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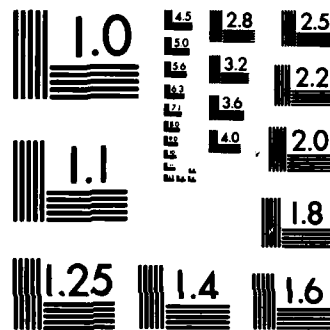
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BASIC STUDIES OF THE LITHIUM SECONDARY BATTERY

FINAL REPORT

(Technical Report No. 1)

May 1, 1984 to April 30, 1985

Prepared by

J. S. Foos, S. M. Erker and L. M. Rembetsy

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approx.
0.5e⁻² per quinone unit. Similar results were observed in the initial cycles in Li cells, however, the capacity of the electrode degraded on cycling.

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(U.S. Steel, used as-received). The 2-methyltetrahydrofuran (2-MeTHF) (Aldrich) and tetrahydrofuran (THF) (Burdick and Jackson) were distilled from CaH_2 and treated with alumina. The propylene carbonate (PC) (B&J), and acetonitrile (AN) (B&J) were used as-received.

Synthesis and Cyclic Voltammetry of PDMB I. The electrochemical oxidation was done in a cylindrical, undivided cell using stainless steel (SS) electrodes and under an Ar atmosphere. The cell was filled with 0.5M LiClO_4 in PC containing excess DMB (Eastman). Typically the films were formed using a constant current which was increased over the period of 4-5 hr to a maximum of 0.4A (2.6 mA/cm^2). After approximately four hours at a cell voltage of $\sim 4.9\text{V}$ ($\sim 4.1\text{V}$ at O.C.) a black layer 1-2 mm thick had formed. During the reaction, first, metallic Li and then gas bubbles (H_2) formed on the counter electrode. When the deposition was completed, the polymer was removed from the electrode, filtered, and washed with acetonitrile. The yield was $\sim 3.6\text{g}$ and ranged from 85 to 91% (based on $2e^-$ per monomer). This material is insoluble in all common solvents and, although initially black, becomes light brown upon exposure to the atmosphere. No melting point was observed up to 400°C .

An analytical sample was prepared by adding the original black material to H_2O with stirring, followed by filtration and drying for ~ 3 hrs at 100°C . Elemental analysis (Galbraith); Calcd for $\text{C}_8\text{H}_8\text{O}_2$: C, 70.58; H, 5.92; O, 23.50. Found: C, 70.43; H, 5.77; O, 23.74; IR (KBr) 2980(m), 2925 (m), 2925(m), 2820(m), 1485(s), 1460(s), 1390(m), 1365(m), 1260(m), 1200(s), 1170(m), 1035(s), 860(m), 795(w), 750(m) cm^{-1} . The peak at 1035 cm^{-1} (O- CH_3 str.) and a small OH peak indicated that the methyl groups were not lost in the polymerization.

The cyclic voltammetric (CV) work was done using an ECO 551 potentiostat, 566 function generator, and a Hewlett-Packard 7015B X-Y recorder. Scans were done at 50 mV/sec. The cell utilized an isolated Li reference and SS counter electrode. The PDMB film was formed on a 1 cm SS wire (1 mm dia) from 0.5M LiClO_4 in PC containing 0.03M DMB. The CV analysis of the PDMB electrode done in electrolyte contain no excess DMB.

Synthesis of PHQ II. The PDMB I (3.6g) was finely ground and treated with 100 ml of 48% HBr. The solution was stirred and heated for approximately 24 hrs under argon at a constant temperature of $130-140^\circ\text{C}$. The reaction was followed by monitoring the loses of the 1035 cm^{-1} peak (O- CH_3 stretch) in the IR spectrum. The polymer was isolated by adding H_2O to the suspension, filtering, and washing with H_2O and finally acetone. Drying was done under vacuum at $>50^\circ\text{C}$. The product is a dark powder with no mp up to 400°C . It is insoluble in all solvents except for those containing base. The powder completely dissolves at pH 10 which typically requires approximately 4 meq. of base per gram of material. The IR spectrum shows the loss of the peaks at 2980, 2925, 2820 (alkyl C-H str.) and 1035 cm^{-1} indicating the removal of the methyl groups. The IR (KBr) includes a broad absorption at 3300(s), plus 1630(m), 1500(m), 1430(s), 1325(m), 1195(s), 865(m), 800(s).

The elemental analysis of this material invariably shows appreciable excess H over the expected $C_6H_4O_2$ approaching one H per monomer. This excess may imply low molecular weight, see Results and Discussion.

An alternative synthesis of PHQ involved the treatment of PDMB (0.8g) with 18g of pyridium hydrochloride (Aldrich) at $230^\circ C$ for 1 hr (13). The melt was poured into water and the PHQ isolated as above. The IR of this material was virtually identical to that obtained previously. The elemental analysis showed less H (4.05%, calc. 3.70%) than earlier samples, however the sample apparently contained residual pyridine (N, 2.00%).

