Rechargeable iodine batteries based on charge transfer materials having mixed conduction

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Solid-state galvanic cells based on semiconducting charge transfer materials with mixed conduction have been fabricated and tested. The charge transfer complexes of iodine with phenothiazine, 2-chloro-phenothiazine, 2-acetyl-phenothiazine in 3:2 molar ratio and with benzidine in 1:1 ratio have been found to be mixed conductors along with usual electronic conductivities. The pressed pellets of these materials have been used as cathodes in contact with anode metals like aluminium, copper, zinc, titanium and nickel. The electrochemical characteristics of the cell such as open circuit voltages, short-circuit currents, their time and temperature dependence, and rechargeability of these cells have been studied. Dielectric behaviour of the cells have also been studied with a view to establish the nature of electrode reactions. Battery configurations have been fabricated and tested. The advantages and limitations of these batteries have been outlined.

Charge transfer materials containing iodine have been extensively utilized for the commercial production of lithium-iodine batteries. These batteries yield high and stable voltages and power densities over an extended period of time. Highly reactive lithium metal is used as anode in cell fabrication. Although, it gives high open circuit potential, it undergoes corrosion in idle period. A non-reactive polymer film was inserted in between the anode metal, i.e., lithium and the cathode material, a C-T complex of iodine so that it inhibits the spontaneous reaction of lithium with iodine. The film was removed at the time of use of the battery. The charge transfer materials were placed in contact with solid electrolytes so as to minimize the internal resistance of the cell.

Gutmann et al. have investigated electrochemical behaviour of iodine complexes with different metallic contacts. The highest open circuit voltage ($V_{oc}$) for the cell Mg/phenothiazine-iodine/Pt,C or Au was reported to be 1.75 V and short circuit current ($I_{sc}$) as 2.8 to 8.0 mA. A reaction mechanism for both free and iodine complex cell reactions has also been proposed. Mg/phenothiazine/Pt cell was studied for its reaction mechanism and it was concluded that the formation of metal halide as the energy producing reaction. It was found that the cell performance can be improved by exposing it to different environments, particularly to the atmospheric moisture, which acts as a reactant and not as a catalyst.

Louzos et al. have reported a cell which consists of a conductive ionic solid KCN-4AgI as electrolyte for silver and perylene-iodine complex system. This system is reported to have long shelf life due to low impedance, it has $V_{oc}$ of 0.64 V and $I_{sc}$ of 50 mAh/inch.

The synthetic of a new solid electrolyte Hgl-Rbl-TII and its usage in a cell assembly between silver anode and iodine-graphite complex cathode has been reported. They have obtained $V_{oc}$ as 0.69 V and $I_{sc}$ as 1.0 mAh/cm$^2$ at room temperature.

Solid state cells like Li/benzidine-iodine, Li/perylene-iodine were fabricated by Scrosati and Torroni and they found a very high cell voltage of 2.8 V at room temperature. Chandra et al. used a pellet of Ag$_x$KI 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.

Various carbon allotrope forms (graphite, active carbon and carbon black) were used as cathode materials for rechargeable lithium batteries, for their chemical stability and favourable cycling characteristics for charge-discharge study. The effect of structure of carbon on the performance of the cell was also discussed on the basis of charge-discharge and cyclic voltammogram.

Phthalocyanines have been used as cathode materials in secondary lithium cells by Yamaki and Yamaji and proposed a probable reaction mechanism. Matsumato and Matsunaga have reported a solid state cell Ag/Agl/phenothiazine-iodine, and studied its electrochemical behaviour as a
function of iodine composition \( (n = 1, 1.5, 2, 2.5, \ldots) \) and temperature. The \( V_{oc} \) of the cell increases with the increase in iodine composition from 0.62 V at \( n = 2.5 \) to 0.66 V at \( n = 3.0 \). Thermodynamic data, e.g., \(-\Delta G\), \(-\Delta H\), \(-\Delta S\) and \(\Delta G/n\) for the complex formation reactions have also been determined.

