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**AEROSPACE POWER SCHOLARLY
RESEARCH PROGRAM**

**Delivery Order 0007: Single Lithium Ion
Conducting Polymer Electrolyte**



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14. ABSTRACT This report focuses on the development of a lithium-ion conducting channel as a solid-state electrolyte for rechargeable lithium batteries. Dilithium phthalocyanine (Li₂Pc) has been used in this development since it can undergo molecular self-assembly to form the ionically conducting channel. The essential features of the channel are that it is designed such that the anion matrix of the unsaturated macrocycle forms the channel through which the lithium ions move, thus making it a single-ion conductor for lithium ions; the ionic transport of lithium depends on the electric field gradient created by the electrodes, thereby minimizing temperature dependence for ionic transport.					
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Introduction

Objective: Synthesize a single ionic conducting polymer electrolyte (lithium ion) which features a constant-solvent-coordination sphere for the lithium ions i.e. a channel for lithium ion conduction.

The original effort in this area was the preparation of a polymeric porphyrin ladder structure as shown in Figure 1. The generation of the requisite components was

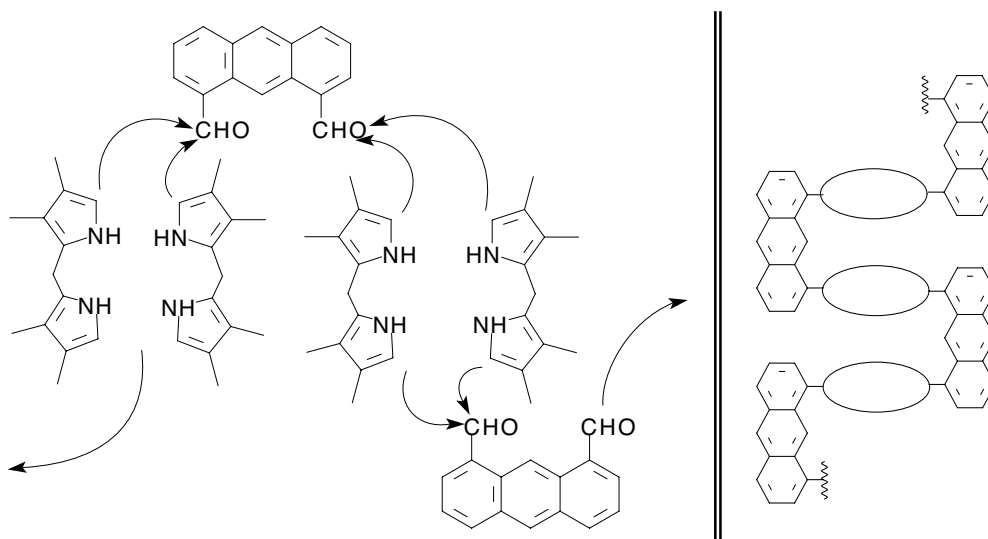


Figure 1. (left) The proposed polymerization of a "spacer" and appropriate bipyrrole subunits. (right) The polymeric "channel" produced.

undertaken as proposed Figure 2. This approach was abandoned in favor of a new

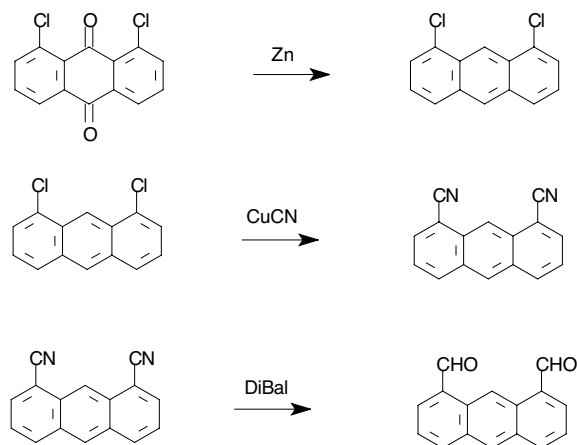


Figure 2. The proposed synthesis of the "spacer" unit.

material, dilithium phthalocyanine, Li_2Pc (Figure 3), that forms a channel-array by

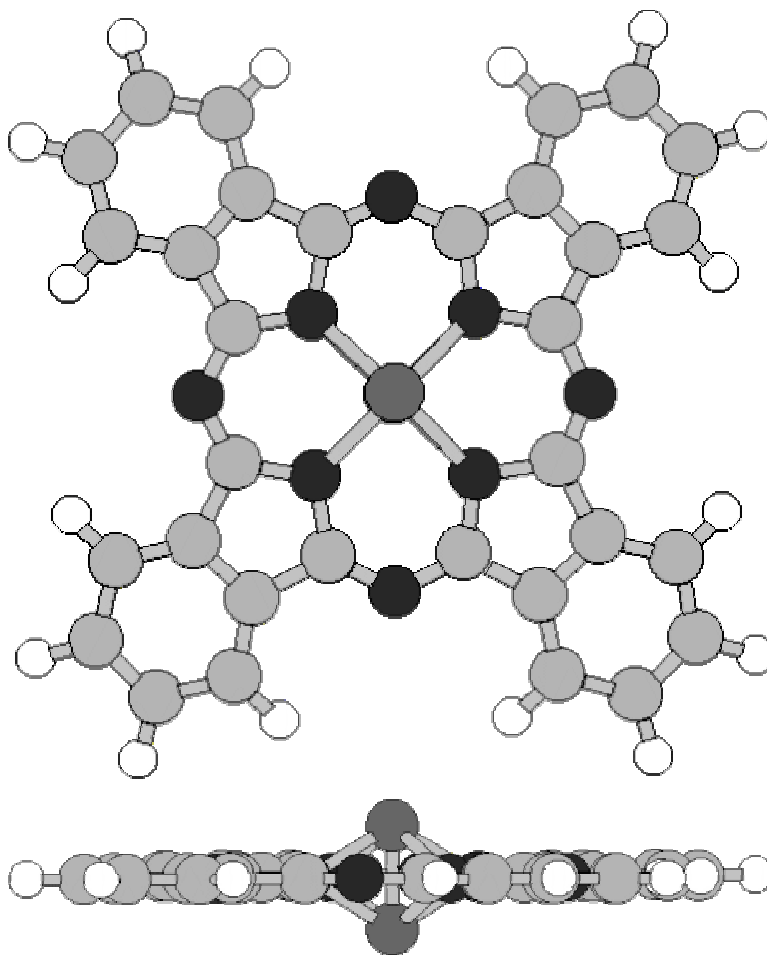


Figure 3. The structure of dilithium phthalocyanine.

molecular self-assembly on a nanoscale. The preparation and purification of dilithium phthalocyanine has been the focus of the current research. A procedure (paper #1 Experimental) for the purification of commercially available dilithium phthalocyanine was developed and allowed for the determination of the data presented in the attached papers. We are currently investigating the in-house preparation of Li_2Pc because commercially available material is in short supply and of low quality. Several samples from vendors contain unknown impurities and give low yields that are unacceptable for electrochemical experiments as described in the publications attached.

The following papers were prepared during the course of the investigation and provide detailed descriptions of the accomplishments of this research.

