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Charge-discharge characteristics of polyacetylene solid-state batteries

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Summary

The performances of solid-state batteries using polyacetylene, $(CH)_x$, as electrode material have been investigated. Two kinds of solid electrolytes, $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$, have been used with silver anodes. Both types of cells are able to discharge at room temperature. The performances of cells such as internal resistance, electromotive force, discharging ability, capacity, etc., have been measured under different conditions. The secondary effect of the solid-state batteries is investigated also. Moreover, the differences between the two kinds of cells have been compared and discussed.

Introduction

Polyacetylene, $(CH)_x$, film has been much attractive for the application as the electrode material of secondary batteries [1-3]. The battery using $(CH)_x$ electrode has the advantages of lighter weight, higher energy and power densities. So far, most of the reports about polyacetylene films used as electrode material have been limited to liquid electrolyte batteries. There are few reports about polyacetylene solid-state batteries [4-6]. They indicated that solid-state batteries have some advantages which are lacking in liquid electrolyte batteries. These include, (i) ease of miniaturization, (ii) free of electrolyte vaporization or leakage out of cells, (iii) capable of operation over a wide temperature range, not causing catastrophic loss of electrolyte conductivity and (iv) long shelf life.

In this paper, two kinds of solid electrolytes, $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$, were chosen as the electrolyte materials. Both electrolytes exhibit high ionic (Ag^+) conductivities with practically no electronic conductivity at room temperature. $RbAg_4I_5$ has the highest ionic conductivity in the silver iodide and rubidium iodide system ever known [7]. $Ag_{26}I_{18}W_4O_{16}$ has been known to have better stability in iodine atmosphere than the rest of silver ion conductors ever known [8]. Two types of solid-state batteries, $Ag+RbAg_4I_5/RbAg_4I_5/(CHI_y)_x$ and $Ag+Ag_{26}I_{18}W_4O_{16}/Ag_{26}I_{18}W_4O_{16}/(CHI_y)_x$, were constructed. The performances of both types of batteries were described and compared through the measurements of battery parameters. Besides, secondary effect of the batteries has also been investigated in this study.

Experimental

Polyacetylene films were synthesized by the method of Shirakawa et al.

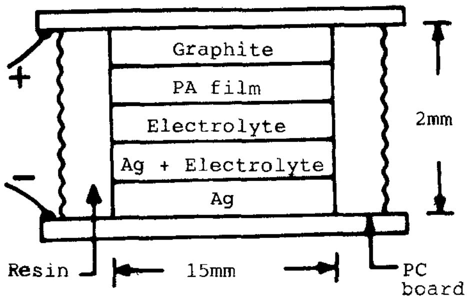

Fig. 1. Schematic diagram of the polyacetylene solid-state battery.

[9]. The films were prepared at low temperature (-78°C) and therefore existed in the cis form. Trans-films can be obtained by heating the cis-films at 180°C under vacuum for 30 minutes. Because cis-$(CH)_x$ films are more flexible and tough than trans-$(CH)_x$ films, we choose the cis-$(CH)_x$ as the electrode material in this study. The thickness of $(CH)_x$ films is about 22-100um with an apparent density of about 0.3-0.4g/cm³. Doping was carried out by exposing the $(CH)_x$ films to iodine vapor. The concentration of dopant in $(CH)_x$ was measured by weight up-take.

Solid electrolytes $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$ were synthesized according to the processes reported [7-8]. Because $RbAg_4I_5$ will decompose sluggishly when the temperature is below 27°C [7], it was kept above 27°C under vacuum before use. The transport numbers of silver ions in solid electrolytes were measured by Tubandt's method [10]. Electronic conductivity was measured by Wagner's polarization method [11]. In order to avoid polarization effect, a cell, Ag/Ag+Electrolyte/Electrolyte/Ag+Electrolyte/Ag, was constructed to measure the ionic conductivities of solid electrolytes using a 1 kHz ac impedance bridge.

The polyacetylene solid-state battery is schematically shown in Fig.1. It has a cylindrical form of 15mm diameter and 2mm thickness. The cell consists essentially of an anode layer, a mixed layer of silver and electrolyte, an electrolyte layer and a cathode layer.

Since the electrolytes, $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$, are all silver ion conductors, the anode must employ silver as the active element. In order to increase the effective contact area between anode and electrolyte, silver powder is mixed with electrolyte powder. The so called complex type electrode will also reduce the contact resistance at the anode-electrolyte interface. Since the anode mixture formulation will influence the utilization of cells, a preliminary experiment shows that the anode polarizations are reduced to minimum at the weight ratios of silver to $RbAg_4I_5$ electrolyte in 1:2 and $Ag_{26}I_{18}W_4O_{16}$ electrolyte in 1:3.