Synthesis of PQ III. A sample of PHQ was added to distilled H_2O . Aqueous NaOH (0.1N) was added to this solution until all of the PHQ was dissolved. Aqueous HCl (0.1N) was then added to precipitate the polymer. A potentiometric titration, employing a SCE as the reference electrode and a Pt wire as the indicator electrode, was performed. The titrant used was a freshly prepared solution of .51 ml of Br_2 in 100 ml of distilled H_2O . The potential was measured after the addition of each successive increment of titrant. A steady potential ranging from .840V to .850V indicated the end point. The stoichiometry of the Br_2 oxidation is in approximate agreement to that expected for oxidation of hydroquinone to quinone. The black quinone was isolated by centrifugation or filtering, washed with H_2O , and dried under vacuum at $100^\circ C$.

The IR shows a strong absorption at 1650 cm^{-1} associated with the quinone carbonyl. Other absorptions include (KBr): 1565(s), 1415(m), 1320(m), 1185(s), 965(w), 910(m) cm^{-1} . Residual absorptions remain above 2000 cm^{-1} presumably due to hydration H_2O left after drying at $100^\circ C$. Elemental analysis showed incorporation of Br (19%) which was not expected using this technique (14). Analysis (Galbraith); calcd for $C_6H_2O_2Br_{0.33}$: C, 54.39; H, 1.51; O, 24.17; Br, 19.92. Found: C, 53.61; H, 1.53; O, 23.99; Br (by diff.), 20.87.

An alternative oxidation technique used iodine at neutral pH. The PHQ (0.3-0.4 g) was dissolved and reprecipitated as described above using care to re-establish a neutral solution. Buffer (pH 7, Fisher) was added and the solution titrated using KI_3 (0.1M) to a potential of $\sim 0.34V$. Periodic additions of dilute NaOH were made to keep the solution neutral. The quinone was isolated as above.

This procedure gave a material which was much lighter in color than the earlier procedure and gave an IR with much sharper absorptions and much less absorption above 2000 cm^{-1} . IR (KBr): 3400(w), 1650(s), 1565(m), 1425(w), 1320(m), 1185(s), 965(vw), 910(m). The elemental analysis (Galbraith) showed some iodine incorporation and excess H: Calcd for $C_6H_{2.33}O_2I_{0.1}$: C, 60.49; H, 1.96; O, 26.88; I, 10.67. Found: C, 61.70; H 1.99; O, 25.89; I (by diff.), 10.42.

The ceric ion oxidation of PHQ was done under Ar in acetic-sulfuric acid solutions using 0.101N ceric sulfate in 0.5 NH_2SO_4 as the titrant (15). The titrations were done potentiometrically using a Pt electrode vs.

SCE. Potential readings were taken 5 min. after the ceric addition. The titanous reduction was done by adding excess titanous solution prepared by diluting commercial 20% TiCl_3 (Fisher) one volume to ten. The reduction was complete in 20 min.

Synthesis of PQ III on Carbon (1:1). To 100 ml of distilled H_2O , three drops of Triton X-100 (Fisher) was added followed by 0.3-0.5g of acetylene black (Shawinigan). After stirring, PHQ was added and treated with sufficient NaOH to completely dissolve the PHQ. The solution was then slowly neutralized with aqueous HCl. This procedure was followed by the potentiometric titration described previously. The product was isolated by filtration, washed with H_2O , and dried under vacuum at 80°C .

Li Cell Preparation and Cycling. The PQ III on carbon (PQ/C) was mixed with 20% carbon/Teflon and pressed onto fine Ni Exmet in a steel die at 4300 psi to give a circular pellet 1.3 cm dia. and ~1.5 mm thick. The density of the pellet was $\sim 1.2\text{g}/\text{cm}^3$ (exclusive of Exmet). The electrode was then placed against the inner wall of a 5.9 x 3.9 x 1.3 cm prismatic glass cell. The electrode was held in place and under compression by the balance of the cell material consisting of a Celgard 2400 separator, a 10 mil propylene wick, and a 10 mil Li counter electrode backed by a solid polypropylene sheet. Compression was maintained by a leaf spring made from stainless steel shim stock (10 mil). Approximately 20 ml of electrolyte was used to fill the cell. The cells were discharged and charged at constant current between voltage limits.

The coulometric titration was done by discharging (charging) the cell at constant current for one hr at 1.00 mA. The cell was then allowed to set at open circuit for 2 hrs and the voltage recorded. This was continued until the cell polarized to 1.60V (vs. Li) during the discharge. The open circuit voltages were then plotted vs. charge.

RESULTS AND DISCUSSION

When DMB is oxidized in 0.5M LiClO_4 solution in propylene carbonate (PC) a black material forms on the substrate which is easily grown to 1-2 mm thickness. This material is a doped semiconductor with a maximum observed conductivity of $3.7 \times 10^{-4} \text{ S}/\text{cm}$ for isolated samples. The measured conductivities are variable and dependent on the doping level.