1. L. G. Scanlon, L. R. Lucente, W. A. Feld, G. Sandí, D. J. Campo, A. E. Turner, C. S. Johnson, R. A. Marsh. Lithium-Ion Conducting Channel. Proceedings of the International Workshop on Electrochemical Systems. A. R. Landgrebe, R. J. Klingler (editors). Vol. 36, 326-339, (2000).
2. L. G. Scanlon, L. R. Lucente, W. A. Feld, G. Sandi, D. J. Campo, A. E. Turner, R. Csencsits and S. J. Rodrigues, Lithium-Ion Conducting Channel, 7th Workshop for Battery Development, Philadelphia, June, 2001.

LITHIUM-ION CONDUCTING CHANNEL

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Computational Chemistry has been used to design a solid state ionically conducting channel for lithium ions whereby the transport mechanism for lithium ions depends on the electric field gradient established between the electrodes of an electrochemical cell. In this fashion, the temperature dependence for ionic conduction is minimized and one can expect high ionic conductivity at ambient and subambient temperatures. This transport mechanism differs from oxygen based polymer electrolytes where in that case lithium ion transport depends primarily upon polymer segmental motion and is therefore very much temperature dependent. An additional benefit associated with the lithium ion channel is that the transference number for lithium is one and therefore under high current loads any voltage drop across the electrolyte is minimized. The transference number of one for lithium is by design since the anion matrix that forms the lithium ion conducting channel is immobile. A schematic of a one dimensional single ion conductor for lithium ions as shown in Figure 1 illustrates this point. The macrocyclic ring shown in the figure is an unsaturated macrocyclic complex such as dilithium phthalocyanine. It is by design that one uses an unsaturated macrocyclic complex because with it there is electron delocalization around the ring that keeps the lithium ion centered within the macrocycle. Correspondingly, this is where the negative

electrostatic potential is at a maximum. It is through proper spacing of the unsaturated macrocyclic rings with respect to one another, that allows one to create a channel where the negative electrostatic potential remains relatively constant throughout the molecular system. It is this feature that is primarily responsible for changing the lithium ion transport mechanism so that it depends upon the electric field gradient established between the electrodes of a cell.

In order to test the concept of an ionically conducting channel designed for lithium ions, dilithium phthalocyanine (Li_2Pc) was chosen as the molecular system. Gaussian 98, a software package from Gaussian, Inc. for doing computational chemistry, was used to investigate the molecular structures for Li_2Pc , $(\text{Li}_2\text{Pc})_2$ and $(\text{Li}_2\text{Pc})_3$ by doing Hartree-Fock calculations.⁽¹⁾ The molecular structure for $(\text{Li}_2\text{Pc})_3$ is shown in Figure 2. The spacing between the phthalocyanine rings is about 3.5 Å. This close spacing is a result of electrostatic attraction between the lithiums and nitrogens on adjacent dilithium phthalocyanine molecules. The calculated bond energy for this molecular system is on the order of 76 kcal/mole. Calculations are on going that factor in different basis sets and methods of calculation for determining the bonding energy. The importance of this result is that it suggests that molecular-self assembly

can be important in the formation of the lithium ion conducting channel. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) photomicrographs of dilithium phthalocyanine are shown in Figure 3 a and b, respectively. The long columnar structure illustrated in these figures is consistent with the calculated results reflecting a strong molecular electrostatic bonding predominately along one axis. As an additional collaboration of the calculated results, a Differential Scanning Calorimetry (DSC) was run on dilithium phthalocyanine since it was expected that one should have an endotherm peak reflecting the molecular-self assembly process. The DSC results showed an endotherm at 89.4°C and an absorption energy of 202.9 J/g. The preliminary calculated results for the bond energy of $(\text{Li}_2\text{Pc})_3$ formed by the reaction of three moles of dilithium phthalocyanine in the gas phase is 76 kcal/mole or 201.3 J/g.

So far, the discussion has focused on the molecular structure of the electrolyte. In order to test the validity of the concept, two electrode cells have been constructed using lithium foil as the counter and reference electrode and a thin film of copper as the working electrode. Li_2Pc in the form of a pellet 589 μm thick and 1cm^2 was used as the electrolyte. The cyclic voltammogram of this test cell run at -10°C is shown in Figure 4. The smallest electrode area used in the cell was that of the lithium electrode at 0.385 cm^2 . The profile of the cyclic voltammogram is virtually identical to that reported by Angell for his single lithium ion conductor based upon an inorganic polymer anion.⁽²⁾ His cyclic voltammogram at ambient temperature, which is Figure 3 of his paper, is dominated by the deposition and stripping of lithium as shown in Figure 4. The resistance of the cell shown in Figure 4 is 0.6 ohms and corresponds to a specific conductivity of $2.5 \times 10^{-1}\text{ S/cm}$ at -10°C . The plating and stripping

of lithium, as shown in Figure 4, is consistent with the transport of lithium ions through the solid state ionically conducting channel.

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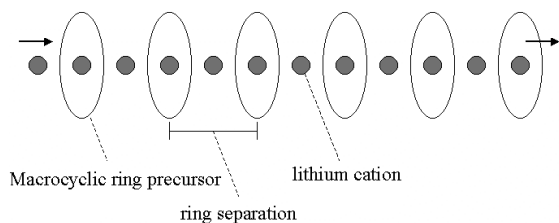


Figure 1. Schematic diagram for a one dimensional single ion conductor for lithium ions.

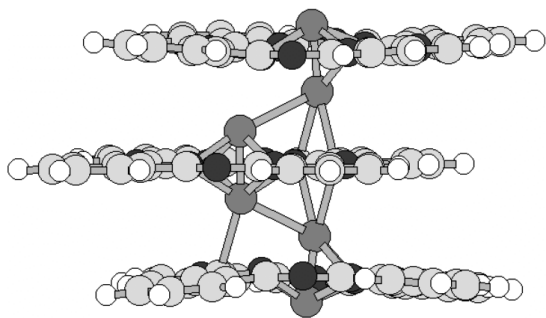
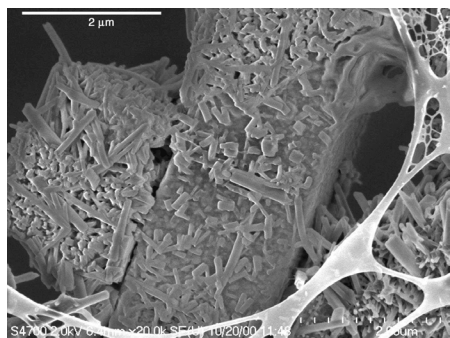
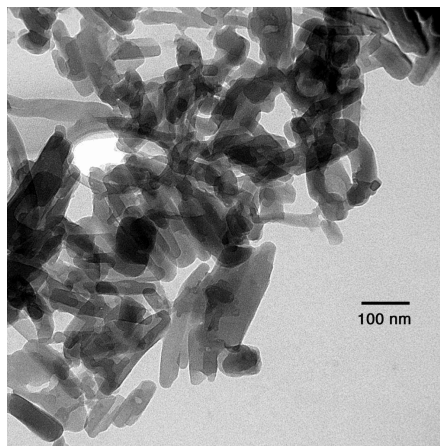


Figure 2. Structure for $(\text{Li}_2\text{Pc})_3$ based on Gaussian 98 calculated results.



