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Electrochemical Impedance Studies of Dilithium Phthalocyanine

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Metal phthalocyanines have been investigated for several electrochemical studies including applications in batteries.[1] Dilithium phthalocyanine (Li_2Pc) has been examined for Li^+-ionic conductivity with a possible application in solid-state Li-ion batteries.[2] In the present study, electrochemical impedance characteristics of Li_2Pc are investigated.

Pellets of Li_2Pc were made by pressing a mixture of Li_2Pc (85 wt %) and polyvinylidene fluoride (15 wt %) in a suitable die, and symmetrical cells – SS/Li_2Pc/SS (SS stands for stainless steel) were assembled in argon atmosphere.

A typical impedance diagram of SS/Li_2Pc/SS symmetrical cell is shown in Figure 1. The Nyquist impedance consists of a pair of distinguishable semicircles, with the high frequency end intercepting at origin. The low frequency end intercepts on the real axis and Warburg impedance is absent. It has been known that phthalocyanines possess semi conducting properties owing to conjugate bond structure.[3] It has also been reported that the metal center of phthalocyanine ring is mobile.[2] As a result, Li_2Pc is considered to possess both electronic conductivity and ionic conductivity. For this mixed conductor, the electronic resistance (R_e) and ionic resistance (R_i) are considered to be present in parallel in the electrical equivalent circuit,[4] as shown in Figure 2. The geometrical and interfacial capacitances are represented by constant phase elements, C_g and C_i, respectively. At low frequencies, the diameter of the big semicircle is considered equal to the electronic resistance, R_e. At high frequencies, the impedance data due to relatively large interfacial capacitance (C_i) becomes insignificant, and hence the equivalent circuit consists of C_g, R_i and R_e in parallel arrangement. Thus the diameter of the small semicircle (R_1) is a measure of R_i and R_e in parallel. Thus $R_i = R_1 R_e / (R_e – R_1)$. The values of R_i and R_e are obtained by fitting the impedance data to non-linear least squares fitting program. From the data measured in temperature range 20 – 80 ^{0}C, Arrhenius plots are drawn for specific conductivities (σ) obtained from R_e and R_i, and shown in Figure 3. There is a significant contribution of both ionic and electronic resistances at all temperatures. The activation energy values are calculated. Further results obtained on influence of voltage on impedance and dc chronopotentiometry will be presented.

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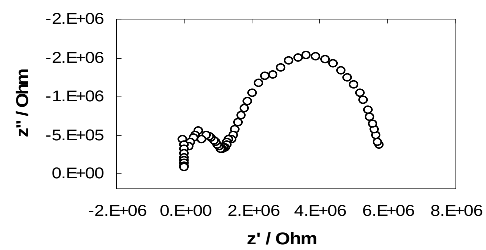

Figure 1. Nyquist impedance of SS/Li_2Pc/SS cell at 45 ^{0}C. Area of Li_2Pc = 0.78 cm^2 and thickness = 250 μm

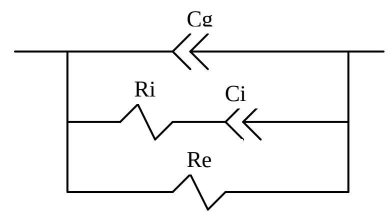

Figure 2. Equivalent circuit.

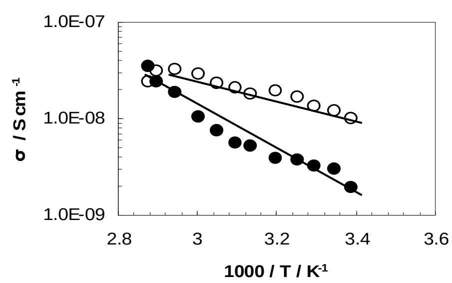

Figure 3. Arrhenius plots of specific conductivities (σ) obtained from R_i (o) and R_e (●)