only after the cell discharge. We believe that the phthalocyanine cathodic reduction is:

(a) lithium intercalation between layered phthalocyanine molecules, since:

the reaction with n-butyl lithium gives octane as a reaction co-product, and because of

the good rechargeability of the Li/H₂Pc cell in the voltage range of 1 - 2.6 V/Li;

(b) the phthalocyanine ring reduction leading to a soluble carbanion in the P(EO) electrolyte (this was demonstrated in § 2.3); the loss of capacities observed in the electrochemical cells is certainly maintained by this second reaction.

In order to clarify this mechanism the relative contributions of these reactions are being studied at present.

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References

- 1 M. S. Whittingham, *J. Electroanal. Chem. Interfacial Electrochem.*, 118 (1981) 229.
- 2 A. Le Mehaute, *J. Power Sources*, 9 (1983) 167.
- 3 H. Alt, H. Binder, A. Kohling and G. Sundsted, *Electrochim. Acta*, 17 (1972) 873.
- 4 S. I. Tobichima and J. I. Yamaki, *J. Electrochem. Soc.*, 131 (1984) 57.
- 5 D. MacInnes, M. A. Druy, P. Nigrey, D. P. Nairns, A. MacDiarmid and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, (1981) 317.
- 6 J. I. Yamaki and A. Yamaji, *J. Electrochem. Soc.*, 129 (1982) 5.
- 7 J. H. Sharp and M. Lardon, *J. Phys. Chem.*, 72 (1968) 3230.
- 8 F. Dalard, D. Deroo, H. Djellab, J. Mercier and J. P. Cohen Addad, *J. Power Sources*, 14 (1985) 71.
- 9 M. Fouletier, *Thèse Doctorat d'Etat*, Grenoble, 1983.
- 10 C. A. Melendres and S. Q. Xu, *J. Electrochem. Soc.*, 131 (1984) 466.