COMPOSITE CATHODE WITH LI_2PC

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Computational chemistry calculations performed with Gaussian 98 were used to develop an experimental method that facilitates ionic connection between the solid-state electrolyte dilithium phthalocyanine (Li_2Pc) and manganese dioxide (MnO_2) (1). Li_2Pc has been under development in our lab as a solid-state lithium-ion conducting channel (2).   Attempts at preparing galvanic cells with lithium metal anodes, Li_2Pc and transition metal cathodes have been very difficult to achieve. It is quite possible that failure to fabricate these cells is due to poor ionic connectivity between the solid-state electrolyte and the solid state cathode; the planar configuration of the phthalocyanine ring and the fact that the lithium ions are very close to the ring may sterically hinder effective ionic coupling between Li_2Pc and any potential cathode. This same argument has been used for understanding the insertion and removal of magnesium from phthalocyanine (3). Figure 1 shows the sandwich structure for $(Li_2Pc)_2$ that has been optimized using the density functional method, B3LYP, and the 6-31G(d) basis set. The extension of the lithium ions above/below the phthalocyanine ring is approximately 0.45 Å. For the monomer, Li_2Pc, the extension above/below the phthalocyanine ring is 1.0 Å. Figure 2 shows the optimized structure of the MgPc dimer as reported in reference 3 using B3LYP/6-31G(d). This optimization was performed on the MgPc dimer in order to test the methods of calculation since X-ray structural analysis results are not available for $(Li_2Pc)_2$. The calculated displacement of the magnesium ion from the plane of the inner nitrogen atoms as shown in Figure 2 is 0.528 Å. X-ray structural results show that the magnesium ion is displaced 0.496 Å above the plane of the inner nitrogen atoms. The significance of the extension of magnesium above the phthalocyanine plane is to make the magnesium more labile in order for it to react with other chemicals. Kinetic studies as reported in reference 3 support this conclusion.   In view of the apparent difficulty in making a good ionic connection between Li_2Pc and MnO_2, it was decided to investigate the influence of a curved carbon lattice, such as corannulene, on the displacement of lithium above the plane of the phthalocyanine ring. Figure 3 shows the optimized structure for the electrostatic interaction of Li_2Pc with corannulene using B3LYP/6-31G(d).   The lithium ion is extended above the phthalocyanine plane by 1.56 Å. In order to test the theoretical results, an electrically conducting carbon with a curved lattice was used in the fabrication of an all solid-state electrochemical cell with a lithium metal foil anode, Li_2Pc electrolyte and a MnO_2 cathode. The solid-state electrolyte was composed of Li_2Pc and 8% by wt. KYNAR vinylidene fluoride resin (KYNAR FLEX 2801). The cathode consisted of MnO_2, Li_2Pc, carbon and 8% by wt. KYNAR FLEX 2801. The reversible open circuit potential at 75°C is 2.77 Volts. The cell has been charged and discharged at constant potentials of 3.0 and 2.0 Volts, respectively, with a current density of 10 $\mu A/cm^2$. The fact that there is a reversible cell voltage of 2.77 Volts suggests effective ionic coupling between Li_2Pc and MnO_2 has been achieved

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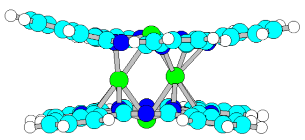

Figure 1. Calculated structure for $(Li_2Pc)_2$ using RB3LYP/6-31G(d) for geometry optimization

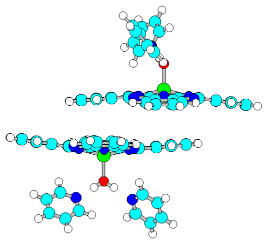

Figure 2. Calculated structure for $(MgPc\text{-}H_2O\text{-}2C_5H_5N)_2$ using RB3LYP/6-31G(d) for geometry optimization.

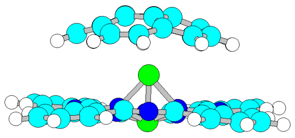

Figure 3. Calculated structure for Li_2Pc-corannulene using RB3LYP/6-31G(d) for geometry optimization.