A solid-state storage battery comprising of Ag as anode, \( \text{RbAg}_4\text{I}_5 \) as a solid electrolyte separated by polyethylene film from composite containing iodine:graphite:polyethylene in 6:3:1 ratio as a cathode has been fabricated. This battery has long shelf life (3 years), because of the plastic film attached to casing material.

Solid-state galvanic cells\(^1\) based on a benzidine-iodine complex as cathode material and various commonly available metals as anodes have been reported. A stable open circuit voltage of 0.8 V for the cell configuration \( \text{Cu/benzidine-iodine/Al} \) has been found.

In this paper, a detailed study on four iodine complexes with five anode metals is reported. It is established that the cathode materials themselves act as mixed conductors. Various electrochemical parameters like open circuit voltages, short circuit currents and their dependence on time and temperature, polarization, and charge-discharge characteristics have been studied. Batteries were fabricated and tested. The above studies helped us to make the best solid state galvanic cells using common and less reactive metals.

**Experimental Procedure**

**Materials and their purifications**—Phenothiazine, 2-chloro-phenothiazine, 2-acetylphenothiazine (Aldrich), benzidine (Stains) and iodine were purified. The purities were checked from their melting points and thin layer chromatography and found the purities greater than 99.9%.

The charge transfer materials were prepared by weighing donors and iodine for a particular composition and grinding them together in an agate mortar with a few drops of benzene. The traces of the solvent evaporated by exposing to a 250 W infrared lamp for about one minute. The pellets (0.2 to 0.3 cm thick, 1.3 cm diameter) were prepared out of these materials (each of quantity approximately 300 mg) at a pressure of 10 kbar on hydraulic press (Spectralab, India). Various metal plates having dimension of 1.5 \( \times \) 1.5 cm\(^2\) are used as anodes.

**Fabrication of cell**—The cells were assembled on a rig made of brass and insulated by teflon (PTFE) by placing the cathode pellets in between the anode and inert metals. Care was taken to ensure complete contact between different materials. This cell assembly was placed in an evacuated glass chamber in order to protect it from atmospheric moisture.

**Measurements**—The electrical parameters of the cell were determined using a source measure unit (Keithley 236) and a precision digital LCR meter (Vasavi Electronics, Hyderabad, Model VLCR 7). The temperature was controlled and measured using a temperature indicator-controller unit (Century, India, Model CT 806). All the measurements were repeated at least three times to check reproducibility of data which were found to vary within the limits of experimental error.

**Results and Discussion**

**Mixed conduction in charge transfer materials**—Mixed conduction in charge transfer materials has been reported by Akamatu et al.\(^{14}\) The dc electrical resistivity of perylene-bromine complex in contact with silver metal was found to increase with time. Consequently, a part of total conductance was attributed to the transference of some ions. Ionic conductances were found to be 3-5 times as large as electronic conductance in freshly prepared samples, thereafter it increased to 10-20 times. The transference number determined from the ratio of ionic conductance to total conductance lies in the range of 0.8-0.99, characteristic of superionic conduction.

Most of the other data reported in literature do not mention the role of ionic or superionic conduction in charge transfer materials. However, we have found that the dc electrical conductivities of many charge transfer materials conducting polymers decrease with time even when non-reactive contacts like platinum or graphite are used. A representative example of variation of electrical conductivity with time for 2-acetylphenothiazine-iodine complex has been shown in Fig. 1. The cell is Pt/CTC/Pt, pellet of charge transfer complex (CTC) in contact with Pt or graphite electrodes. The electrical conductivity of the material decreases exponentially with time and attains a saturation value. Similar results have been obtained for the other systems as well. The existence of polyiodides in such complexes has been proposed earlier\(^{15}\), which takes part in ionic conduction in these molecular electronic materials. The details of this work has been reported earlier\(^{16}\). But this study indicates that the charge-discharge behaviour of the solid-state cells depends largely on the mobile ions present in the cathode materials itself. We need not add other superionic conductors in these materials for improving the cell characteristics.