The polymer as formed is oxidatively doped, but unlike polypyrrole, this doping appears unstable in electrolyte. A doped film of PDMB can be grown during successive cyclic voltammetric sweeps (Fig. 1. top), however when the excess monomer is removed the size of the peaks decrease on cycling (Fig. 1, bottom). This lack of stability may result from reaction with electrolyte, however it has been observed in both LiClO_4/PC and $\text{LiAsF}_6/\text{acetonitrile}$ electrolyte. Alternatively, the doped polymer may be inherently unstable.

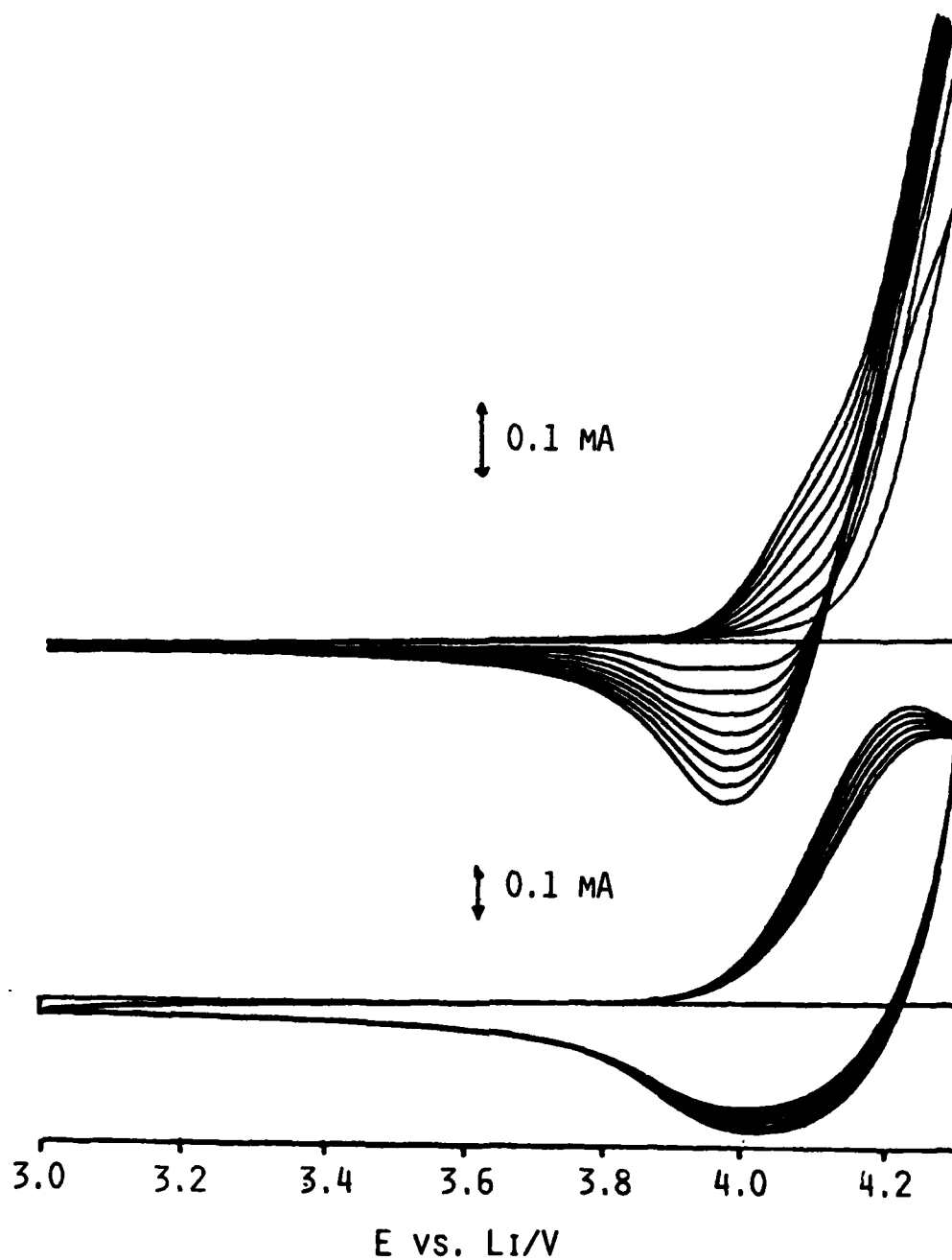


Fig. 1. Top: The formation of PDMB from DMB solution with currents increasing with cycling. Bottom: The oxidation and reduction of PDMB film with currents decreasing with cycling.

