Studies on electrochemical cells based on polymer composites of charge-transfer materials

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The low mechanical strengths of the charge-transfer materials have restricted their applications as cathode materials in the solid-state batteries. To improve the mechanical strengths, the polymer composites of these materials have been prepared and used in the fabrication of solid-state electrochemical cells. The pressed pellets of the polymer composite of \( o \)-tolidine-iodine charge-transfer complex in poly (vinyl chloride) and polystyrene have been used as cathodes in contact with zinc as anode metal. The electrochemical characterization of these cells such as open circuit voltages, short circuit currents, their time and temperature dependence charge-discharge characteristics and rechargeability of these cells have been studied. The impedance and dielectric behaviour of these cells have been studied to understand the nature of the electrode reactions.

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Solid-state electrochemical cells using charge-transfer (CT) complexes as cathode materials have attracted considerable attention\(^1\text{,}^4\). Scrosati and Torroni\(^5\) have fabricated solid-state lithium cells based on benzidine-iodine and perylene-iodine and found that these cells have very high cell voltage of 2.8 V at room temperature. Electrochemical behaviour of iodine complexes with different metallic contacts such as barium, calcium, magnesium and aluminum, as anodes and CT complexes as cathodes and platinum, gold or carbon as counter electrodes has been studied\(^7\). Chandra et al.\(^6\) have used pellet of Ag\(_2\)KI\(_3\) as the solid electrolyte, silver foil as anode and graphite-iodine complex as the cathode. This cell yields an open circuit voltage of 0.68 V at room temperature.

Gutmann et al.\(^7\) has proposed a reaction mechanism for cells based on both iodine free and iodine complexes and it was concluded that the formation of metal halide is the energy producing reaction. Scrosati et al.\(^8\) have reported the formation of insulating layer between cathode and anode as a result of the metal halide formation. Due to the formation of metal halide, the resistive layer continuously growing on the metal electrode surface, as a result of this there is expansion of semicircle between real and imaginary impedance. It was reported that the electrode resistance of these batteries increases continuously whereas the grain and grain boundary resistance is almost constant in the impedance analysis of these batteries which further confirms the formation of insulating layer between the anode and cathode\(^9\).

Recently, rechargeable organic batteries based on CT complexes of iodine with aromatic diamines in different mole ratios have been fabricated. Various non-stoichiometric complexes of benzidine-iodine, \( o \)-tolidine-iodine and \( N,N'\)-diphenylbenzidine-iodine were prepared on which detailed study of time, composition, temperature dependence and discharge against a fixed external load and charging after discharging have been made\(^1\text{,}^10\).

The low mechanical strengths of the CT complexes restrict their potential application in device fabrication\(^11\). These problems have been overcome by preparing composite of CT complexes with insulating polymers\(^12\). These composite materials have high mechanical strengths while retaining other properties, such as electrical conductivity. In this paper, a detailed study of composites of \( o \)-tolidine-iodine (1:1) in poly vinyl (chloride) and polystyrene as cathode materials and zinc as anode materials has been reported. Various electrochemical parameters like open circuit-voltage, short circuit current and their dependence on time and temperature and charge-discharge characteristics have been studied. The ac impedance and dielectric behaviour of these batteries have been also studied in order to understand the nature of electrode reactions.

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Experimental Procedure

o-Tolidine (S.D.Fine Chem.) was used after recrystallization in benzene; iodine (S.D.Fine chem.) was used after purification by sublimation from KI +I₂ mixture (1:2.5). The purities were checked from their melting points and thin layer chromatography. The poly (vinyl chloride) and polystyrene (G.S.C., India, A.R. grade) were used as received. All other chemicals used were of A.R. grade. The CT complex of o-tolidine-iodine (1:1) (o-Tol-I₂) was prepared by mixing hot solutions of required amount of donor and acceptor in benzene\textsuperscript{13}. The composite of CT complex with poly (vinyl chloride) (PVC) has been prepared by dissolving CT complex in chloroform and was introduced in insulating polymer (PVC) matrix by diffusion\textsuperscript{14}. And for preparation of polystyrene (PS) composites, the o-tolidine-iodine and polymer were dissolved separately in chloroform and mixed them, and then the solvent was evaporated with constant stirring. The cell was fabricated in a pellet holder made of brass by placing cathode pellets in between the anode and inert electrode like platinum. The diagrammatic assembly of the cell is given in Fig. 1.

The electrical measurements were done on a Source Measure Unit (Keithley-236), Picoammeter (Keithley-485), LCZ meter (Keithley-3330) and temperature controller (Centure, India). The mechanical strengths were measured on Amsler Universal Testing Machine.