Cis-$(CH)_x$ film with thickness of about 22-100um is used as cathode material. Both doped and undoped films can be used; however, the cells adopting undoped films must be charged before ready to use, which will create a partial electrolysis of electrolytes according to the reactions:

$$2RbAg_4I_5 \longrightarrow Rb_2AgI_3 + 7Ag + 7/2I_2$$

or

$$Ag_{26}I_{18}W_4O_{16} \longrightarrow Ag_8W_4O_{16} + 18Ag + 9I_2$$

and the subsequent doping of $(CH)_x$,

$$(CH)_x + 1/2xyI_2 \longrightarrow (CHI_y)_x$$

So, we use multi-pieces of doped cis-$(CH)_x$ films to fabricate the solid-state batteries. A thin layer of graphite powder is used as an inert cathode collector. The cell is finally encapsulated with a resin coating.

Results and Discussion

The ionic conductivity of solid electrolyte was determined with an 1 kHz ac impedance bridge at the temperature ranging from -25°C to 100°C. Figure 2 shows the plots of logarithm of specific conductivity multiplied by the absolute temperature (σT) vs. the reciprocal temperature. At room temperature (25°C), the ac total specific conductivities are 0.25 and 0.042S/cm for $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$, respectively. The activation energy of $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$ obtained from the slopes of curves in Fig.2 are about 2Kcal/mole and 4Kcal/mole. The silver ion transport numbers measured by Tubandt's method are about 0.989 and 0.993 for $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$, respectively, which shows that the conduction of both electrolytes is almost due to the Ag^+ movement. The elctronic conductivities of both $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$ measured by Wagner's method are of the order of about 10^{-8}S/cm. From the results obtained above, it is obvious that both types of solid electrolytes possess high ionic and negligible electronic conductivities, which makes them to be very suitable for the application of solid-state batteries.

The electromotive force of solid-state batteries depends on three different factors. The first factor found to influence the electromotive force is the iodine content doped in polyacetylene films. Figure 3 shows the influence of dopant concentration on the electromotive force of both kinds of cells. It was found that the electromotive force increases sharply when the iodine content increases from 0 to 4-5%, after then it increases slowly. Finally, the electromotive force can be increased up to 650mV when the iodine content attains ca.22%. If the iodine content increases continuously, it will be approaching to the theoretical EMF associated with the reaction:

$$Ag + 1/2I_2 \longrightarrow AgI$$

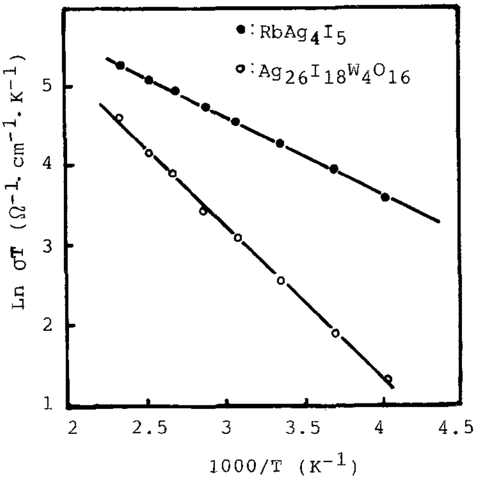

Fig. 2. Ionic conductivities vs. temperature for $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$ electrolytes.

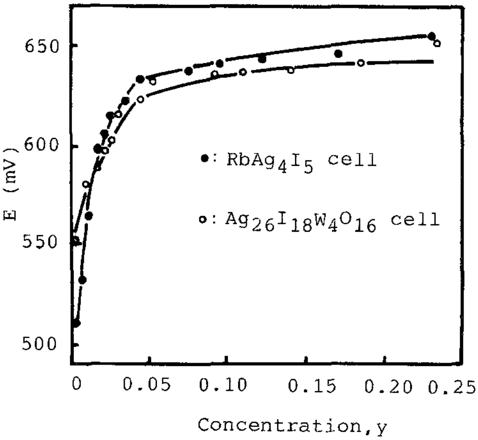

Fig. 3. Influence of the iodine content y of the $(CHI_y)_x$ cathode on the electromotive force at 25°C.

which has been given from Nernst equation and the standard free energy of formation of AgI: $E^o = 0.687V$ [12]. From the phenomenon described, we can suggest that the discharging reaction of the cell should be written as:

$$xyAg + (CHI_y)_x \longrightarrow xyAgI + (CH)_x$$

which is similar to the Owens's battery using a charge transfer complex [13]. The experimental dependences of E vs. y shown in Fig.3 is difficult to interpret. It may be supposed that the tendency in Fig.3 is with relation to the conductivity of the films because the two curves of Fig.3 are very similar to that of conductivity vs. concentration plot [2].