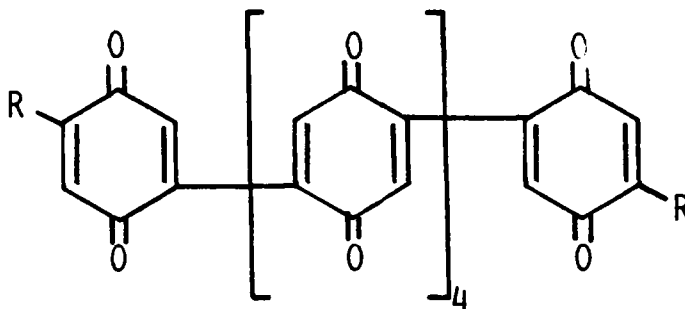
After reaction with water, the doped polymer gives a light brown material that is insoluble in all common solvents, does not melt up to 400°C, and gives an elemental analysis (C₈H₈O₂) which corresponds to the anticipated polymer PDMB, I. The IR spectrum shows the retention of the methyl groups by the alkyl oxygen-carbon stretch at 1035 cm⁻¹ and by the absence of absorptions attributable to phenolic hydrogens. Due to the low solubility of this polymer, molecular weight determinations were not done. However, oligomers of DMB up to the tetramer are known and have been reported to have melting points below 400°C and some solubility (13). Therefore PDMB must have a higher molecular weight than these compounds. The observed elemental analysis, with no excess hydrogen, implies even a higher degree of polymerization.

PDMB was converted to the polyhydroquinone, PHQ, by treatment with aqueous HBr. The product is a dark brown or black powder which is insoluble in all common solvents except aqueous base at pH 10. The powder can be converted to a voluminous (high surface area) precipitate by dissolution followed by reprecipitation. This step was necessary so that the subsequent oxidation could be done at a reasonable rate and as a means to deposit the PHQ on high surface area carbon.

The IR spectrum of PHQ is in agreement with the proposed structure, however, the elemental analyses were consistently high in hydrogen. This may be due to incomplete removal of the methyl groups, the presence of low molecular weight oligomers, or reduction (hydrogenation) of some of the unsaturation in the polymer chain. The first two of these explanations seem most likely. It might be expected that there would be residual methoxy groups due to the insolubility of the starting material and product, i.e., heterogeneous reaction conditions. In addition, the rigorous conditions required to cleave the methoxy groups might also cleave the bonds between monomers. Oligomers up to the trimer have been characterized (13) and would be expected to be soluble in washes used in the isolation of PHQ. The possible existence of oligomers will be further addressed in the discussion of the polyquinone. A second method, investigated briefly for converting PDMB to PHQ, utilizes pyridinium hydrochloride at 230°C. The IR spectrum of this material was unchanged from that previously recorded. The elemental analysis was somewhat improved but the result was clouded by the presence of residual pyridine.

PQ was synthesized from PHQ using bromine water. This reagent has been reported to be useful in oxidizing hydroquinones in redox polymers (14) and is particularly useful because both bromine and bromide are water soluble and thus the isolation of product is simplified. The PHQ is rapidly oxidized to PQ in acid solution using approximately an equivalent of bromine.

The IR spectrum shows clearly the formation of the quinone in an absorption at 1650 cm^{-1} . Unfortunately significant bromine is found in the elemental analysis. The amount of bromine is relatively consistent among samples (0.3-0.4 bromine per monomer) and along with the analysis for carbon, hydrogen, and oxygen suggests that this PQ is the dibromohexamer, IV.



IV R = BR, V R = H

This is in agreement with the observed excess hydrogen in the analyses of PHQ implying lowered molecular weight probably resulting from cleavage of the polymer during ether cleavage. If a hexameric polyhydroquinone were formed it might be expected that it could be rapidly brominated at its termini (13). The interior hydroquinone groups would be sterically hindered to bromination (like redox polymers) and be oxidized instead.

To minimize halogenation, the oxidation was done using iodine, instead of bromine, which normally undergoes nucleophilic substitution only with difficulty. The product was a soft brown powder instead of the brittle black solid produced previously. The IR spectrum of this material had the same absorptions as before but they were much sharper and the background, especially above 2000 cm^{-1} was much decreased. In this case the elemental analysis showed little incorporated iodine, however, there was sufficient excess hydrogen to suggest the presence of the hexamer V.

As in the case of the hydroquinone, the excess hydrogen may also be due to incomplete reaction of the precursor. If the oxidation of the PHQ to PQ were incomplete, the excess hydrogen would be the phenolic hydrogen. This would be expected to show up in IR spectra and absorbances in the O-H stretch region are observed although they are minimal in the case of the iodine-oxidized PQ. Such materials might also react intramolecularly in a Michael addition (12) causing the O-H absorption and unsaturation to be lost.