Results and Discussion

Mechanical properties

The mechanical strengths for the composite of o-tolidine-iodine (1:1) with PVC and PS have been measured on a pellet of uniform dimension by taking fixed weight of the materials\textsuperscript{15}. The pellet was compressed by applying pressure between the compression anvils. The pressure, at which the pellet was broken, has been recorded. The results have been reported in Table 1. It is observed that the mechanical strengths of these charge transfer complexes increases with an increase of insulating polymer contents and reaches approximately to pure polymer for 20% composite. It is evident from this study that the preparation of composite improves the mechanical strengths of pure charge transfer complexes.

Shelf life

Due to the direct contact of the cathode and anode spontaneous reaction goes on in cell even when it is in idle period, which reduces the life of the cell. Scrosati et al.\textsuperscript{8} have introduced a non-reactive polymer film in between the cathode materials and anode metals to overcome this problem, which has to be removed at the time of use of battery. In this study, the open circuit voltage ($V_{OC}$) and short circuit current ($I_{SC}$) of the cell without putting any load to the cell have been measured. It has been observed that the $V_{OC}$ and $I_{SC}$ were decreasing with time which shows that the spontaneous reaction goes on in these cells and the cells have shelf life of about 100 h, if no insulating film is inserted between the anode and cathode. The shelf life of these cells could be many months if such a non-reactive films were inserted between the anode and cathode.

Discharge-charge characteristics

The charge-discharge characteristics of the pure CT complex and their composites have been studied. The variation of $V_{OC}$ and $I_{SC}$, as a function of time against 10 kΩ external load for the composite of o-Tol-I₂ (1:1) with PVC and PS has been shown in Figs 2 and 3 respectively. It has been observed that the initial $I_{SC}$

<table>
<thead>
<tr>
<th>% Composition</th>
<th>Compressive strength*(kg/cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Poly (vinyl chloride)</td>
</tr>
<tr>
<td>100</td>
<td>255.3 ± 0.2</td>
</tr>
<tr>
<td>80</td>
<td>361.4 ± 0.1</td>
</tr>
<tr>
<td>60</td>
<td>472.4 ± 0.3</td>
</tr>
<tr>
<td>40</td>
<td>568.9 ± 0.1</td>
</tr>
<tr>
<td>20</td>
<td>584.2 ± 0.2</td>
</tr>
<tr>
<td>Pure polymer</td>
<td>648.5 ± 0.3</td>
</tr>
</tbody>
</table>

*Compressive strengths were measured for samples of dimension $A = 0.786$ cm\textsuperscript{2}, $l = 2.00 ± 0.2$ cm

Fig. 1—A diagrammatic representation of the cell assembly.
is decreasing on increasing the concentration of insulating materials in the composites whereas the initial $V_{OC}$ for pure CTC and the composites are almost equal. This can be explaining on the basis of internal resistance of the cell. On decreasing the concentration of CT complex in the composites the internal resistance of the cell increases, which reduces the current in the cell$^{12}$. Also the number of reactive iodine molecules per unit contact area of the anode metal decreases as the amount of CT complex in composite decreases leading to lower amount of electrochemical reaction and hence the short circuit current$^9$. The cell was discharged for 100 h and then charged on 1.0 mA current for 45 min. It has been observed that nearly same $V_{OC}$ and $I_{SC}$ were obtained again after charging as found for the freshly prepared cells. The electrochemical cell reaction is given below

$$I_2 + 2e^- \rightarrow 12I^-$$

$$Zn + 2I^- \rightarrow ZnI_2 + 2e^-$$

During operation salt layer (ZnI$_2$) deposited at anode works as a separator between cathode and anode because it is electronically insulating but ionically conducting. Hence, these metal halides works as solid-state electrolyte$^{2,7}$. The detailed electrochemical data for different composition of CTC in insulating polymers have been listed in Table 2. These data confirm the rechargeability of these solid-state galvanic cells based on composite of CT complex with insulating materials. These results indicate that the electrochemical regeneration of discharged cell improves the cell characteristics. It is also evident that these cells give stable voltage output for about 100 h even a high load of 10 kΩ.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Fresh cell</th>
<th>After 100 h</th>
<th>After charging the cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time=0 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$V_{OC}$ (V)</td>
<td>$I_{SC}$ (μA/cm$^2$)</td>
<td>$V_{OC}$ (V)</td>
</tr>
<tr>
<td>o-Tol-Idine-I$_2$ (1:1)</td>
<td>0.96</td>
<td>38.42</td>
<td>0.83</td>
</tr>
<tr>
<td>o-Tol-Idine-I$_2$:PVC (80% CTC)</td>
<td>0.94</td>
<td>30.41</td>
<td>0.82</td>
</tr>
<tr>
<td>o-Tol-Idine-I$_2$:PS (60% CTC)</td>
<td>0.89</td>
<td>21.95</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Table 2—Charge-discharge data of cells with 10 kΩ external load at room temperature