(a)



(b)

Figure 3. SEM (a) and TEM (b) photomicrographs of Li_2Pc .

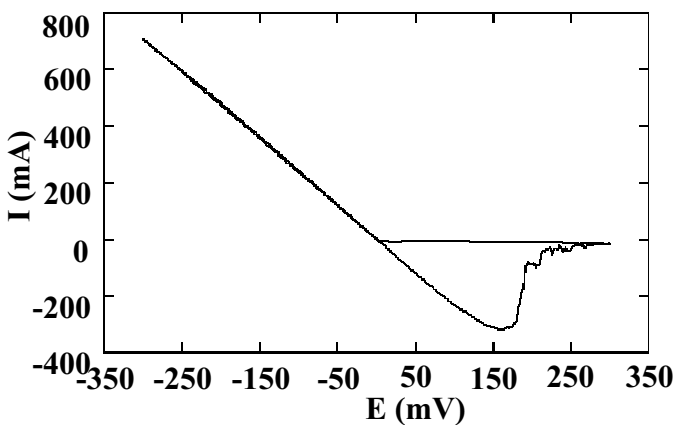


Figure 4. Cyclic voltammogram of the ionically conducting channel, Li_2Pc , at -10°C showing the deposition and stripping of lithium. Electrode area is 0.385 cm^2 and the scan rate is $20 \mu\text{V/s}$. Lithium is used as the counter and reference electrode, copper is used as the working electrode.

LITHIUM-ION CONDUCTING CHANNEL

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Computational chemistry has been used to design a solid state ionically conducting channel for lithium ions. Molecular self-assembly which can occur between molecular units is required for channel formation and is an important feature of this design. In this design, the anion matrix forms the channel through which the lithium ions move. Calculations have shown that the bond energy between two or three molecular units using dilithium phthalocyanine is either 42.1 or 73.4 kcal/mol, respectively. Preliminary experimental results based on dilithium phthalocyanine have shown that specific conductivities greater than 10^{-3} S/cm are attainable at ambient and subambient temperatures. Cyclic voltammograms of a two electrode cell with lithium as the counter and reference electrode, copper as the working electrode and the channel as the solid state electrolyte show nucleation and discharge peaks consistent with the deposition and stripping of lithium and transport of lithium ions through the solid state ionically conducting channel. These tests were done at 26, -10 and -31 °C.

INTRODUCTION

For oxygen based solid polymer electrolytes, absent of any non-aqueous plasticizer, lithium ion transport depends upon polymer segmental motion. Because of this, ionic conductivity is poor at ambient and subambient temperatures. The idea associated with lithium ion transport in an ionically conducting channel is that it would depend upon the electric field gradient established between the electrodes of an electrochemical cell. In this fashion, one can minimize the temperature dependence for ionic conduction and therefore improve ambient and subambient temperature performance. In order to accomplish this requirement, it would be important to establish a coordination sphere for lithium ions that was invariant along the axis of symmetry of a cylinder (i.e., ionically conducting channel). Since the coordination of lithium ions is through electrostatic attraction, one can take advantage of the negative electrostatic potential associated with the dianion, of an unsaturated macrocycle, in order to achieve this condition. With proper spacing of the unsaturated macrocyclic rings, the contours of the negative

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electrostatic potential overlap sufficiently to provide a “constant potential” throughout the channel. In this paper, an unsaturated macrocyclic compound, dilithium phthalocyanine, has been investigated for the formation of lithium ion conducting channels.

COMPUTATIONAL METHODS AND EXPERIMENTAL

Gaussian 98 was used to perform the geometry optimizations for dilithium phthalocyanine (Li_2Pc), $(\text{Li}_2\text{Pc})_2$ and $(\text{Li}_2\text{Pc})_3$ in the gas phase (1). The Hartree-Fock method of calculation was used for these optimizations with a 3-21G basis set. Electronic energy differences between products and reactants at 0 K were calculated as a measure of the bond energy between adjacent dilithium phthalocyanine molecules in $(\text{Li}_2\text{Pc})_2$ and $(\text{Li}_2\text{Pc})_3$. Hyper Chem was used to calculate and display the negative electrostatic potentials for two porphyrin dianions separated by 7 Å. Each porphyrin dianion had first undergone a geometry optimization prior to the Hyper Chem calculation using the Hartree-Fock method of calculation and the 6-31G(d) basis set.

Dilithium Phthalocyanine was purchased from Aldrich and dried under reduced pressure at 80°C for 18 hours. This was accomplished in a vacuum oven antechamber attached to our Vacuum Atmospheres dry box that uses helium for the inert atmosphere. The phthalocyanine was then brought into the dry box from this chamber and pellets were fabricated using a Carver press. Approximately 80 mg of dilithium phthalocyanine was used for each pellet. The area of the pellet was on the order of 1 cm² and thickness was approximately 500 µm. Pellets prepared from this dried material were then used in the assembly of two electrode cells for electrochemical characterization. Lithium metal was used as the counter and reference electrode, copper as the working electrode and dilithium phthalocyanine as the solid state electrolyte. In the discussion that follows, test cell # 1 and test cell # 2 were prepared as stated above for electrochemical characterization. Test cell # 1 was used for electrochemical characterization at ambient and subambient temperatures. The purpose of test cell # 2 was to verify the experimental results of test cell # 1 at ambient temperature (i.e., to demonstrate the transport of lithium ions in a solid state electrolyte). A third two electrode electrochemical cell, test cell # 3, was prepared using dilithium phthalocyanine again purchased from Aldrich, but with a different Lot Number from the dilithium phthalocyanine used in test cells #1 and #2. In addition, the dilithium phthalocyanine used in test cell # 3 was purified by a procedure developed by Feld that was a slight modification of the procedure in *Inorg. Synth.*, 20, 159 (1980). The procedure is as follows. All solvents were dried over 3A molecular sieves for 24 h. Dilithium phthalocyanine was dissolved in anhydrous acetone (1 g/100 mL). The mixture was stirred for 15 min and then filtered. The solid was discarded and the filtrate was concentrated (one-tenth volume) on a rotary evaporator. The concentrated solution was slowly added over a period of 20 min to a stirring mixture of anhydrous toluene/hexanes (100 mL 49:1). This mixture was allowed to stir at room temperature for 15 min, and then was placed in a refrigerator for an additional 60 min. After cooling, the mixture was filtered and the solid was dried at 50°C for 72 hours.

The electrochemical impedance measurements for determining ionic conductivity were accomplished using a two electrode cell using EG&G impedance spectrometer model 398 software interfaced with an EG&G potentiostat/galvanostat model 273A and

EG&G lock-in amplifier model 5210 taken in the frequency range from 0.1 Hz to 100 kHz. The measurements were obtained without polarization and used a sinusoidal signal of 5 mV. The voltammetric and galvanostatic plating/stripping data were produced using a two electrode cell and the same EG&G equipment. The electrochemical measurements were performed inside the dry box as there was an electrical interface through the dry box to the EG&G equipment. Electrochemical characterization at subambient temperatures was performed using an insulated glass vessel that contained the electrochemical cell under a helium atmosphere and was partially submerged in a controlled temperature bath. The glass vessel was equipped with electrical wires and a thermocouple that allowed one to connect the cell with the EG&G equipment and measure the temperature of the cell as well.

