

Multilayer thin-film batteries with poly(vinyl alcohol)

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Abstract

Poly(vinyl alcohol) is considered as a potential material in thin-layer 'all solid' batteries. By adding an appropriate doping agent, intrinsic ionic conduction is observed leading to its use as a solid electrolyte in zinc/halogen and zinc/metal oxide batteries. The association of zinc metal powder and conjugated salt in poly(vinyl alcohol) leads to a composite anode which acts as a proton generator or protode when the system is a proton conductor.

Introduction

Electrically conductive materials have been the subject of intense interest in the last decade. Plastic ionic conductors have the advantage of combining the typical properties of polymers (good mechanical parameters, easy processing, low volatility and specific gravity) and the conductivity performance required for electrolytes.

Attractive and potentially useful polymers with π -conjugated bonds such as poly(acetylene) [1], poly(*p*-phenylene) [2], polypyrrole [3–6], polyfuran [6–9] have been used as electronic conductors and host networks. Other polymers such as poly(ethylene oxide) (PEO) [10–13], polyvinylidene [14] and poly(vinyl acetate) [15] have been proposed as potentially useful solid ionic conductors. Most promising polymer electrolytes seem to be polyethers and particularly poly(ethylene oxide) which acts as a real solvent by its ability to complex alkali metal salts as demonstrated by Fenton *et al.* [16]. Polymeric membranes of PEO doped with LiClO_4 have been extensively studied by Armand *et al.* [11] and by Chiodolli and coworkers [12, 13] in lithium systems. A new class of conducting polymers was introduced using poly(ethylene imine) and poly(acrylamide) associated with HSO_3 [17] or the ormolyte and amminosil group [18, 19]. The good physical properties of plastics lead to a new generation of systems and devices as sensors, electrochromic displays and batteries. With regard to the battery technology, numerous polymers have been studied as potential electrode materials:

- (i) polypyrrole in a zinc/bromine battery with a liquid electrolyte [20, 21];
- (ii) nylon 6,6-poly(acrylonitrile) and poly(vinyl chloride) in a zinc/iodine battery with a liquid electrolyte [22];
- (iii) poly(vinyl acetate) and poly(ethylene oxide), respectively, as cathodic additive and electrolyte in a lithium solid battery using TiS_2 and MoS_2 as host materials [23], and

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(iv) more recently, poly(vinyl alcohol) (PVA) has been used as substrate and binding agent in a polymetallic hydride negative electrode [24].

PVA doped with H_3PO_4 shows a conductivity around $10^{-5} \Omega^{-1} \text{cm}^{-1}$ at room temperature as determined by Polack *et al.* [25] in its use as a hydrogen sensor. Masao [26] used a plastic plate coated with PVA to prepare an ion-sensitive field-effect transistor (ISFET) for pH and glucose detection. Zhang *et al.* [27] used a cross-linked PVA as substrate for immobilizing an indicator in optic fibre chemical sensors. In this case the conduction seems to be induced by adding HCl to an aqueous solution of PVA.

The aim of the present work is to examine the use of PVA as a potential solid electrolyte in 'all solid' batteries in association with its role as binding agent in the electrodes of zinc/halogen and zinc/metal oxide batteries. Zinc/halogen batteries have been extensively studied with liquid electrolytes [20–22, 28, 29], but the liquid electrolyte presents some inconveniences due to leakage, evaporation and dissolution of halides from the electrodes. These problems can be reduced by solid configurations.

Several publications describe the solid-conducting protonic batteries in combination with various solid electrolytes [30–32]. The best results were obtained with uranyl phosphate acid (HUP). But the application is limited by dehydration of HUP at low temperatures (less than 40 °C). Polymer membranes with PVA are less temperature sensitive in a broad temperature range and seem to be an attractive alternative.

Experimental

Polymer films are prepared by dissolving PVA (mol. wt. = 75 000) in de-ionized water and adding in various ratio of $n:1$ of PVA repeat unit to appropriate doping. The solution is placed in an evaporation dish for several days at room temperature. For electrolyte use, PVA was mixed with formic acid. The classical method with two blocking electrodes is used to determine the conductivity of films with the a.c. impedance spectroscopy between 100 kHz and 0.1 Hz.

