Low Energy of Activation
Lithium-Ion Conducting Channel

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Low Energy of Activation Lithium-Ion Conducting Channel
Outline

• Lithium Ion Conducting Channel
• Negative Electrostatic Potential field
  – Electron Delocalization
• Low Energy of Activation
  – Single Crystals
  – Thin Film
• Conclusion
Conceptualized Lithium-Ion Conducting Channel

Macrocyclic ring precursor

ring separation

lithium cation
Channel Concept Based on Tetracene Bridging Unit with Dilithium Porphyrins Attached
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Negative Electrostatic Potential Contours for Two Porphyrin Dianions Separated by 7 Å. ($E_2$, $E_1$ - Electrostatic Potential)

$|E_2 - E_1| = 0.01 \text{eV}$
Dilithium Phthalocyanine (Li$_2$Pc)
Calculated Electrostatic Potential Contours Obtained from Configurations Representative of Molecular Self-assembly of Li$_2$Pc Molecules; Side View (Above Left), Calculated Contours are for the Li$_2$Pc Molecule in the Middle; Profiles of Electrostatic Potential Contours as Viewed from the Top (Right and Below) of the Molecular System.

X-ray Crystal Structure of Li$_2$Pc

Arrhenius Plot of Ionic Conductivity for a Pressed Pellet of Single Crystals of Li$_2$Pc Sandwiched Between Gold Electrodes (710 µm Thick; 1.6 cm$^2$)

$E_a = 0.038$ eV

$y = 7.16949E-04e^{-4.43368E+02x}$

$R^2 = 9.33118E-01$

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Nyquist Plots of SS/Thin Film Li$_2$Pc Cast Onto an MnO$_2$ Cathode/SS at -50, -25, 0, +25, and 50°C
Arrhenius Plot of Ionic Conductivity for a Thin Film of Li$_2$Pc Cast Onto an MnO$_2$ Cathode at -50, -25, 0, +25, and 50°C

\[ y = 0.0257e^{-7.25094E+02x} \]

\[ R^2 = 0.9998 \]

\[ \sigma = 2.7 \text{ mS/cm} \]

\[ E_a = 0.063 \text{ eV} \]

\[ \sigma = 1.0 \text{ mS/cm} \]
Conclusions

The energies of activation for ionic conduction within the pressed pellet of single crystals (0.038 eV) and the thin film of Li$_2$Pc dried at 160°C (0.063 eV) would suggest a very similar conduction mechanism.

The lithium ion conduction pathway might be parallel to the a-axis between the phthalocyanine rings since there is a negative electrostatic potential field between the parallel phthalocyanine rings and in effect provides a constant sphere of solvation for the lithium ion throughout the crystal lattice.
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