The second factor which influences the electromotive force is temperature. The variations of electromotive force with temperature for both kinds of cells with lightly doped films are shown in Fig.4, in which, the expected straight lines are in accordance with the Nernst equation. The temperature coefficients are 0.096mV/°C and 0.185mV/°C for $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$ cells, respectively. From the results got, the variation of electromotive force with temperature for $RbAg_4I_5$ cell is smaller than that of $Ag_{26}I_{18}W_4O_{16}$ cell. The reason may be due to the larger conductivity and smaller activation energy of $RbAg_4I_5$ in the cell.

Another factor to affect electromotive force is a strange phenomenon. This phenomenon was also found in the fabrication of M-S diodes [14]. That is, when the dull side of the polyacetylene film contacts with the graphite layer, the cell gives a normal elctromotive force. However, the cell will give an abnormal electromotive force ranging from 300 to 500mV when the shiny side contacts with the graphite layer. But this phenomenon only exists when the cells are composed of one piece of film, it does not occur when the cells are fabricated with double or more films.

Characteristics of V vs. I of both types of cells are shown in Fig.5. The cells are allowed to discharge on loads of various resistances . Then the potential V and current I are measured immediately before any

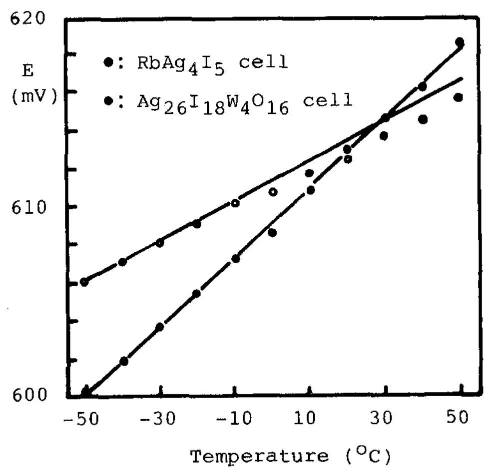

Fig. 4. Temperature dependence of the electromotive force.

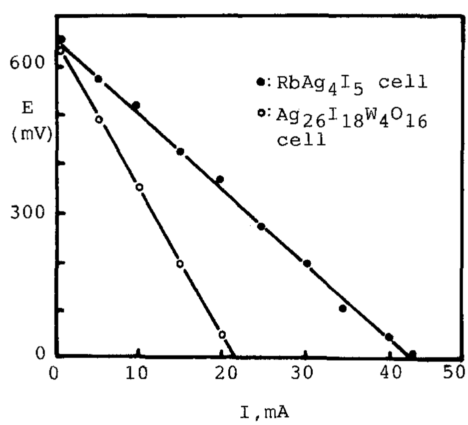

Fig. 5. Galvanostatic measurement of the voltage of both kinds of solid-state batteries.

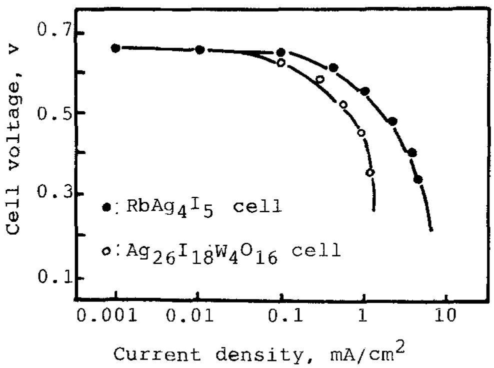

Fig. 6. V-I characteristics of both kinds of solid-state batteries.

polarization occurs. Figure 5 shows that the short-circuit flash currents of $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$ cells are about 25mA/cm^2 and 12mA/cm^2, respectively. The internal resistances derived from Fig.5 are in the ranges of 10-20 ohms for $RbAg_4I_5$ cell and 20-40 ohms for $Ag_{26}I_{18}W_4O_{16}$ cell. The internal resistance of $RbAg_4I_5$ cell is expected to be smaller because of its higher conductivity. Nevertheless, the summation of the separate resistances of the individual layers in both cells gives a much lower value. For example, the electrolyte disk in Fig.1 whose area and thickness are 1.76cm^2 and 0.05cm, respectively, contributes resistance for less than 1 ohm. The conductivities of other layers in cells are larger than that of the electrolyte layer, so they should contribute smaller resistances. From the discussion above, we can suggest that the cell resistances are mainly due to the interfacial resistances.

