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SOLID STATE BATTERIES WITH CONDUCTING POLYMERS

F. Bénière, D. Boils, H. Cánepa, J. Franco, A. Le Corre and J.P. Louboutin

Science des Matériaux, Université de Rennes I, 35042 Rennes, France

Résumé - Les polymères conducteurs comme (CH)x sont très intéressants comme matériaux d'électrodes dans des cellules électrochimiques. Nous avons combiné de telles électrodes avec des électrolytes solides pour fabriquer des piles "tout solide". Les premiers prototypes utilisant une anode d'argent et un électrolyte solide à conduction Ag+ fonctionnent de façon satisfaisante depuis deux ans. Les performances ont été testées sur de nombreuses cellules pour étudier les propriétés électriques ainsi que les paramètres thermodynamiques. Un grand nombre de cycles charge-décharge ont été enregistrés à diverses valeurs de courant maintenu constant. Ceci a permis de déterminer les propriétés essentielles : tension, courant, densité de courant, fiabilité, rendement faradique, rendement énergétique, etc. Les performances ont été également étudiées en fonction de la température, permettant d'obtenir l'enthalpie et l'entropie de la réaction électrochimique. La cinétique de la décharge a été soigneusement mesurée et comparée aux données de diffusion récemment obtenues dans notre laboratoire à l'aide d'isotopes radioactifs. Ceci a donné une explication claire du mécanisme de transport atomique dans le polymère.

<u>Abstract</u> - The conducting polymers like $(CH)_x$ are very interesting materials for electrodes in electrochemical cells. We have combined such electrodes with solid electrolytes to build "all solid-state" batteries. The first prototypes using a silver anode and a silver conducting electrolyte have been working satisfactorily since two years. The performances have been tested with many batteries to study the electrical properties as well as the thermodynamical parameters. A number of cycles of charge-discharge have been recorded at various values of the current kept constant. This has allowed to determine the essential properties : voltage, current, current density, reliability, Faradaic and energetic efficiency... The performances have also been investigated as a function of temperature, allowing to derive the enthalpy and the entropy of the electrochemical reaction. The kinetics of the discharge has been thoroughfully measured and compared to the mass transport data recently obtained in our laboratory by using radiotracers. This has given a clear explanation of the mechanism of mass transport inside the polymer.

I - INTRODUCTION.

Soon after it was discovered by SHIRAKAWA et al. [l] in the U.S.A. that a polymer, namely (CH)_X — initially highly insulating like most plastics — can acquire a surprisingly high electronic conductivity by a simple process, applications were found first in U.S.A. [2], France [3] and Japan [4]. As a matter of fact, polyacetylene doped by suitable donor or acceptor impurities exhibits the two essential properties of a good electrode :

- high electrical conductivity (up to 10³ Ω^{-1} .cm⁻¹) without graphite additive ;

- high capacity of storing the impurities (up to 30 % in mole fraction) which can be easily restituted and become the active material in an electrochemical reaction.

Whereas MAC DIARMID's polyacetylene battery [5] utilizes a liquid electrolyte (especially Li C& 04 in propylene carbonate) our own cells are entirely solid, which means that the electrolyte also is a solid. Among the relatively large number of combinations electrode/electrolyte our oldest battery works on the following principle :

Ag / Rb Ag₄ I₅ /
$$(CHI_V)_x$$

the design of which is schematically shown on Fig. 1 :



Fig. 1 - Solid-state Ag/I₂ polyacetylene battery.

II - THERMODYNAMICS.

In order to investigate separately the influence of the different components, the following cells have been studied :

Pt / Ta / Ag / Ag I /
$$(CHI_y)_x$$
 / Pt
Pt / Ta / Ag / $(CHI_y)_x$ / Pt

This last cell differs from the first one, only by the absence of any initial Ag I. However a thin film of Ag I spontaneously covers the silver anode because of the chemical attraction and grows as electrical power is supplied from the battery. Then, the next cells have been considered :

Pt / Ta / Ag / Rb Ag₄ I₅ /
$$(CHI_y)_x$$
 / Pt
C / Ag / Rb Ag₄ I₅ / $(CHI_y)_x$ / C

The electromotive force E (or open circuit voltage) has been registered versus time (Fig. 2) with a high impedance voltmeter at a number of temperatures ranging from -30 °C to +30 °C (at the atmospheric pressure). The linear dependence E = f(T) on figure 2 refers to the composition y = 0.07. The e.m.f. increases with increasing y according to a logarithmic law without more than one obvious plateau. Though this behavior doest not support the assumption of intercalation with successive and well defined stages [6].

The same values are obtained with the two electrolytes Ag I and Rb Ag₄ I₅ as it must be, which encourages the use of the superconducting ionic Rb Ag₄ I₅ for a smaller internal resistance and therefore higher current density. From our results and the chemical constants of Ag I (standard enthalpy of formation = -14.91 Kcal.mole⁻¹ and standard entropy = 3.14 cal.mole⁻¹.K⁻¹) we may estimate the entropy and enthalpy of the reaction :

$$\frac{1}{2} I_2 + \frac{1}{xy} (CH)_x \longrightarrow \frac{1}{xy} (CHI_y)_x$$
(I)

 $\Delta S = -0.8 \text{ cal.mole}^{-1}$. K⁻¹ and $\Delta H \sim -1 \text{ Kcal.mole}^{-1}$. This surprisingly small ΔH shows a weak interaction between iodine and the polymer chain.