<table>
<thead>
<tr>
<th>Time=0 h</th>
<th>After 100 h</th>
<th>After charging the cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{OC}$ (V)</td>
<td>$I_{SC}$ (μA/cm$^2$)</td>
<td>$V_{OC}$ (V)</td>
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<tr>
<td>0.96</td>
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<td>21.95</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Power output

Variation of power output as a function of time for pure CT complex and their composites have been shown in Fig. 4. It is observed that there was sharp fall in power output within 5-10 h. After then it was almost constant up to 100 h. The power output increases significantly after charging the cell. The initial power output decreases from $1.84 \times 10^{-1}$ VA/kg to $3.65 \times 10^{-2}$ VA/kg and $3.43 \times 10^{-2}$ VA/kg, when the content of CT complex decreases from 100 wt% to 60 wt% in PVC and PS respectively. The decrease in power output with decreasing weight percent of CT complex is due to the power loss against the internal resistance of the cell. The extent of electrochemical reaction will also be less, as the less amount of CT complex will be available at the surface of the pellet in composites having lower weight percent.

Temperature dependence of the cell

The temperature dependence variations of $V_{OC}$ and $I_{SC}$ of these cells have been done to study the effect of temperature on the electrochemical behaviour of these cells. The variation of $V_{OC}$ and $I_{SC}$ as a function of temperature has been shown in Fig. 5. It has been observed that increase in temperature increases the short circuit current but the open circuit voltages remains more or less unaltered. Beyond 368 K, there is fall in $I_{SC}$ of these cells. The increase in $I_{SC}$ may be due to thermal activation of electrochemical reaction and the decrease may be due to increase of internal resistance of the cell, due to liberation of iodine from the cathode materials at high temperature.

Thermodynamic parameters for the cell Zn/o-Tol-I$_2$-PVC/Pt and Zn/o-Tol-I$_2$-PS/Pt (for 80 wt% CT complex) were calculated by using the following equations

\[ \Delta G = -nEF \]  
\[ E = -\Delta H/nF + T \left( \frac{dE}{dT} \right) \]  
\[ \Delta G = \Delta H - T\Delta S \]

The Gibbs free energy for the cell Zn/o-Tol-I$_2$-PVC/Pt and Zn/o-Tol-I$_2$-PS/Pt containing 80% CT complex were found to be 181.4 and 179.5 kJ/mol respectively. The enthalpy and entropy values were found to be 210.6 kJ/mol and 96.5 J/K mol respectively for the cell Zn/o-Tol-I$_2$-PVC, and 208.7 kJ/mol and 96.5 J/K mol respectively for the cell Zn/o-Tol-I$_2$-PS from the temperature dependence of open circuit voltages of these cells.

Nature of electrode reaction

Impedance analyses of these cells have been studied to understand the nature of the electrode reaction. It has been already reported that the metal halides formed due to the cell reactions in these cells, which formed an insulating layer between cathode and anode. The formation of insulating layer can be assessed by the change in the impedance plots as a function of time. The semicircle corresponding to the electrode contribution of the cell increased with the time, indicating the formation of insulating layer between the cathode and anode. Similarly the
capacitance of the cells also increases with the time, which further confirms the formation of insulating layers. The ac impedance and dielectric properties of these batteries have been studied at various time of cell discharge (Table 3). The data were recorded in the frequency range of 40 Hz-100 kHz. A possible equivalent circuit was given to the system by feeding the frequency, real and imaginary impedance data in the complex non-linear least square (CNLS) analysis software developed by EG & G Parc, USA. The best-fitted circuit of the system has been determined by observing the coherence between the experimental and the simulated data in complex impedance and modulus plots, as well as the minimum real and imaginary errors. Then the data were simulated in the frequency range required for the best resolution (10^3-10^11 Hz) using the parameters of the equivalent circuit.

Usually we expect the bulk, grain boundary and electrode contributions to the overall measured electrical properties. So in general we expect the presence of three arcs. The values of bulk and grain boundary contributions are approximately equal. The mathematical expressions for these contributions have been given by Gutmann et al. For (RC)(RC) equivalent circuit, the effective equivalent conductance \(G_P\) and effective equivalent capacitance \(C_P\) was given below:

\[
G_P = \frac{1}{R_P} = \frac{(R_S + C_S) + \omega^2 R_C R_S (R_S C_S^2 + R_C C_S^2)}{(R_S + C_S)^2 + \omega^2 R_C^2 R_S^2 (C_S + C_C)^2}
\]

and

\[
C_P = \frac{R_S^2 C_S^2 + R_C^2 C_C^2 + \omega^2 R_S^2 R_C^2 C_S C_C (C_S + C_C)}{(R_S + C_S)^2 + \omega^2 R_C^2 R_S^2 (C_S + C_C)^2}
\]