The degree of polarization of the batteries can be estimated from the voltage-current characteristics, as shown in Fig.6. The voltage plateau extends from low current density to a higher value, and then polarizations begin to be appreciable. The tendency is similar for both $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$ cells, while the polarization is more serious in $Ag_{26}I_{18}W_4O_{16}$ cell at high current density region, this may be due to its larger internal resistance.

Constant current discharge measurements are carried out at 30°C and

Table 1. The performance of $RbAg_4I_5$ cell under various discharge conditions.

Parameters	Discharge conditions			
	65uA		300uA	
	30°C	50°C	30°C	50°C
Iodine concentration in $(CH)_x$ films, %	20.0	21.1	21.9	22.9
Cell capacity, mA·hr	2.55	2.62	2.76	2.80
Discharge capacity, mA·hr (cutoff voltage=0.2V)	2.06	2.30	2.03	2.27
Coulombic efficiency, %	80.8	87.8	73.7	81.5

Table 2. The performance of $Ag_{26}I_{18}W_4O_{18}$ cell under various discharge conditions.

Parameters	Discharge conditions			
	65uA		300uA	
	25°C	50°C	25°C	50°C
Iodine concentration in $(CH)_x$ films, %	21.8	21.6	23.8	21.0
Cell capacity, mA·hr	2.70	2.72	2.84	2.72
Discharge capacity, mA·hr (cutoff voltage=0.2V)	2.01	2.14	1.86	2.07
Comlombic efficiency, %	74.6	78.8	65.5	76.1

50°C for $RbAg_4I_5$ cells and at 25°C and 50°C for $Ag_{26}I_{18}W_4O_{16}$ cells respectively, with two different discharge currents of 65uA and 300uA. The results are summarized in Table 1 for $RbAg_4I_5$ cells and Table 2 for $Ag_{26}I_{18}W_4O_{16}$ cells. In each case, there is a voltage drop, followed by a voltage plateau that extends out to about 60-80% of discharge capacity, and then additional polarization begins to affect the performances. The discharge performance of $RbAg_4I_5$ cell is better than that of $Ag_{26}I_{18}W_4O_{16}$ cell. It may result from the larger conductivity of $RbAg_4I_5$ electrolyte. In each cell, the discharge capacity decreases as temperature goes down. This may be due to the lowering in the ionic conductivity of both kinds of electrolytes. As shown in Table 1, the coulombic efficiency of $RbAg_4I_5$ batteries under 65uA discharge current can attain 80.8% at 30°C, and even up to 87.8% at 50°C. From Table 2, the coulombic efficiency of $Ag_{26}I_{18}W_4O_{16}$ batteries under the same conditions can attain 74.6% at room temperature and 78.8% at 50°C. The total energy density accounting the total weight of cell is as below as 1 W-h/Kg, however, it will amount to as high as 60-70 W-h/Kg based on the weight of $(CHI_y)_x$ electrode for both types of cells.

In order to examine whether the polyacetylene solid-state batteries can be used as rechargeable batteries or not, the following experiment was made. The cell of each type was discharged at constant current of 300uA to 0.2V. Following this initial discharge, the cell was charged at an applied constant current 0.5mA for five hours (i.e. 2.5mA·hr capacity) and then discharged again at 300uA constant current to 0.3V. This discharge performance is shown as curve 1 in Fig.7 for $RgAg_4I_5$ cell. The charge-discharge cycles were carried on, and resultant discharge performances are shown in curves 2 and 3. The charge-discharge performance of $Ag_{26}I_{18}W_4O_{16}$ cell is similar to that of $RbAg_4I_5$ cell. The recharge efficiencies are considerably high initially, and amount to about 70-75% for both $RbAg_4I_5$ and $Ag_{26}I_{18}W_4O_{16}$ cells. This is an interesting result since the cells after discharge may be stored for any desired length of time, and activated just before use. The shelf life of "polyacetylene solid-state battery" should therefore be prolonged considerably. Although both types of batteries have good performances and high coulombic efficiencies in rechargeability,