**Cell characteristics**

**Time dependence**—The variation of open-circuit
Fairly stable voltages and short circuit currents have been obtained during the first three hours of discharge. For the 2-acetylphenothiazine-iodine complex in contact with carbon and zinc, the open circuit voltage of 0.9 V, short circuit current of 0.68 mA, power output of 0.66 W and current density of 0.51 mA/cm² were found at the time of cell assembly as shown in Fig. 2. The \( V_{oc} \) rose up to 1.05 V in about 20-30 min and remains constant at the same value for about 3h. This may be due to slow diffusion of iodine/iodide into zinc leading to the formation of zinc iodide. When the same cell configuration is connected across a 10 kΩ external load, a stable voltage of 1.03V and reduced current of
With 10 K load

**Fig. 4—Variation of cell voltage and current density with time for the cell configurations Pt/2-chlorophenothiazine-iodine/Zn (----), Pt/2-chlorophenothiazine-iodine/Al (--), carbon/2-chlorophenothiazine-iodine/Zn (-----) and carbon/2-chlorophenothiazine-iodine/Al (----) at 10 k fixed load and without load at room temperature (303.5K).**

0.1mA were found. The Pt-Zn contacts give an initial $V_{oc}, I_{sc}$ as 1.02 V, 1.26 mA respectively which is slowly reduced to 0.95V after one hour of the cell assembly, thereafter, no drop in voltage was seen for 3h. Similar behaviour was found for Pt-Al and C-Al combinations. However, very low voltages and current densities are found in Pt-Cu, Pt-Ni, Pt-Ti and C-Ti, C-Ni combinations probably due to the poor reactivity of anode metals with iodine. The behaviour of phenothiazine-iodine complex with various metallic contacts are shown in Fig. 3: When the pellet of this complex is coupled with carbon and zinc, stable and large power output and current densities are obtained unlike the other metal contacts as shown in the respective tables. In 2-chlorophenothiazine-iodine and benzidine-iodine complexes also, similar results were obtained with carbon and zinc contacts.

The variation of cell voltage over extended period of time has been shown in Fig. 5. It was found that the voltage drop is very small for the first three days of continuous operation but decreases to half its value in 15 days. The detailed electrochemical data for the different systems are presented in Tables 1-4. It is found that the cell voltage increased from 0.98V at the time of assembly to a constant value of 1.05V after about 15 min. It seems to support the mixed conduction mechanism for such galvanic cells which requires some time for the diffusion of iodine/iodide to the anode from the bulk.

**Temperature dependence—** This has been further supported by the study of the effect of temperature on the electrochemical behaviour of the cell, increase in temperature enhances the short circuit current but the open circuit voltages remain more or less unaltered. During the heating cycle for the cell configuration carbon/2-acetylphenothiazine-iodine/Zn, the initial open circuit voltage of 0.98V and short circuit current of 4.9mA are found at room temperature 305.7 K. When the temperature was raised to 333 K, there was little change in open circuit voltage, but its current rose upto 9.2 mA. In cooling cycle, $I_{sc}$ retraces the path of heating cycle. Thus, thermally activated diffusion of ionic conductors may be responsible for the above result. These observations suggest that these cells can be used at elevated temperatures rather more efficiently than at ambient temperatures. Also there is no self discharge of the cell.

Thermodynamic parameters for the cell carbon/2-acetylphenothiazine-iodine/Zn are
Table 1—Variation of cell voltage and current density of 2-acetyl-phenothiazine-iodine (2:3) complex (as cathode) in contact with Pt & C (as inert metals) and various metals (as anodes) at room temperature (303 K)