RESULTS & DISCUSSION

Computational Chemistry

A schematic of a one dimensional single ion conductor for lithium ions is shown in Figure 1. It illustrates that the lithium ions are centered throughout the “channel” which implies there are no unoccupied donor atom sites. This is different from polyethylene oxide based polymer electrolytes where one needs unoccupied sites in order for lithium ion transport to occur. Theoretical calculations show, for the simple porphyrin dianion, the highest negative electrostatic potential is in the center of the unsaturated macrocyclic ring which is where a lithium ion would be located for a lithium porphyrin complex anion. For a similar system, the crystal structure of the lithium complex of the phthalocyanine radical shows that the lithium ion is in the center of the nearly planar phthalocyanine ring (2). The negative electrostatic potential contours for two porphyrin dianions separated by 7 Å are shown in Figure 2. The unsaturated macrocyclic rings are perpendicular to the page. The calculated results show that the difference in potential between the highest value of the potential located in the center of the ring and the mid point between the rings is 0.01 eV. The purpose of this calculation was to determine the possibility of forming a channel based upon the notion of a constant coordination sphere for lithium ions as reflected in the relatively constant electrostatic potential. The small difference in the calculated electrostatic potential between the macrocyclic rings reflects the notion of a constant coordination sphere for lithium ions within the channel. At this point, one still had to be concerned that the lithium ion would be too tightly bonded to the porphyrin and therefore not move under the influence of an electric field gradient. In addition, it was recognized that inter channel hopping by the lithium ion would most likely occur as one would not expect a continuous channel between the electrodes. As illustrated in Figure 2, however, the negative electrostatic potential contours extend beyond the macrocyclic rings and this feature could be important for facilitating lithium ion transport between channels.

The optimized geometry for dilithium phthalocyanine (Li_2Pc) is shown in Figure 3. The calculated electronic energy for this complex is -1662.4368917 Hartrees at 0 K (1 Hartree=627.5095 kcal/mol). The lithium ions are positioned above and below the plane of the phthalocyanine ring which is shown in Figure 3 b. One would expect this,

since the highest negative electrostatic potential is located in the center of the ring and there is electrostatic repulsion between the lithium ions. The optimized geometries for $(\text{Li}_2\text{Pc})_2$ and $(\text{Li}_2\text{Pc})_3$ are shown in Figures 4 and 5. The electronic energies for these complexes at 0 K are -3324.9409051 and -4987.42769845 Hartrees, respectively. The calculated bond energies between these molecules are 42.1 and 73.4 kcal/mol, respectively. The strength of these bonds originates from the electrostatic attraction of lithium ions and nitrogens from adjacent phthalocyanine rings. The nitrogens have a partial negative charge. This suggests that one can take advantage of this attraction for molecular self-assembly of these molecules in order to form the ionically conducting channel. Although Figures 4 and 5 suggest that the ring alignment is not cofacial, the important feature is the ring separation of about 2.5 to 3 Å which should insure that there is good overlap of the negative electrostatic potential contours for lithium ion conduction. Preliminary results of high-resolution TEM conducted at Argonne National Laboratory suggest that the solid state ionically conducting material used in the experiments discussed below, dilithium phthalocyanine, is arranged in a three-dimensional lattice (3).

Test Cell # 1

The cyclic voltammogram of a two electrode cell, test cell # 1, run at -10°C is shown in Figure 6. Lithium foil was used as the counter and reference electrode, a thin foil of copper was used as the working electrode and a pellet of dilithium phthalocyanine, 589 μm thick, was used as the electrolyte. Since the cyclic voltammogram was run at -10°C , the scan rate used was 20 $\mu\text{V/s}$. The smallest electrode area used in the cell was that of the lithium electrode at 0.385 cm^2 . The peak current in the anodic region of the cyclic voltammogram was 316 mA at 157 mV. The profile of the cyclic voltammogram in Figure 6 is virtually identical to that reported by Angell for his single lithium ion conductor based upon an inorganic polymer anion (4). His cyclic voltammogram at ambient temperature, which is Figure 3 of his paper, is dominated by the deposition and stripping of lithium as shown in Figure 6. The electrolyte used by Angell is a melt at ambient temperature and is based on the lithium (poly-urea-sulfonyl imide) complex with AlCl_3 .

The resistance of the electrolyte in test cell # 1 at -10°C was determined by complex impedance. Nyquist and Bode plots used for this determination are shown in Figure 7. The Bode phase angle plot is indicative of ohmic behavior since the phase angle is zero over most of the frequency range as expected for a single ion conductor. The value of the resistance at 0.1 Hz was 0.6 ohms and corresponds to a specific conductivity of $2.5 \times 10^{-1} \text{ S/cm}$ at -10°C . The plating and stripping of lithium, as shown in Figure 6, is consistent with the transport of lithium ions through the solid state ionically conducting channel.

The cyclic voltammogram of test cell # 1, where the temperature of the cell had been lowered to -31°C from -10°C , is shown in Figure 8. The scan rate was 20 $\mu\text{V/s}$. At the lower temperature, the peak current in the anodic region of the cyclic voltammogram was 466 mA at 228 mV. The polarization of the peak current at 228 mV is expected for the lower temperature of -31°C compared to 157 mV at -10°C . However, it is interesting that the peak current increased, perhaps due to reduced vibrations within the molecular

lattice. The resistance of the cell as measured by complex impedance was 0.5 ohms. Cycling was continued for seven more days at the scan rate of 20 $\mu\text{V/s}$. At the end of this testing, the peak current in the anodic region was 442 mA at 253.7 mV. In view of this, there appears to be relatively good electrochemical stability at the lithium metal anode/solid state channel electrolyte interface.

The cyclic voltammogram of test cell # 1 at 25°C is shown in Figure 9. The initial point for the cyclic voltammogram was 0.0 V and it was run first cathodic and then anodic. The scan rate for this voltammogram was 20 mV/s. The peak current in the anodic region was 854.0 mA at 214.3 mV.

Test Cell # 2

The cyclic voltammogram of test cell # 2 at 28°C is shown in Figure 10. The scan rate was 10 mV/s. Dilithium phthalocyanine was made into a pellet with a thickness of 483 μm . The resistance of the cell as determined by complex impedance was 1 ohm at 0.1 Hz. The smallest electrode area, which was the lithium electrode, was 0.636 cm^2 . Based on these parameters, the specific conductivity for the electrolyte is $7.6 \times 10^{-2} \text{ S/cm}$ at 28°C. Once again, the plating and stripping of lithium, as shown in Figure 10, is consistent with the transport of lithium ions through the solid state ionically conducting channel.

