

Solid State Rechargeable Organic Batteries Based on Polymer Composites of Charge-transfer Materials

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Abstract: Solid-state galvanic cells based on charge-transfer complexes have been extensively used. However, the low mechanical strengths of these materials have restricted their applications. To overcome this problem, the polymer composite of these materials have been prepared and used in fabrication of solid-state batteries. The pressed pellet of these materials has been used as cathode 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 and rechargeability of these cells have been studied. The impedance analyses have been done to understand the nature of the electrode reaction.

Key words: Composite, semiconductors, electrochemical cell, impedance spectroscopy

INTRODUCTION

Charge-transfer complexes have attracted considerable attention for fabrication of solid-state batteries^[1-4]. Electrochemical behavior of iodine complexes with different metallic contacts such as barium, calcium, magnesium, aluminum etc, as anodes and charge-transfer complexes as cathodes and platinum, gold or carbon as counter electrodes has been studied^[2]. These batteries have high open-circuit voltage. The performance of these batteries can be improved by exposing it to different environments. It has been found that the atmospheric moisture improves the performance of these batteries to a great extent. It was proposed that the atmospheric moisture acts as a reactant and not as a catalyst^[5].

Solid-state lithium cells based on benzidine-iodine and perylene-iodine have been fabricated and it was found that they have very high cell voltage at room temperature^[6]. Chandra *et al.*^[7] have used a pellet of Ag₄KI₅ as the solid electrolyte, silver foil as anode and graphite-iodine complex as the cathode for fabrication of cell. This cell yields an open-circuit voltage of 0.68 volts at room temperature. Gutmann *et al.*^[8] 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.*^[9] 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 was 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 was almost constant in the impedance analysis of these batteries which further confirms the formation of insulating layer between the anode and cathode^[10].

The charge-transfer materials have low mechanical strengths, which restrict their proper application in device fabrication^[11]. The mechanical strength of these charge-transfer materials can be improved by preparing their composite with insulating polymers^[12]. These composite materials have high mechanical strengths, as well as high electrical conductivities. In this study, an electrochemical behaviour of cells based on composites of benzidine-iodine (1:1.25) in poly (vinyl chloride) and polystyrene as cathode materials and zinc as anode materials has been reported in detail. Various electrochemical parameters like open-circuit voltage, short-circuit current and their dependence on time and temperature and charge-discharge characteristics have been studied. Impedance analyses of these batteries have been done in order to understand the electrode reactions.

MATERIALS AND METHODS

Benzidine (Thomas Baker) 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) were used as received. All other chemicals used were of A.R. grade. The charge-transfer complex of benzidine-iodine (1:1.25) was prepared by mixing hot solutions of required amount of donor and acceptor in benzene^[13]. The composite of charge-transfer complex (CTC), benzidine-iodine (1:1.25) (Bz-I₂) with poly (vinyl chloride) (PVC), has been prepared by dissolving CTC in chloroform and was introduced in insulating polymer (PVC) matrix by diffusion^[14] and for preparation of PS composites, the CTC and polymer were dissolved separately in chloroform and mixed them and then the solvent was evaporated with constant stirring at room temperature. Then the composite was grounded with the help of pastel mortal. The fine powders of the composites were pressed in pellets form under 10 tones load using a hydraulic press.

The cells were fabricated in a pellet holder made of brass, by introducing the pellets of the materials in between the anode metal (zinc) and inert electrode (platinum). The fabricated cell was placed in a glass chamber containing fused calcium chloride in order to protect it from the atmospheric moisture. 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 compressive strengths were measured on Amsler Universal Testing Machine.