where \(R_S\) and \(C_S\) are sample resistance and capacitance respectively and \(R_C\) and \(C_C\) are contact resistance and capacitance respectively. It is generally assumed that because of the tight inter-particle packing, the contact capacitance, \(C_C\), is very much larger than the sample capacitance \(C_S\) and the contact resistance \(R_C\) is at least as large as the sample resistance, i.e., \(C_C \gg C_S; R_C \geq R_S\). Then above relationships are reduced to:

\[
R_P (\omega \to 0) = R_S + R_C
\]

\[
R_P (\omega \to \infty) = R_S.
\]

\[
C_P (\omega \to 0) = C_C.
\]

\[
C_P (\omega \to \infty) = C_S.
\]

From these equations \(R_P\) equals the series DC value at low frequency and becomes equal to the sample resistance at sufficiently high frequency. The real impedance versus imaginary impedance plots of the cell at various time of cell discharge has been shown in Fig. 6. It is clear from this figure that the impedance response of these cells revealed a progressive expansion of electrode contribution with time whereas bulk contribution was almost constant. It shows that the change in total impedance is due to change in electrode resistance and electrode capacitance.

![Fig. 6—Expansion of electrode resistance in complex impedance plot for \(o\)-tolidine-iodine-PVC (80% CTC) system (a) at the time of cell assembly (b) after 48 h of discharge (c) after 96 h of discharge](image)

<table>
<thead>
<tr>
<th>Time after assembly (h)</th>
<th>Impedance (Ohm)</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 Hz</td>
<td>1 kHz</td>
</tr>
<tr>
<td>0</td>
<td>1.55 \times 10^5</td>
<td>1.47 \times 10^5</td>
</tr>
<tr>
<td>24</td>
<td>1.72 \times 10^5</td>
<td>1.56 \times 10^5</td>
</tr>
<tr>
<td>48</td>
<td>1.81 \times 10^5</td>
<td>1.73 \times 10^5</td>
</tr>
<tr>
<td>72</td>
<td>1.96 \times 10^5</td>
<td>1.89 \times 10^5</td>
</tr>
<tr>
<td>96</td>
<td>2.02 \times 10^5</td>
<td>1.97 \times 10^5</td>
</tr>
</tbody>
</table>
The capacitance of different cells at different frequencies was measured. Some of these data for 80% CT complex have been given in Table 4 as a representative of all these systems. It is evident from these data that the capacitance of 6.72 nF, 2.94 nF, 1.72 nF and 0.42 nF at 100 Hz, 1 kHz, 10 kHz and 100 kHz respectively, increases to 10.77 nF, 5.12 nF, 3.02 nF and 0.69 nF respectively after 24 h for the 80% CT complex composite with PVC. This also confirms the formation of insulating layer between cathode materials and anode metals.

Table 4—Variation of capacitance of cell with time at 1 kΩ load for composite of o-tolidine-iodine with poly(vinyl chloride) and polystyrene (80% CTC).

<table>
<thead>
<tr>
<th>Time after assembly (h)</th>
<th>o-Tolidine -iodine-PVC (80% CTC)</th>
<th>o-Tolidine -iodine-PS (80% CTC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 Hz</td>
<td>1 kHz</td>
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<td>0</td>
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<td>5.12 nF</td>
</tr>
<tr>
<td>48</td>
<td>20.23 nF</td>
<td>6.99 nF</td>
</tr>
<tr>
<td>72</td>
<td>34.71 nF</td>
<td>11.72 nF</td>
</tr>
<tr>
<td>96</td>
<td>45.32 nF</td>
<td>17.12 nF</td>
</tr>
</tbody>
</table>

The capacitance of different cells at different frequencies was measured. Some of these data for 80% CT complex have been given in Table 4 as a representative of all these systems. It is evident from these data that the capacitance of 6.72 nF, 2.94 nF, 1.72 nF and 0.42 nF at 100 Hz, 1 kHz, 10 kHz and 100 kHz respectively, increases to 10.77 nF, 5.12 nF, 3.02 nF and 0.69 nF respectively after 24 h for the 80% CT complex composite with PVC. This also confirms the formation of insulating layer between cathode materials and anode metals.

Conclusions

The data presented here on the composition, time and temperature dependence of solid state galvanic cells shows that the rechargeable cells can be fabricated using composite of charge transfer materials with insulating polymer. These cells have high mechanical strengths, although the short circuit current for these composite cathode was lower than the pure charge transfer materials, the open circuit voltage of these systems were comparable. Therefore, these polymer composites could be used as an alternative for preparing the rechargeable organic batteries.

Acknowledgements

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References