Fig. 2 - Temperature dependence of the Electromotive force of the Ag/I₂ battery with $(CHI_{0.07})_X$.

III - KINETICS.

a. Absorption and desorption.

An essential quality for an electrode is its capability to store a large amount of active material. This condition is well fulfilled for polyacetylene which is able to store as much as 30% in mole fraction [7] of acceptor impurities (e.g. iodine) as well as donor impurities (e.g. sodium). However, it is also essential that the active material can rapidly be exchanged at the electrode interface in order to prevent a significant concentration overvoltage. We have measured [8] the rate of absorption and the rate of desorption of the active material of the cathode polyacetylene/iodine. This is based on the measurement as a function of time of the radioactivity of the polyacetylene cathode immersed in a solution of labelled iodine in pentane (Fig. 3). In



Fig. 3 - Absorption and desorption of iodine in and out from a polyacetylene film immersed in a pentane solution of radioactive iodine.

addition, to get a better understanding of the diffusion mechanisms at the microscopic level, the distribution of radioactive iodine has been measured after a given diffusion time [9]. For that purpose, the sample is sliced into parallel sections of one micron thickness with a microtome. A number of distribution profiles have been obtained for several concentrations in the temperature range -60 + 20 °C. The penetration mechanism has been elucidated and the diffusion coefficients determined : 10^{-5} and 10^{-17} for the inter- and intra-fibril diffusion coefficients and 10^{-9} for the overall process [10]. In addition, the kinetics of reaction (I) was also obtained in the same experiment. Reaction (I) is only slightly thermally activated with the activation enthalpy $\Delta H_1 = 2 \text{ Kcal.mole}^{-1}$.

b. Kinetics of current discharge.

Consider a cell initially charged at the mole fraction y. When it is short-circuited, the whole stored electricity is delivered in a few minutes only (Fig. 4). Because



Fig. 5 - Short-circuit current of a battery containing 10 mg of (CH)_X and the respective mole fractions y of iodine : ∆:0.014, V:0.03, ■:0.047, •:0.067, as a function of t^{-1/2}.

of the high ionic conductivity of the solid electrolyte, the rate of discharge of the present battery is expected to be controled by the motion of the iodine from the cathode to the cathode/electrolyte interface. In such a case, the time dependence on the current density i should obey the equation :

$$i = \frac{FC}{\sqrt{\pi t}} \frac{\sqrt{D}}{y}$$
(II)

where F is the Faraday, C the concentration of polyacetylene (in mole of CH per unit volume), t the time and D the diffusion coefficient. The experimental results like those of Fig. 4 for a given y are plotted as a function of $t^{-1/2}$ on Fig. 5. The simple theoretical equation (II) is well satisfied : one observes a linear dependence of i-vs-t^{-1/2}. Furthermore, the same data are represented as $(\Delta i / \Delta t^{-1/2})$ -vs-y on Fig.6.



One observes a new straight line passing through the origin also in accordance with equation (II). From the slope of this line, one derives the value $D = 1.5 \times 10^{-9}$ cm². sec⁻¹ in good agreement with the tracer data [8,10]. One can therefore conclude that the rate at which electricity is supplied from our Ag/I₂ battery is controled by the diffusion of iodine. However, the present results do not eliminate the possibility that some part of the iodine also diffuses through the RbAg₄ I₅ electrolyte, according to a diffusion process which would be characterized by a smaller diffusion coefficient. Such a diffusion, even small, would have the baneful effect of self-discharging the cell. Up to now, it has not been possible to keep the stored energy over a few months. The different causes of self-discharge, including diffusion of iodine molecules through the electrolyte, are being investigated.

III - PERFORMANCES.

The Ag/I₂ polyacetylene solid state battery shows the following characteristics :

- operational at room temperature,
- waterproof,
- shock-resistant,
- extended lasting, probably over ten years in its discharged state,
- many possible recharges,
- current density up to 50 mA.cm⁻²,
- voltage of 0.65 V. Our standard sets combine three elements to get a voltage of 2V,
- internal resistance : 10 Ω ,
- energy density : 10 Wh.kg⁻¹,
- best field of applications : supply of electronic devices or liquid crystal displays utilizing electric currents in the range 1-100 VA,
- best quality : can be prepared in the discharged state and then stored for many years with no damage.

IV - CONCLUSIONS.

In this short description of our Ag/I_2 polyacetylene battery, we have been faced to both fundamental and applied aspects.

The applied aspects concern the feasibility of a solid-state battery using polyacetylene, which possesses the interesting properties briefly summarized in section III. In addition, the Ag/I_2 battery work has also been very useful to the comprehension of the polyacetylene cathode, the same that we are now also successfully using in our Na/I₂ polyacetylene battery.

The fundamental part concerns the results that we have obtained when trying to understand the working mechanisms of the battery. Those results fall into two categories :

- thermodynamical properties : enthalpy and entropy of association polyacetyleneiodine. The present study has shown that there is a chemical reaction polyacetylene+iodine characterized by a very small energy of attraction. This study is to be combined with the structural investigations : X-ray [11], N.M.R. [12], E.P.R. [13], I.R. [14], Raman [15], etc...;
- kinetical properties : We have also measured the kinetical parameters of the reaction of association. Another kinetical aspect essential for the operative conditions of the battery concerns the motion of iodine through polyacetylene. The present study has shown the nature of the mechanisms and the diffusion constants, by using the radiotracer techniques and the electrochemical methods.

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