To further substantiate the structures of PHQ, freshly precipitated samples were chemically oxidized using aqueous Ce^{IV} , reduced with Ti^{III} , and reoxidized with Ce^{IV} (15). The same procedure was applied to hydroquinone for comparison, see Figure 2. In the initial potentiometric titration, the potential is constant with a rapid rise at the endpoint when titrating hydroquinone and the theoretical equivalency is observed. With

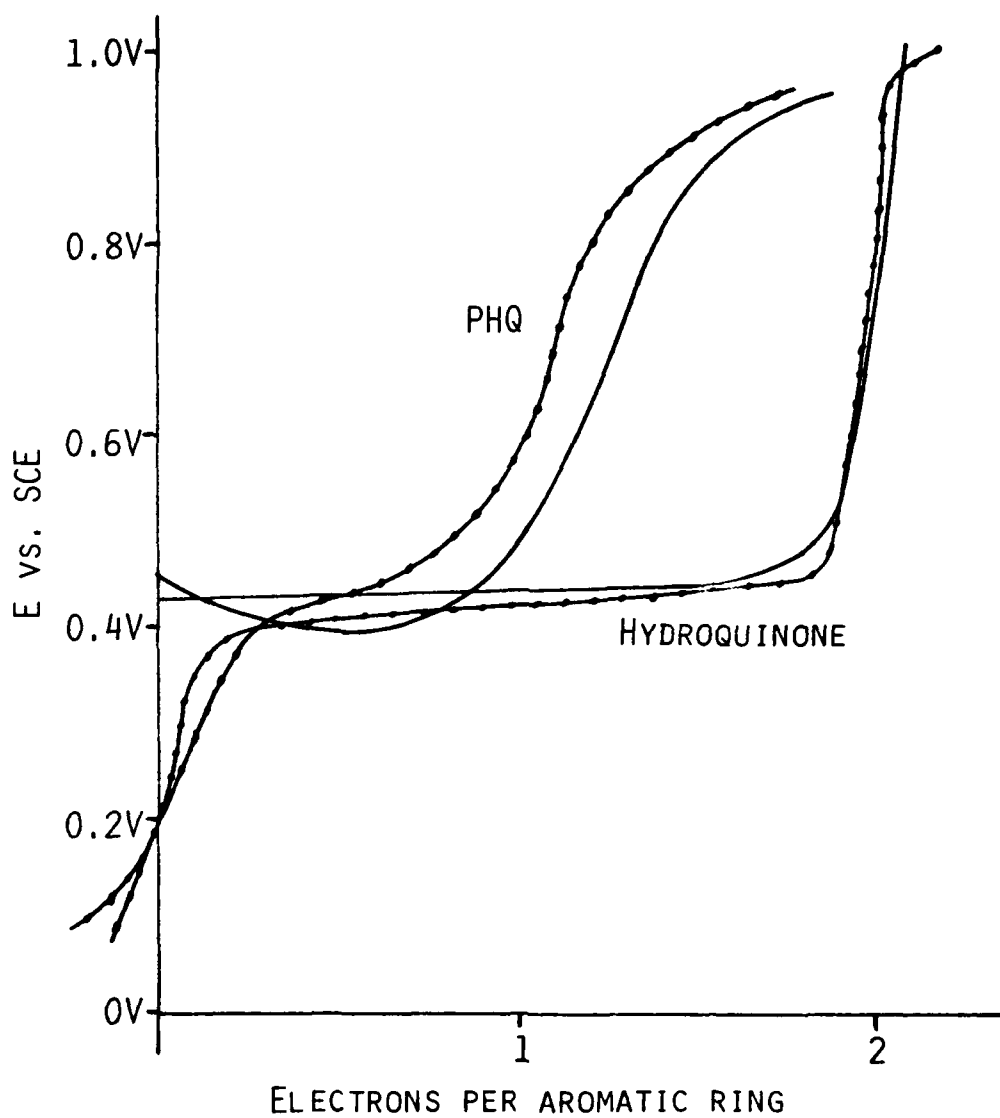


Fig. 2. Potentiometric titration of hydroquinone and PHQ with ceric ion. The solid lines are the first titrations. The dotted lines are the second titrations.

PHQ the titration curve is similar but shows gradual potential changes which reflect the slow equilibration due to the two phase reaction. The observed capacity is ~70% of the theoretical in the initial oxidation. After titanous reduction, the hydroquinone is reoxidized in nearly 100% efficiency whereas the PHQ shows decreased capacity on this second oxidation. Nonetheless, the substantial redox capacity of the PHQ is demonstrated.

The conductivity of the doped PDMB suggested that the derived hydroquinone and quinone might also be conductive. Although occasional samples have shown some slight conductivity ($\sim 10^{-7}$ S/cm, 2-probe) generally the conductivity of the samples was low ($< 10^{-8}$ S/cm). Attempts were made to reductively dope PQ in non aqueous solvents, using sodium naphthalide and sodium benzophenone ketyl without success. There was no apparent reaction suggesting that the PQ was not wetted by the aprotic solvents. This might have been expected because only freshly precipitated samples of PHQ react at appreciable rates in aqueous suspension. As an alternative, a half-oxidation of PHQ by ceric ion was done to measure the effect of oxidative doping on PHQ. An increase in conductivity was observed, however, the conductivity remained low (10^{-7} S/cm, 2-probe). The conductivity observed in earlier samples of PHQ and PQ must indicate incomplete reduction or oxidation.