Test Cell # 3

In the experiments described above for test cells # 1 and # 2, the dilithium phthalocyanine was used as received from sample containers with the same Lot Number. In the context of verifying experimental results, it was decided to use dilithium phthalocyanine that was from a different Lot Number and purified. The cyclic voltammogram of test cell # 3 at 27°C, using the purified electrolyte, is shown in Figure 11. The scan rate was 10 mV/s. The pellet of dilithium phthalocyanine was 495 μm thick. The smallest electrode area, which corresponds to the lithium electrode, was 0.785 cm^2 . The peak current in the anodic region was 233 mA at 72 mV. The resistance of this cell was 0.5 ohms at 0.1 Hz as determined by complex impedance analysis. The specific conductivity of the electrolyte based on the aforementioned parameters was $1.26 \times 10^{-1} \text{ S/cm}$. A high impedance ohm meter was also used to measure the resistance of the cell which was 0.7 ohms. The agreement of the resistance values by the two techniques is consistent with the electrolyte being a single ion conductor. If both the cation and anion were conducting, one would not expect to see such agreement. Shriver found similar results for a polymer electrolyte where sodium ions were the only mobile species (5).

A constant current charging and discharging experiment was run on test cell #3 after the cyclic voltammogram. This is shown in Figures 12 a and b. The current was 10 mA and the charging/discharging time was set for 3 hours. The constant current charging profile shows voltage fluctuations perhaps due to unstable interface contact, however, the discharge profile is free of these fluctuations. After running the discharge experiment for

8.264 X 10³ seconds, the voltage was 6 mV. This would correspond to a cell resistance of 0.6 ohms similar to that observed in the prior experiment. However, at 9.011 X 10³ seconds the voltage rises sharply to 0.9 volts suggesting that lithium was depleted from the working electrode. These results would correspond to a coulombic efficiency of 83%. The resistance of the cell after the charging/discharging experiment was completed was 4.6 ohms as determined by complex impedance. The increase in resistance that was observed when the cell was over discharged is perhaps to be expected since the electroneutrality of the electrolyte is being affected in the over discharged state and resistance increases.

CONCLUSIONS

A solid state ionically conducting channel based on dilithium phthalocyanine has been prepared. Results of computational chemistry suggest the possibility of molecular self-assembly for ionic channel formation. The key feature is that the unsaturated macrocyclic anion provides the negative electrostatic potential that remains relatively constant between the rings because of their close spacing. Electrochemical experimental results are consistent with lithium ion transport in a solid state media at ambient and subambient temperatures with specific conductivities as high as 10⁻¹ S/cm.

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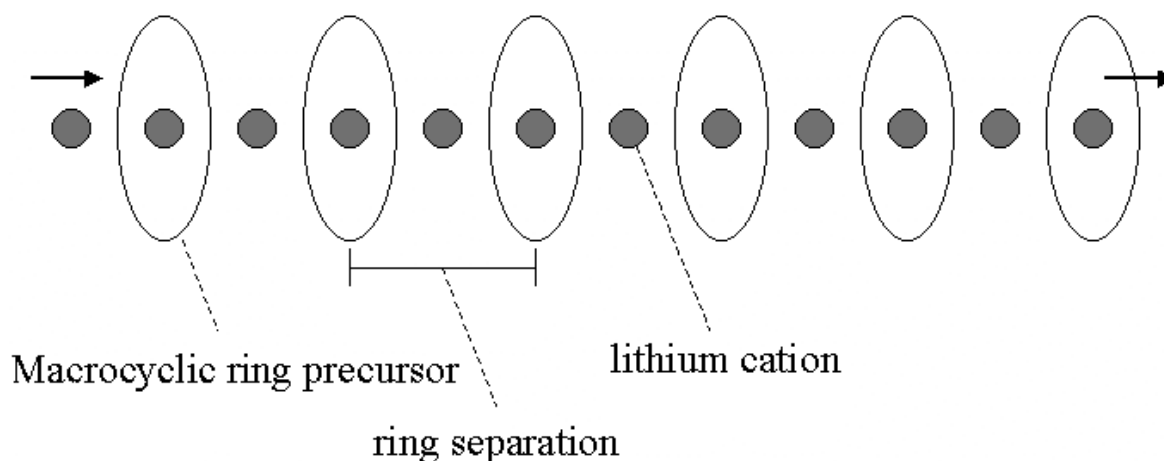


Figure 1. Schematic diagram for a one dimensional single ion conductor for lithium ions.

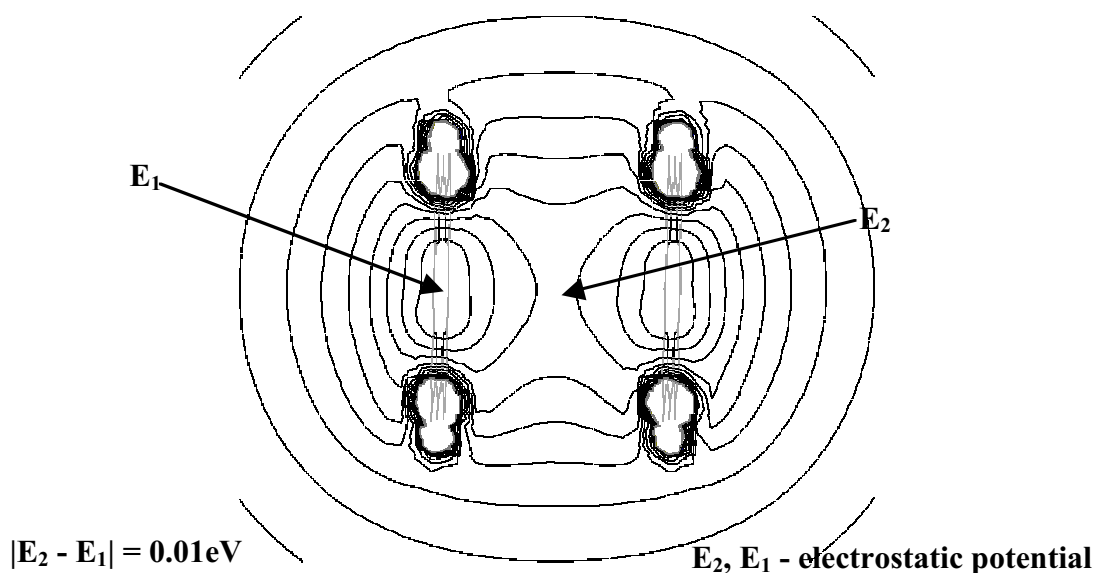


Figure 2. Negative electrostatic potential contours for two porphyrin dianions separated by 7 Å.