RESULTS AND DISCUSSION

Mechanical properties: The compressive strengths for the composite of benzidine-iodine (1:1.25) with PVC and PS have been measured (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: Spontaneous reaction goes on in cell, when it is in idle period due to the direct contact of cathode and anode, reduces the life of the cell. To overcome this problem a non-reactive polymer film was introduced in between the cathode materials and anode metals, which has to be removed at the time of use of battery^[9]. This study, measured the open circuit voltage (V_{OC}) and short circuit current (I_{SC}) of the cell without putting any load to the cell. It has been observed that the V_{OC} and I_{SC} were decreasing very slowly with time which shows that the

Table 1: Mechanical strength of the composites of benzidine-iodine (1:1.25) with poly (vinyl chloride) and polystyrene

% Composition of CTC	Compressive Strength* (kg cm ⁻²)	
	Poly (vinyl chloride)	Polystyrene
100	265.3	265.3
80	364.8	322.6
60	472.2	395.3
40	561.9	451.2
20	584.0	481.3
Pure polymer	648.5	567.8

* Compressive strengths were measured for samples of dimension A = 0.786 cm², l = 2.00 ± 0.2 cm

spontaneous reactions go on slowly in these cells and the cells have shelf-life of about 150 h even if no insulating films was inserted between the anode and cathode.

Discharge-charge characteristics: The variation of V_{OC} and I_{SC} as a function of time against 10 k Ω external load for the composite of Bz-I₂ (1:1.25) with PVC and PS has been shown in Fig. 1 and 2, respectively. It has been observed that the initial V_{OC} for pure CTC and the composites are almost equal, but the initial I_{SC} is found to be decreasing on increasing the concentration of insulating materials in the composites. This can be explaining on the basis of internal resistance of the cell. On decreasing the concentration of CTC 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 CTC in composite decreases leading to lower amount of electrochemical reaction and hence the short circuit current^[10].

For Zn/Bz-I₂/Pt cell, the V_{OC} and I_{SC} at the time of cell assembly were 0.90V and 24.5 $\mu\text{A cm}^{-2}$, respectively after 24 h V_{OC} of 0.63 V and I_{SC} of 18.79 $\mu\text{A cm}^{-2}$ was obtained. The cell was charged by applying the initial current for 1 h. After charging the V_{OC} of 1.10 V and I_{SC} of 43.21 $\mu\text{A cm}^{-2}$ was obtained which decreases to 0.67 V and 3.72 $\mu\text{A cm}^{-2}$ after discharging for 170 h. For 80% composite in PVC, the initial V_{OC} and I_{SC} were 1.0 V and 14.45 $\mu\text{A cm}^{-2}$, respectively, whereas for 80% composite in PS, the initial V_{OC} and I_{SC} were 1.10V and 18.45 $\mu\text{A cm}^{-2}$, respectively, after 48 h of discharge of the V_{OC} and I_{SC} of the cell for 80% CTC in PVC decreased to 0.93V and 6.98 $\mu\text{A cm}^{-2}$ whereas for 80% CTC in PS it was 0.94 V and 12.56 $\mu\text{A cm}^{-2}$, respectively. The detailed electrochemical data for different composition of CTC have been listed in Table 2. These data confirm the rechargeability of these solid state galvanic cells based on composite of CTC with insulating materials. These results indicated 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 k Ω .

Table 2: Charge-discharge data of cells with 10 k Ω external load at room temperature

Composite		Fresh cell				After charging the cell			
		At time of cell assembly		After 100 h		At time of cell assembly		After 72 h	
		V_{OC} (V)	I_{SC} ($\mu A cm^{-2}$)	V_{OC} (V)	I_{SC} ($\mu A cm^{-2}$)	V_{OC} (V)	I_{SC} ($\mu A cm^{-2}$)	V_{OC} (V)	I_{SC} ($\mu A cm^{-2}$)
Benzidine-I ₂	% CTC	0.90	24.50	0.22	1.99	1.10	43.21	0.64	3.71
Benzidine-I ₂	80	1.00	14.45	0.53	0.71	1.00	22.91	0.90	3.16
PVC	60	0.99	7.45	0.66	0.71	1.02	13.12	0.81	1.98
	40	0.96	0.87	0.61	0.22	0.95	1.01	0.69	0.61
	20	0.92	0.09	0.63	0.05	1.01	0.18	0.65	0.07
Benzidine-I ₂	80	1.10	18.45	0.63	1.59	1.29	15.36	0.91	4.87
PS	60	0.99	8.77	0.61	0.63	1.04	9.87	0.75	3.02
	40	0.97	0.62	0.52	0.11	0.98	0.55	0.75	0.10
	20	0.95	0.10	0.56	0.03	1.05	0.09	0.73	0.02