Electrochemistry of PQ in Nonaqueous Electrolyte. Initial studies showed that pressed powder electrodes formed from PQ or PQ physically mixed with carbon/Teflon or graphite showed very little electrochemistry in non-aqueous electrolytes, such as THF/LiAsF₆, 2MeTHF/LiAsF₆, and PC/LiClO₄. To maximize the contact between the PQ and carbon, PHQ was precipitated in a stirred carbon suspension. This was then oxidized to give PQ on carbon (PQ-C). This in turn was mixed with a small amount (20%) of carbon-Teflon binder in making the electrodes. These electrodes were much improved and were evaluated in the electrolytes mentioned earlier.

The most satisfactory electrolyte for the electrochemical reduction and oxidation of the PQ-C electrodes formed using bromine (i.e., PQ-C/Br) was THF/LiAsF₆. The PC/LiClO₄ gave sluggish behavior presumably due to poor wetting or high viscosity; and the 2-MeTHF/LiAsF₆ was more easily oxidized perhaps due to the 2-Methylfuran impurity (16). The coulombic titration of PQ-C/Br is shown in Figure 3. The capacity was 0.53 electron per monomer and the reduction appears fairly reversible. The observed hysteresis however suggests irreversibility (or incomplete equilibration in the coulombic titration).

This material (PQ-C/Br) was also cycled, typically at 0.5-1.0 mA (0.38-0.75 mA/cm²). The first discharge and subsequent charge were similar to the coulombic titration in both capacity and voltage profile. Unfortunately on subsequent cycles the capacity drops off rapidly with both the charge and discharge voltages showing second plateaus, see Figure 4. These new plateaus suggest that the electrode chemistry is changing with cycling. The apparent agreement between the coulombic titration and first cycle,

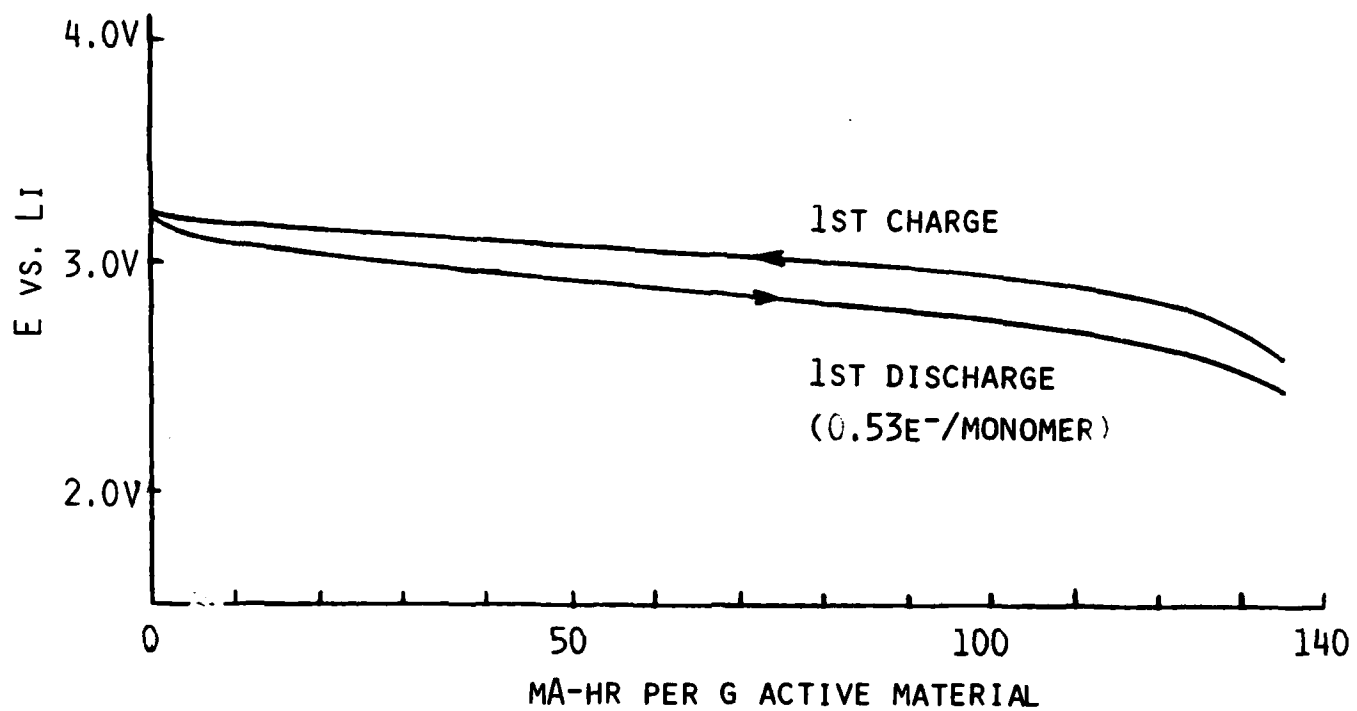


Fig. 3. Coulometric titration of an electrode containing PQ-C/Br in THF/
LiAsF₆.