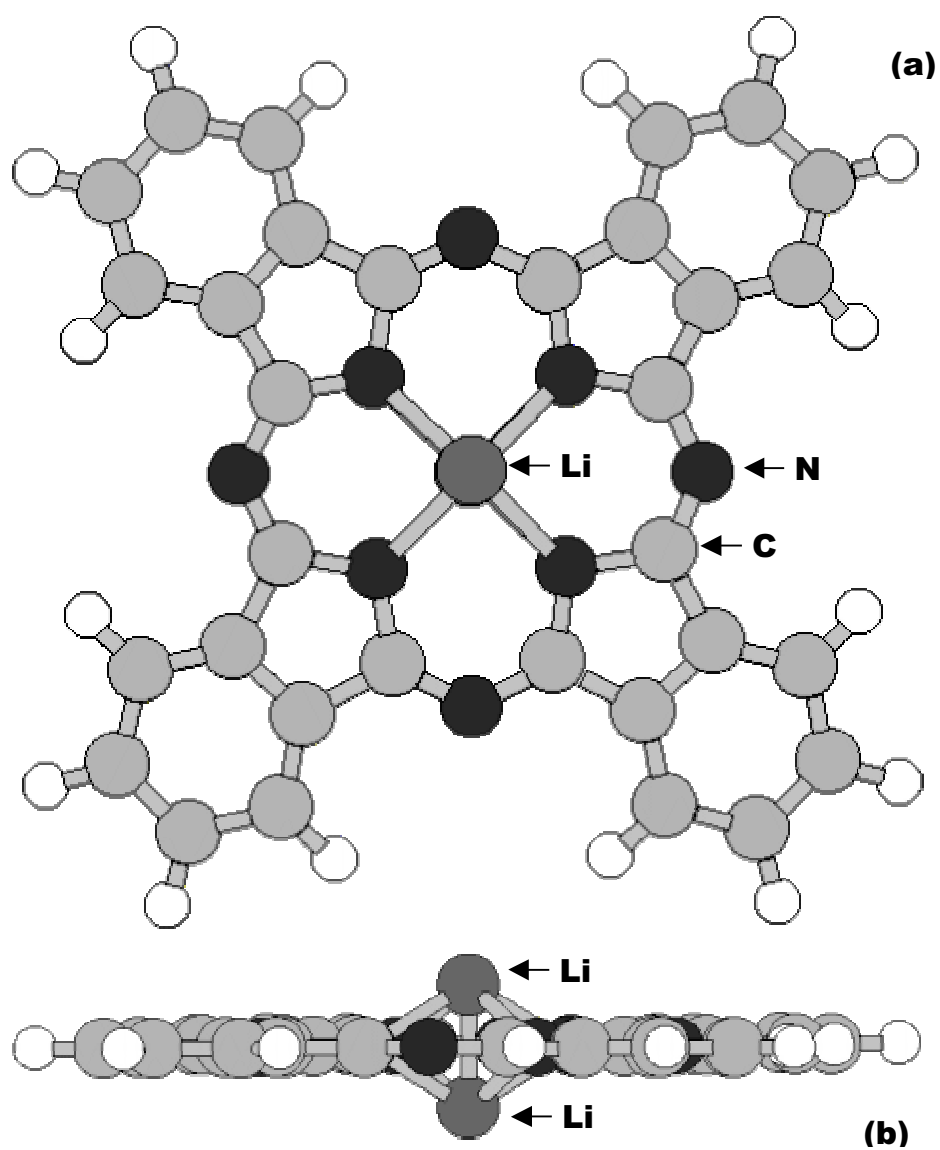


Figure 3. Optimized geometry for dilithium phthalocyanine (Li_2Pc) (a) top and (b) side views.

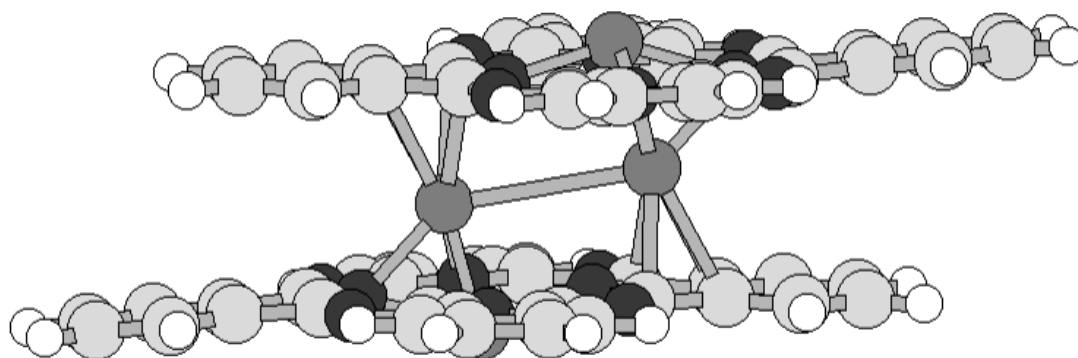


Figure 4. Optimized geometry for $(\text{Li}_2\text{Pc})_2$.

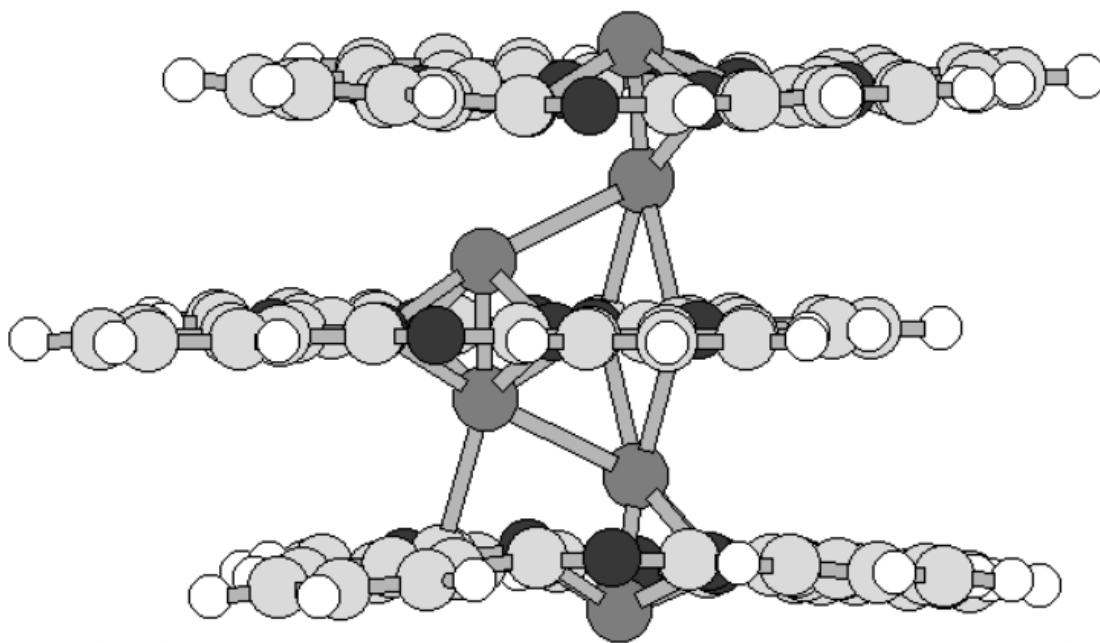


Figure 5. Optimized geometry for $(\text{Li}_2\text{Pc})_3$.