Table 3: Variation of capacitance of cell with time at 10 k Ω load for composite of Benzidine-Iodine with poly (vinyl chloride) and polystyrene (80% CTC)

Time after assembly (h)	Benzidine-iodine-PVC (80 % CTC)				Benzidine-iodine-PS (80 % CTC)			
	100 Hz	1 kHz	10 kHz	100 kHz	100 Hz	1 kHz	10 kHz	100 kHz
0	3.77nF	972.10pF	316.30pF	99.2pF	2.34nF	412.10pF	117.20pF	56.10pF
24	8.43nF	1.52nF	397.50pF	112.4pF	2.97nF	877.20pF	577.70pF	82.30pF
48	15.77nF	2.83nF	897.20pF	432.4pF	6.32nF	1.22nF	948.10pF	972.30pF
72	24.82nF	4.01nF	1.02nF	779.4pF	8.77nF	1.48nF	1.11nF	1.01nF
96	31.72nF	5.11nF	1.62nF	837.2pF	21.23nF	2.24nF	1.401nF	1.22nF

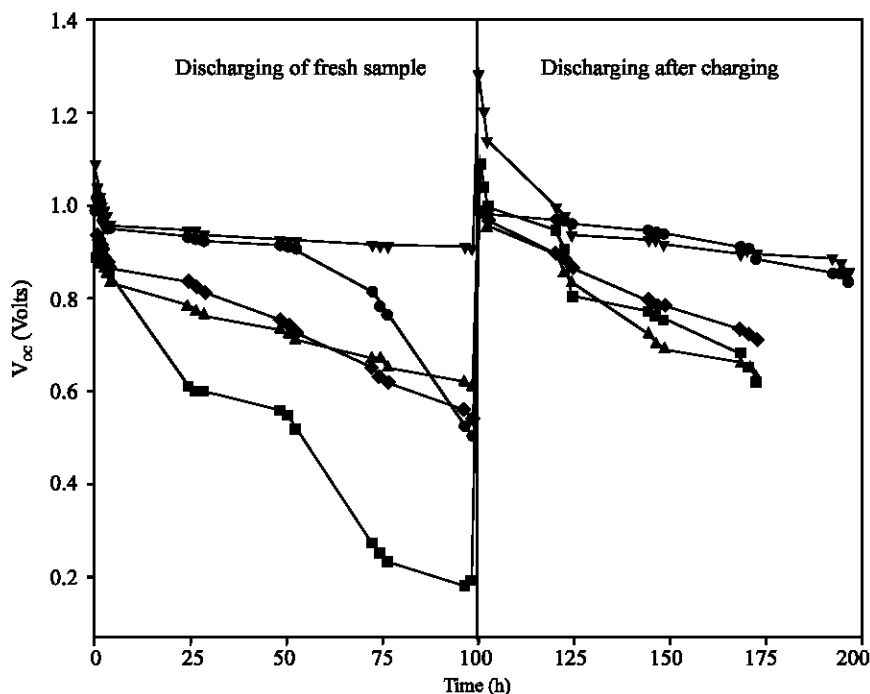


Fig. 1: Variation of open-circuit voltage with time at 10 k Ω load for:

(■) Bz-I₂ (●) Bz-I₂-PVC (80% CTC) (▲) Bz-I₂-PVC (20% CTC) (▼) Bz-I₂-PS (80% CTC) (◆) Bz-I₂-PS (20% CTC)