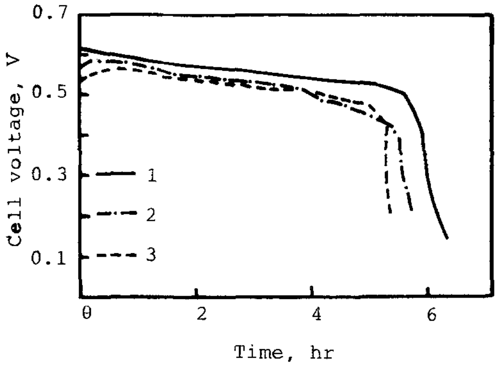

Fig. 7. Rechargeability of $RbAg_4I_5$ cell at 300uA discharge and 500uA charge currents (30°C).

after several recharging cycles, the following discharges became unsatisfactory, then the cell performances deteriorated. However, it seems that $Ag_{26}I_{18}W_4O_{16}$ cell exhibits more charge-discharge cycles than that of $RbAg_4I_5$ cell, which may be due to the less stability of $RbAg_4I_5$ in iodine atmosphere as time elapsed during the test. After a few charge and discharge cycles, both cells were decomposed for examination. Inspection of materials showed that the deposition of silver in dendritic form on the negative electrode surfaces occurred. Scrosati and Butherus [15] have shown that planar silver electrodes behave reversibly at low-current levels. When a considerable amount of charge is passed through the cell, however, the dendritic deposition of silver occurs at the negative electrode. This evidence indicates that the charging process preferably should be carried out at low current densities for the best efficiency and performance.

Conclusions

In conclusion, we have shown that polyacetylene films can be used as the electrode material in solid-state batteries working at room temperature. For comparison, the $RbAg_4I_5$ cell has better performances than the $Ag_{26}I_{18}W_4O_{16}$ cell. This is due to the larger conductivity of $RbAg_4I_5$ itself and less polarization of cell during charge-discharge cycle. However, the $Ag_{26}I_{18}W_4O_{16}$ cell may exhibit much longer storage period than that of $RbAg_4I_5$ cell because of the better stability of $Ag_{26}I_{18}W_4O_{16}$ in iodine atmosphere.

In order to improve the performance of polyacetylene solid-state battery, polarization between electrodes and solid electrolytes must be reduced to a minimum, which will increase the current and energy densities. Some technology must be employed to ensure good contacts between electrodes and electrolytes.

References

1. P. J. Nigrey, D. Maclnnes, Jr., D. P. Nairns, A. G. MacDiarmid and A. J. Heeger, J. Electrochem. Soc., Electrochem. Sci & Technol., 128, 1651 (1981).
2. C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis and A. G. MacDiarmid, J. Chem. Phys., 69, 5098 (1978).
3. K. Kaneto, M. Maxfield, D. P. Nairns, A. G. MacDiarmid and A. J. Heeger, J. Chem. Soc., Faraday Trans. I, 78, 3417 (1982).
4. C. K. Chiang, Polym. Commun., 22, 1454 (1981).
5. F. Beniere, D. Boils, H. Canepa, J. Franco, A. Le Corre and J P. Louboutin, J. Electrochem. Soc., 132(9), 2100 (1984).

6. T. Nagatomo, C. Ichikawa and O. Omoto, J. Electrochem. Soc., 134(2), 305 (1987).
7. S. Geller, Phys. Rev. B, 14, 4345 (1976).
8. L. Y. Y. Chan and S. Geller, J. Solid State Chem., 21, 331 (1977).
9. T. Ito, H. Shirakawa and S. Ikeda, J. Polym. Chem. Ed., 12, 11 (1974).
10. T. Takahashi and O. Yamamoto, Electrochimica Acta, 11, 779 (1966).
11. J. B. Wagner and C. Wagner, J. Chem. Phys., 26, 1597 (1957).
12. T. Takahashi, O. Yamamoto and K. Kuwabara, presented at the 17th meeting of C. I. T. C. E. , Tokyo, Sept. (1966).
13. B. B. Owens, J. S. Sprouse and D. L. Warburton, in "proceeding of the 25th Power Sources Conference", Atlantic City, NJ, May 23-25, (1972), p.8.
14. J. Tsukamoto, H. Ohigashi, K. Matsumura and A. Takahashi, Synth. Met., 4, 177 (1982).
15. R. J. Brook, W. L. Pelzman and F. A. Kroger, J. Electrochem. Soc., 118, 185 (1971).

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