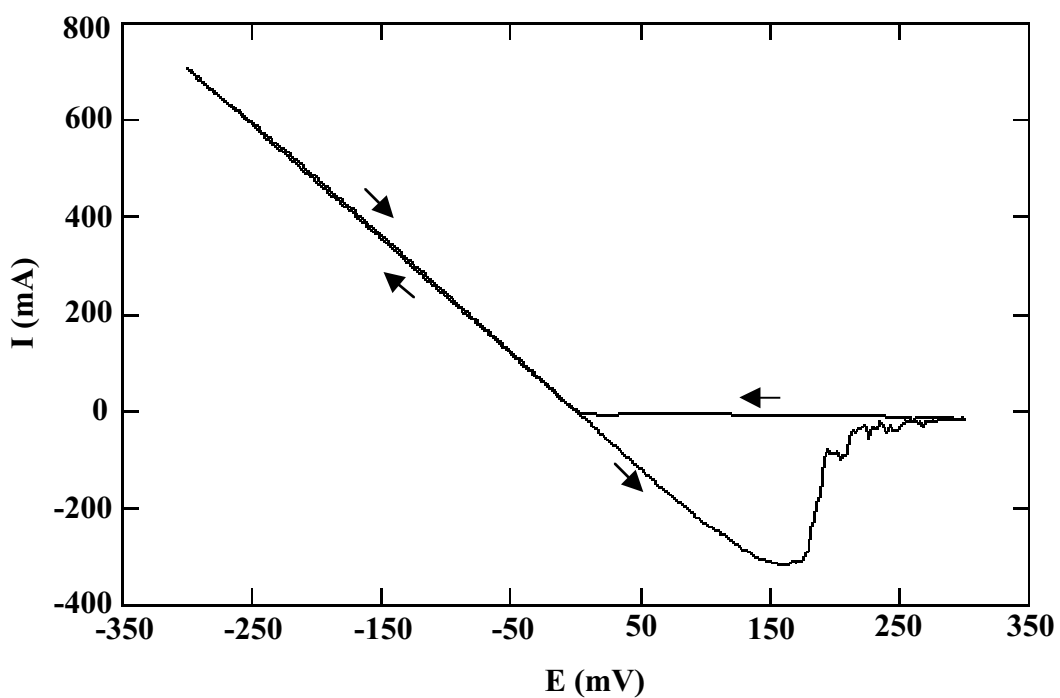


Figure 6. Cyclic voltammogram of the ionically conducting channel, Li_2Pc , at -10°C showing the deposition and stripping of lithium. Electrode area is 0.385 cm^2 and the scan rate is $20\text{ }\mu\text{V/s}$. Lithium is used as the counter and reference electrode, copper is used as the working electrode.

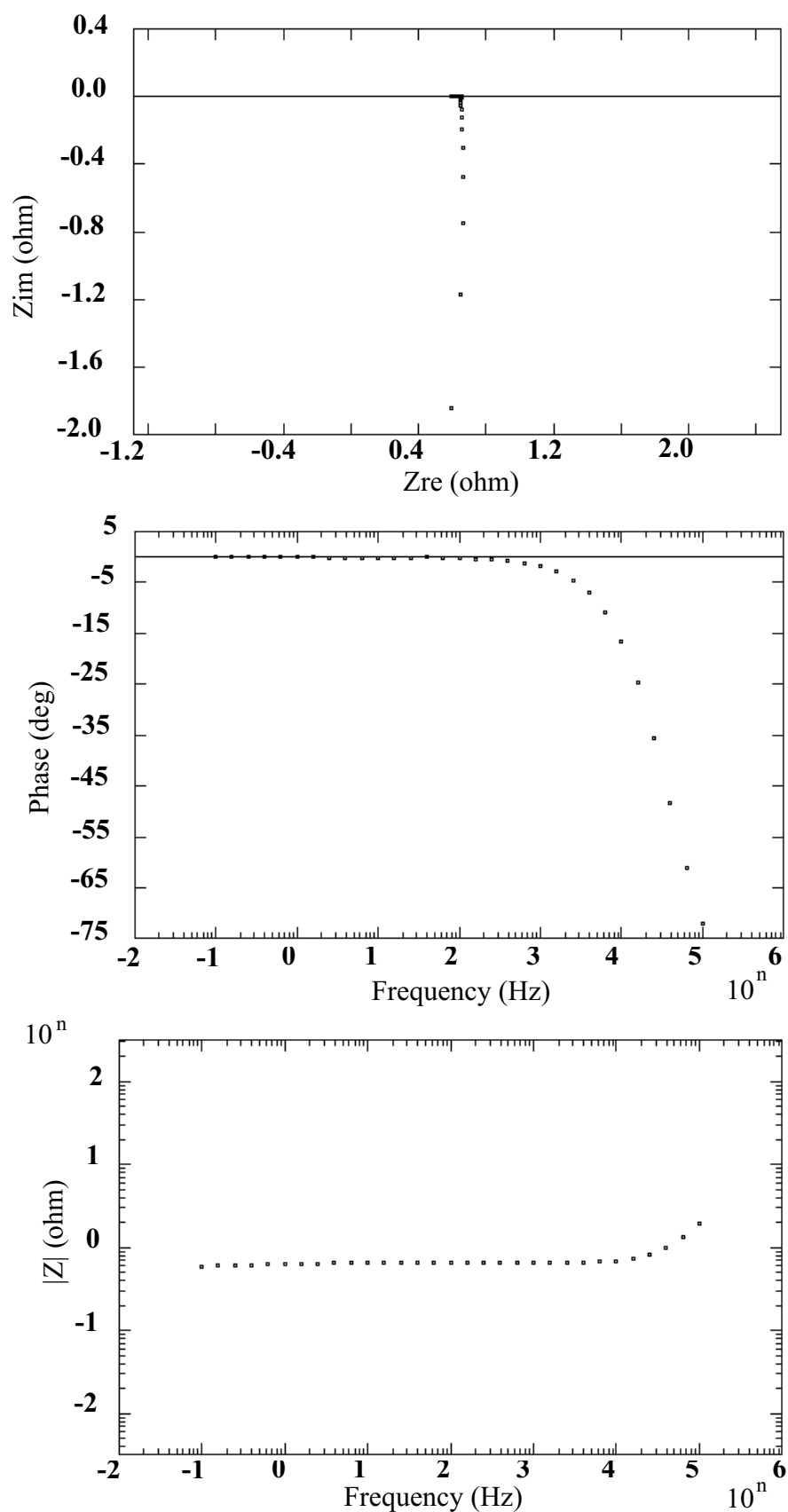


Figure 7. Complex impedance plots (a) Nyquist, (b) Bode phase and (c) Bode absolute impedance for the two electrode cells at -10°C with Li_2Pc as the ionically conducting channel.

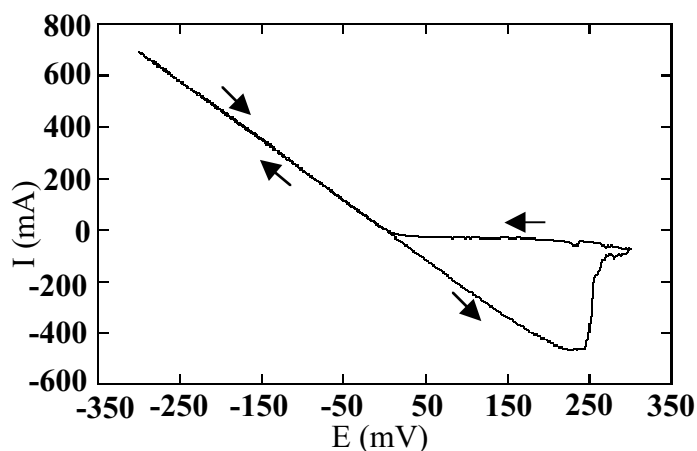


Figure 8. Cyclic voltammogram of the ionically conducting channel, Li_2Pc , at -31°C showing the deposition and stripping of lithium. Electrode area is 0.385 cm^2 and the scan rate is $20\text{ }\mu\text{V/s}$. Lithium is used as the counter and reference electrode, copper is used as the working electrode.