Power out put: Variation of power out put as a function of time for pure charge transfer complex and their composites have been shown in Fig. 3. It is observed that there was sharp fall in power out put within 5-10 h. After than it was almost constant up to 100 h. The power out put increases significantly after charging the cell. The initial power out put decreases from 8.65×10^{-2} to 4.32×10^{-4} and 4.28×10^{-4} VA Kg⁻¹, when the content of CTC decreases from 100 to 20 wt % in PVC and PS, respectively. The

decrease in power out put with decreasing weight % of CTC 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 CTC 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

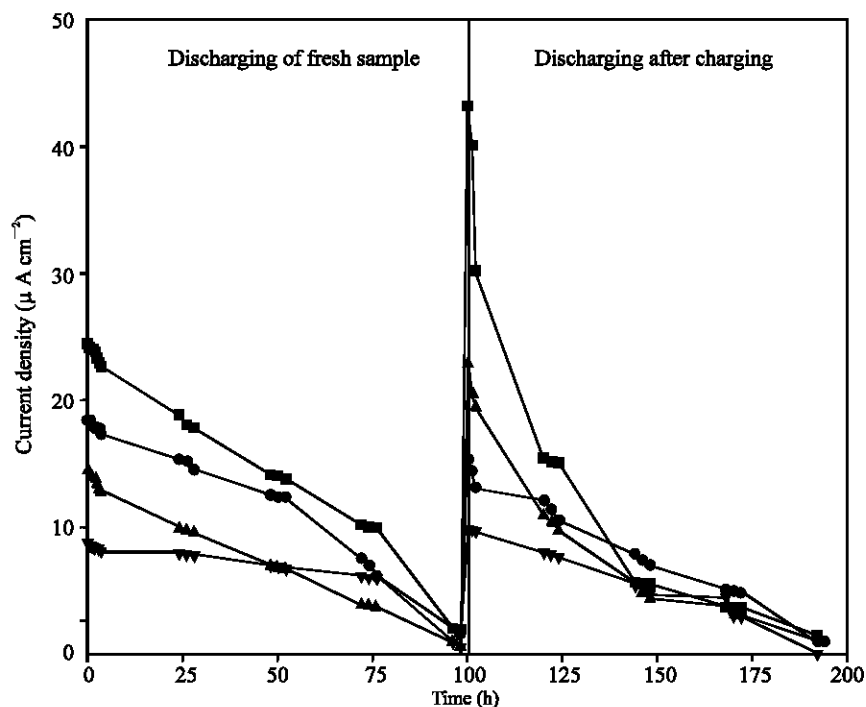


Fig. 2: Variation of short-circuit current density with time at 10 k Ω load for:
 (■) Bz-I₂ (●) Bz-I₂-PVC (80% CTC) (▲) Bz-I₂-PS (80% CTC) (▼) Bz-I₂-PS (60% CTC)

been done to study the effect of temperature on the electrochemical behavior of these cells. 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/ Bz-I₂-PVC (80% CTC)/ Pt are calculated by using the following equations

$$\Delta G = -nEF \tag{1}$$

$$E = -\Delta H/nF + T [dE/dT] \tag{2}$$

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

The Gibbs free energy for the cell was found to be 106.2 kJ mol⁻¹. The enthalpy and entropy values were found to be 76.91kJ mol⁻¹ and 99.0 J K⁻¹, respectively, from the temperature dependence of the cell^[4].

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^[9]. 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. The data were recorded in the frequency range of 40 Hz to 100 kHz and the measured data were simulated in the frequency range of 10⁻³ Hz to 10¹¹ Hz using a Complex Non-linear Least Square (CNLS) analysis software developed by EG and G Parc, USA. Usually the bulk, grain boundary and electrode contributions to the overall measured electrical properties are expected. So in general we expect the presence of three arcs. The values of bulk and grain boundary contributions are approximately equal. The impedance response of these cells revealed a progressive expansion of electrode contribution (Fig. 4). It shows that the change in total impedance is due to change in electrode resistance and electrode capacitance.