<table>
<thead>
<tr>
<th>Inert metal</th>
<th>Anode metal</th>
<th>Without any load</th>
<th>With 10K Ω fixed load</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>At the time of cell assembly After 3 h</td>
<td>At the time of cell assembly After 3 h</td>
</tr>
<tr>
<td>Pt</td>
<td>Al</td>
<td>0.705 1.156 0.730 17.827</td>
<td>0.745 0.045 0.760 0.053</td>
</tr>
<tr>
<td>Pt</td>
<td>Cu</td>
<td>0.003 0.109 0.003 0.019</td>
<td>0.390 0.038 0.160 0.012</td>
</tr>
<tr>
<td>Pt</td>
<td>Zn</td>
<td>1.020 0.947 0.950 1.113</td>
<td>1.090 0.060 1.055 0.075</td>
</tr>
<tr>
<td>Pt</td>
<td>Ti</td>
<td>0.090 &lt; 1 μA 0.150 &lt; 1 μA</td>
<td>0.055 0.002 0.060 0.004</td>
</tr>
<tr>
<td>Pt</td>
<td>Ni</td>
<td>0.002 0.016 0.129 0.387</td>
<td>0.019 &lt; 1 μA 0.021 0.003</td>
</tr>
<tr>
<td>C</td>
<td>Al</td>
<td>0.701 0.371 0.763 38.293</td>
<td>0.760 0.053 0.760 0.057</td>
</tr>
<tr>
<td>C</td>
<td>Cu</td>
<td>&lt; 1 mV 0.002 &lt; 1 mV 0.002</td>
<td>0.008 &lt; 1 μA 0.008 &lt; 1 μA</td>
</tr>
<tr>
<td>C</td>
<td>Zn</td>
<td>0.970 0.511 1.050 3.722</td>
<td>0.103 0.068 0.102 0.083</td>
</tr>
<tr>
<td>C</td>
<td>Ti</td>
<td>&lt; 1 mV &lt; 1 μA &lt; 1 mV &lt; 1 μA</td>
<td>0.028 0.002 0.011 0.008</td>
</tr>
<tr>
<td>C</td>
<td>Ni</td>
<td>&lt; 1 mV 0.002 0.032 0.671</td>
<td>0.010 &lt; 1 μA 0.035 0.003</td>
</tr>
</tbody>
</table>

Table 2—Variation of cell voltage and current density of phenothiazine-iodine (2:3) complex (as cathode) in contact with Pt & C (as inert metals) and various metals (as anodes) at room temperature (303.5 K)

<table>
<thead>
<tr>
<th>Inert metal</th>
<th>Anode metal</th>
<th>Without any load</th>
<th>With 10k Ω fixed load</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>At the time of cell assembly After 3 h</td>
<td>At the time of cell assembly After 3 h</td>
</tr>
<tr>
<td>Pt</td>
<td>Al</td>
<td>0.935 0.102 0.765 0.511</td>
<td>0.925 0.030 0.765 0.049</td>
</tr>
<tr>
<td>Pt</td>
<td>Cu</td>
<td>0.580 0.123 0.535 0.015</td>
<td>0.570 0.035 0.590 0.012</td>
</tr>
<tr>
<td>Pt</td>
<td>Zn</td>
<td>1.070 0.211 0.785 0.128</td>
<td>1.005 0.021 0.780 0.029</td>
</tr>
<tr>
<td>Pt</td>
<td>Ti</td>
<td>0.175 0.004 0.115 0.004</td>
<td>0.120 0.003 0.100 0.003</td>
</tr>
<tr>
<td>Pt</td>
<td>Ni</td>
<td>0.050 0.009 0.120 0.007</td>
<td>0.270 0.016 0.250 0.019</td>
</tr>
<tr>
<td>C</td>
<td>Al</td>
<td>1.045 0.259 0.760 21.898</td>
<td>0.851 0.045 0.740 0.053</td>
</tr>
<tr>
<td>C</td>
<td>Cu</td>
<td>0.584 0.135 0.595 0.143</td>
<td>0.213 &lt; 1 μA 0.595 0.035</td>
</tr>
<tr>
<td>C</td>
<td>Zn</td>
<td>0.980 3.278 1.050 3.263</td>
<td>1.050 0.075 1.070 0.075</td>
</tr>
<tr>
<td>C</td>
<td>Ti</td>
<td>0.005 &lt; 1 μA 0.004 &lt; 1 μA</td>
<td>0.040 0.002 0.034 0.002</td>
</tr>
<tr>
<td>C</td>
<td>Ni</td>
<td>0.014 0.014 0.070 0.050</td>
<td>0.050 0.008 0.090 0.008</td>
</tr>
</tbody>
</table>

calculated by using the following equations (i) \( \Delta G = -nEF \); (ii) \( E = -\Delta H/nF + T[dE/dT] \); (iii) \( \Delta G = \Delta H - T\Delta S \). The Gibbs free energy for the cell was found to be 182.4 kJ mol\(^{-1}\). The enthalpy and entropy values were found to be 100.3 kJ mol\(^{-1}\) and 0.9 JK\(^{-1}\) mol\(^{-1}\) respectively, from the temperature dependence of cell\(^{17}\).