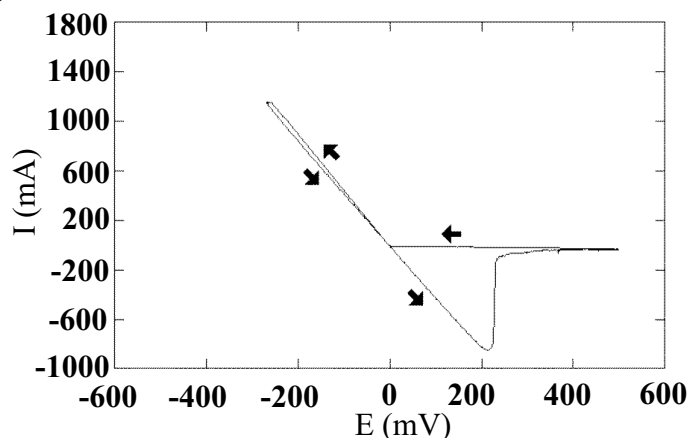


Figure 9. Cyclic voltammogram of the ionically conducting channel, Li_2Pc , at 25°C showing the deposition and stripping of lithium. Electrode area is 0.385 cm^2 and the scan rate is 20 mV/s . Lithium is used as the counter and reference electrode, copper is used as the working electrode.

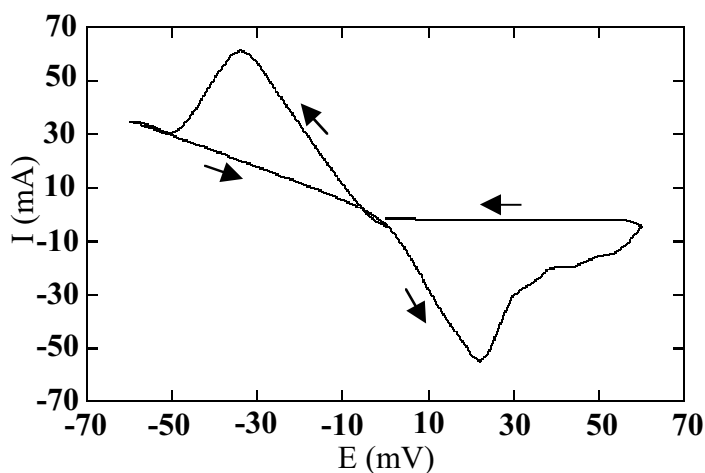


Figure 10. Cyclic voltammogram of the ionically conducting channel, Li_2Pc , at 28°C showing the deposition and stripping of lithium. Electrode area is 0.636 cm^2 and the scan rate is 10 mV/s . Lithium is used as the counter and reference electrode, copper is used as the working electrode.

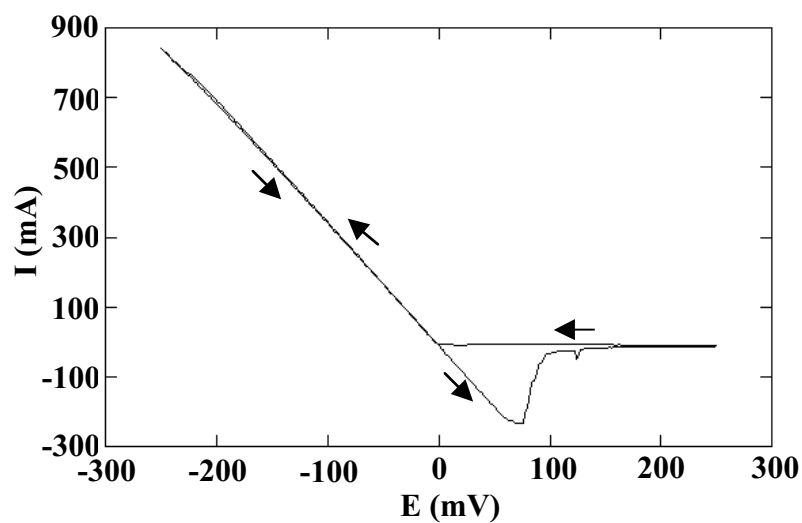


Figure 11. Cyclic voltammogram of the ionically conducting channel, Li_2Pc , at 27°C showing the deposition and stripping of lithium. Electrode area is 0.785 cm^2 and the scan rate is 10 mV/s . Lithium is used as the counter and reference electrode, copper is used as the working electrode.

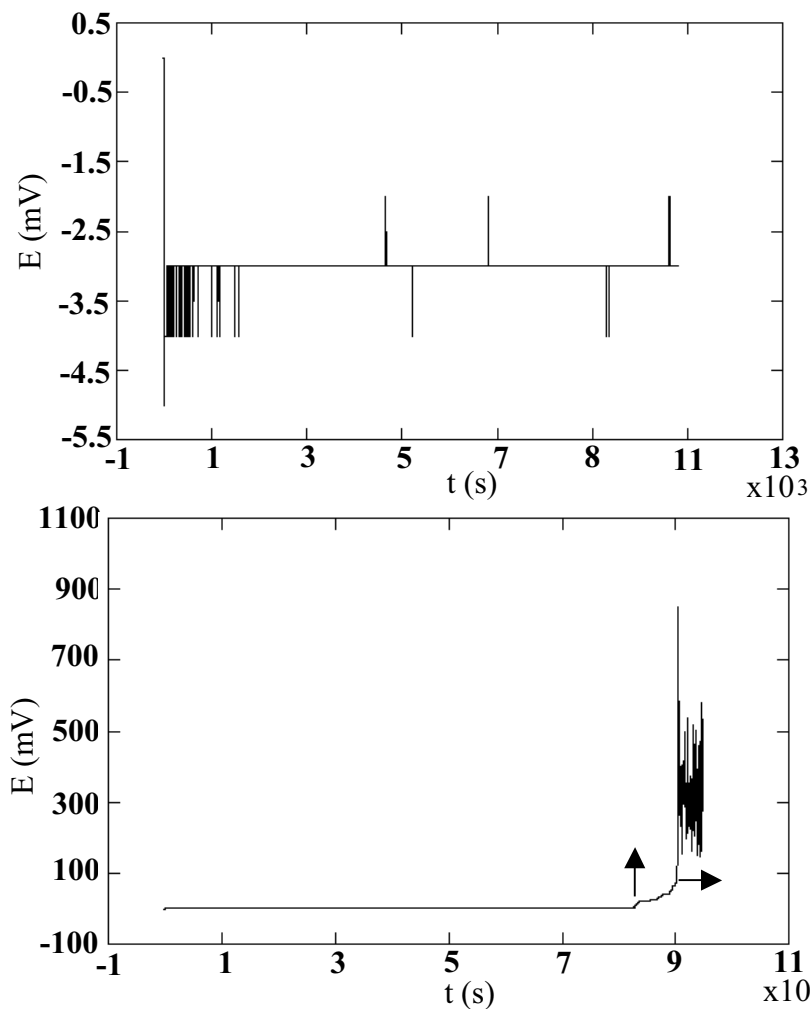


Figure 12. Galvanostatic (a) plating and (b) stripping of lithium on a copper working electrode at 27°C and 10 mA with Li_2Pc as the electrolyte. Electrode area is 0.785 cm^2 and lithium is used as the counter and reference electrode.