The capacitance of different cells at different frequencies was measured. Some of these data for 80% CTC have been given in Table 3 as a representative of all

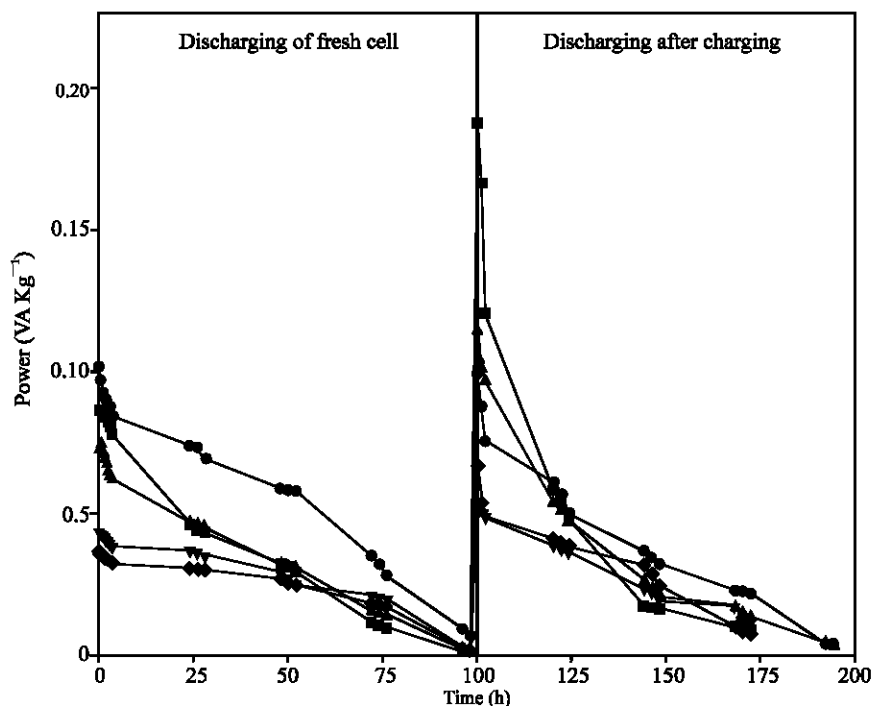


Fig. 3: Variation of power output with time at 10 k Ω load for:
 (■) Bz-I₂ (●) Bz-I₂-PS (80% CTC) (▲) Bz-I₂-PVC (80% CTC) (▼) Bz-I₂-PS (60% CTC) (◆) Bz-I₂-PVC (60% CTC)

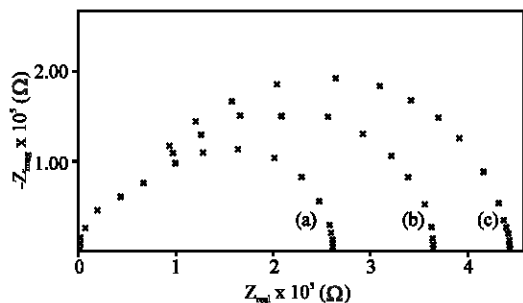


Fig. 4: Expansion of electrode resistance in complex impedance plot for benzidine-iodine-PVC (60% CTC) system, a) At the time of cell assembly, b) After 48 h of discharge, c) After 96 h of discharge

these systems. It is evident from these data that the capacitance of 3.77 nF, 0.972 nF, 0.316 nF and 99.2 pF at 100 Hz, 1 kHz, 10 kHz and 100 kHz, respectively, increases to 8.43 nF, 1.52 nF, 397.5 pF and 112.4 pF, respectively after 24 h for the 80% CTC composite with PVC. This also confirms the formation of insulating layer between cathode materials and anode metals.

CONCLUSION

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.

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