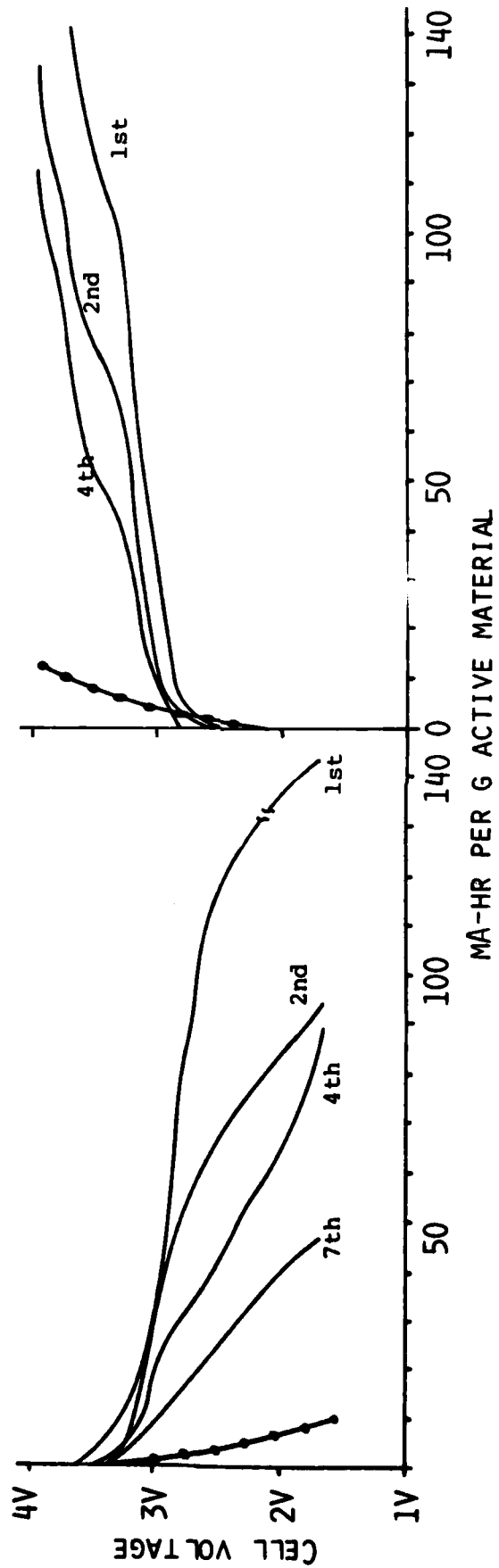


Fig. 4. Cycling of an electrode containing PQ-C/Br at 0.5 mA (0.38 mA/cm²). The dotted line is the background due to the discharge and charge of carbon treated with bromine in the absence of PHQ. The contribution due to the carbon/Teflon is negligible.

despite the fact that the time period for the coulombic titration is much greater, supports the observation that the charge loss is related to the extent of cycling and not just time.

The bromine was suspected of playing a role in the electrochemistry of the electrode. If the bromine were present as molecular bromine, then it could be responsible for up to half of the discharge capacity (20% of 100 mg of PQ). However, the electrode material was washed well with water and acetone; and dried before use at elevated temperatures ($>50^{\circ}\text{C}$ under vacuum for several hrs). These procedures should be effective in removing molecular bromine or bromine derived salts.

Alternatively, covalently bonded bromine might be reduced, not the quinone groups. The apparent reversibility on the first charge implies that this is unlikely because the reduction of bonded bromine would be highly irreversible. Additionally the cell voltage is higher than would be expected for such a reaction (17).

Because oxidation with iodine gave a more halogen-free material, PQ-C which had been prepared using iodine (PQ-C/I) was compounded into an electrode. The general behavior on cycling was similar to the above, however, the mid-discharge voltage on the initial discharge was lowered significantly. Using THF/ LiAsF_6 the mid-discharge voltage was lowered from 2.8V for PQ-C/Br to 2.55V for PQ-C/I. In THF/ LiClO_4 the mid-discharge voltage was lowered to 2.35V for PQ-C/I, see Figure 5. This lowering in voltage is in agreement with the effect of halogen substitution on the redox potential of quinones and is the opposite to what would be expected for the reduction of the halogen substituent itself (17).