**Polarization studies**

The current-voltage characteristics of the carbon/2-acetylphenothiazine-iodine/Zn system has been shown in Fig. 6. When positive voltage of 0.5 to 5.0V were applied to the system, the current rose upto 45.0 mA from 0.25 mA at 5.0V applied to cell. When negative voltages were applied in the same fashion, the current increased very slowly in the beginning. Thereafter a sharp increase upto -75.0 mA was found when -5.0V was applied to the cell. It is evident from Fig. 6 that the \( I-V \) characteristics are not the same in the forward and reverse bias. This may be due to the favoured migration of charge carriers in the reverse bias rather than in the forward bias in which behaviour is more or less ohmic. Similar results have been obtained for other systems.

**Rechargeability**

The rechargeability of the batteries has been reported in Fig. 7. It is found that a cell discharged for
80 h could be recharged to the initial voltage by passing a current of 6.5 mA for only about 5 min. This may be due to ionic conduction within the cathode material, leading to electrolysis of reaction products into original components. The current efficiency calculated from the ratio of charge delivered during discharge and charge used in charging process was found to be 37.0%.

Dielectric studies

The capacitance of the different cells along with the loss factor at 1 kHz were determined with a view to establish the formation of metal halides. In Pt/2-acetylphenothiazine-iodine/Al cell system, 526 nf of capacitance and tan δ of 0.922 was noted at the time of its assembly. After 3h, capacitance and tan δ rose upto 195 μF and 1.936 respectively. The same complex in contact with carbon and Al also shows the similar behaviour, capacitance rose upto 744 μF from 163.4 nf. For the same charge transfer complex coupled with Pt and Zn, the capacitance and loss factor increased with time in all the systems indicating the formation of halides which are the energy producing reactions. Later these halides form polyiodides with the molecular iodine, which helps in mixed conduction.
Batteries

2-cell and 3-cell battery configurations have been fabricated by using these charge transfer complexes with carbon and Zn contacts and their discharge characteristics were studied over a long period. The battery configurations are (i) C/2-acetylphenothiazine-iodine/Zn//C/2-acetylphenothiazine-iodine/Zn and (ii) C/2-acetylphenothiazine-iodine/Zn//C/2-acetylphenothiazine-iodine/Zn//C/2-acetylphenothiazine-iodine/Zn.

When each cell is connected in series, their individual voltages are added up to deliver the total emf. In the case of battery (i), $V_{oc}$ of 2.10 V and $I_{sc}$ of 0.50 mA are noted at the time of assembly. After continuous discharge for 300 h, $V_{oc}$ reduced to 0.61 V and $I_{sc}$ also reduced to 0.11 mA, about 25-30% discharge. While in battery configuration (ii), $V_{oc}$ of 3.21 V and $I_{sc}$ of 0.36 mA are observed at the time of its assembly. At the end of 260 h of continuous discharge, $V_{oc}$ reduced to 2.64 V and $I_{sc}$ decreased to 0.14 mA.

Effect of environment

The possibility of metal-air cell with Pt in contact with dry air has been tested. No emf was observed even after a long exposure (2 days). The zinc plate exposed to ambient temperature containing 90% humidity gave fluctuating emf in the range of 0.1-0.7 mV. Therefore, the emf of about 1 V using the charge transfer materials due to the formation of metal-air cell (Zn-ZnO) is ruled out. In case of hygroscopic metal halides, the atmospheric moisture affects the short circuit current values due to the removal of insulating halides by dissolution so that more metallic area is exposed to the complex leading higher amount of electrochemical reaction and thus higher current values. Similar observations were made by Gutmann et al.3-4,6.

Conclusion

The data presented here show that the rechargeable iodine batteries can be designed and fabricated using common anode metals like zinc and aluminium and a counter electrode. The role of mixed conduction in the performance of these batteries has been emphasized.

Acknowledgements

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References