CONCLUSIONS

The electro-oxidation of DMB offers a convenient synthesis of a protected polyhydroquinone (PDMB). This may be converted chemically to PHQ and PQ. Unfortunately the conductivity manifested in the PDMB during synthesis is for the most part lost in PHQ and PQ. This may result from defects in the synthesis or the cause may lie in the fundamental nature of the polymer. The electrochemistry of these materials was examined in carbon containing composites. The capacity of PQ to reduction was less than expected, however, assuming one electron per quinone nucleus and an imperfect synthesis, the observed values (up to $0.5e^-/\text{ring}$) are promising.

The electrodes unfortunately lose capacity on cycling. It would be expected that at least the one electron reduction of a quinone would operate reversibly (17). The cause may lie in the synthetic techniques, the electrolyte used, or in the unoptimized electrode construction. The lack of conductivity in PQ is certainly important and there is little evidence that the conductivity increases on discharge (reductive doping). In this case, it might be expected that the PQ would lose contact with the carbon on cycling, due to volume changes, and thus the apparent capacity would decrease.

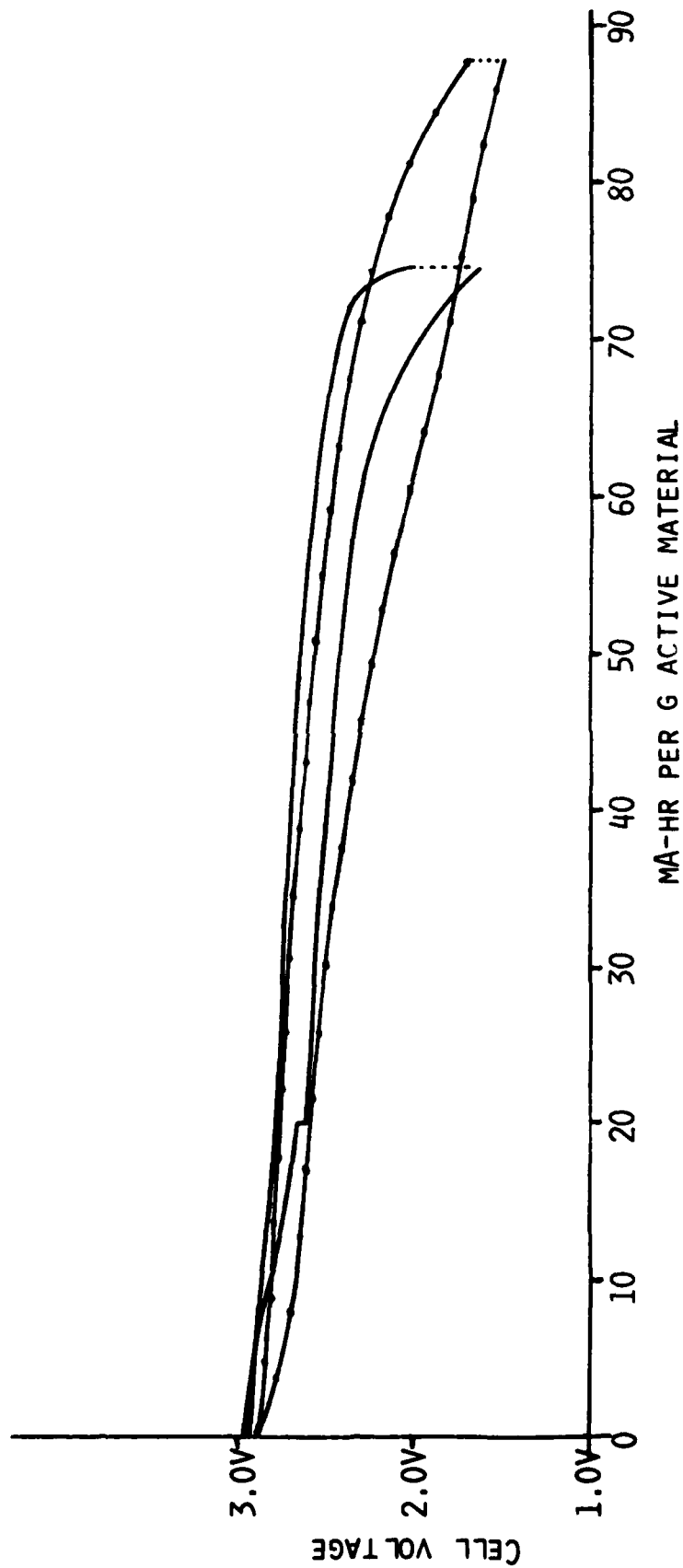


Fig. 5. The first discharge and first charge of electrodes containing PQ-C/I. The solid line shows the discharge done in 1.5M LiAsF₆/THF at 0.75 mA (except for the first 20 mA-hr/g). The dotted line shows the discharge done in 1.5M LiClO₄/THF at 0.50 mA.

Whether or not there is fundamentally irreversible chemistry taking place in the polymer electrode material is not known and polymer quinone electrode materials remain of interest.

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