Battery preparation

The positive electrode for the iodine battery is prepared by mixing iodine and potassium iodide (Merck), PVA (Merck), and black acetylene (SN2A, France) in hot de-ionized water. The evaporation of water at room temperature after a few days leads to a deposition of a black composite material. Positive electrodes for protonic batteries are prepared by the dry mix of $\gamma\text{-MnO}_2$ (WSZ, Sedema, Belgium) and black acetylene (SN2A, France) or PbO_2 removed from lead/acid batteries (X-ray analysis shows a mixed of crystallographic phases α and β) and graphite (Lonza, Switzerland) in a first step. This dry mix is then added to PVA and H_3PO_4 in hot de-ionized water. After evaporation of water, a transparent polymer matrix with incorporated black or brown grains was shown by microscopic examination.

The negative electrode for zinc/iodine batteries was prepared by mixing zinc powder (150 μm) with zinc iodide. Black acetylene (as above) is added in a ratio of 1:3 parts of zinc–zinc salt mix. This composite mix is added, with PVA and tetrabutylammonium iodide, to hot de-ionized water. Evaporation leads to a film containing a mineral matrix. The negative electrode for protonic batteries was prepared in the same way as above replacing zinc iodide by the appropriate zinc salt. The configuration is similar to the anode developed in previous work [33] according to Guittou's configuration [30]. The polymer film is also doped with a mix of phosphoric acid and

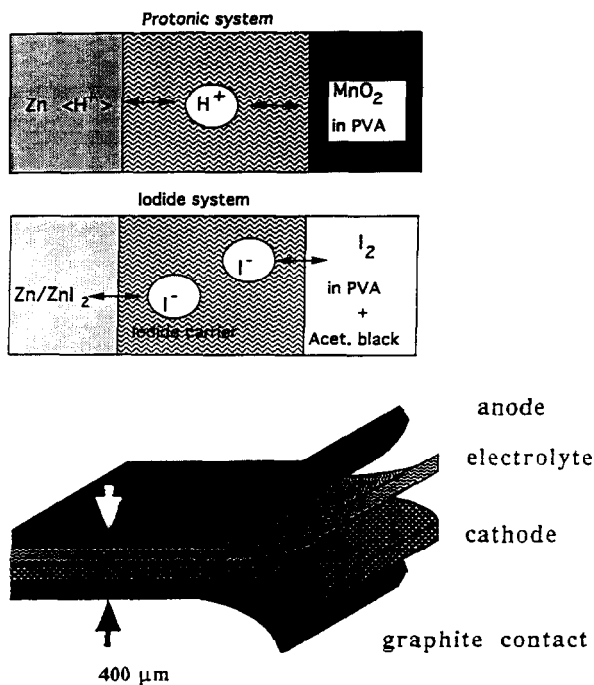


Fig. 1. Electrochemical chain used as thin-film configuration and profil of the multilayered thin-film battery (kindly provided by Dr Armand).

zinc phosphate in order to realize a 'proton-generating anode' configuration or 'protode' as we recently proposed [34].

For each type of battery, the three films are pressed together between two graphite-poly(ethylene) discs leading to a thin-layer configuration as shown in Fig. 1. Charge/discharge curves were carried out under constant current; the voltage of the cell, step-by-step, was recorded versus time.

Results and discussion

Conductivity of doped PVA

It is well known that in ionic conducting polymers no unipolar conduction is observed. By the solvating effect of these polymers, both ions of a the salt move [12, 13]. So, with an appropriate doping agent, PVA can exhibit protonic conduction (as observed by Polack *et al.* [25]) or anionic conduction. Impedance spectra of PVA doped with HCl, H₂SO₄, H₃PO₄, HI, N(C₄H₉)₄I were carried out between 100 kHz and 5 Hz under 5 mV of a.c. voltage. The electrical conductivity was calculated with the intersection of the semi-circle with the real contribution of the impedance. All the specimens gave the same shape of Nyquist plot as reported in Fig. 2. The films obtained exhibited different conductivities according to the doping agent as reported in Table 1. The H₂SO₄-doped polymer became black after evaporation of the solvent. This is probably due to a dehydration of PVA leading to poly(acetylene) (CH)_n, also observed when this sample is heated above 90 °C.

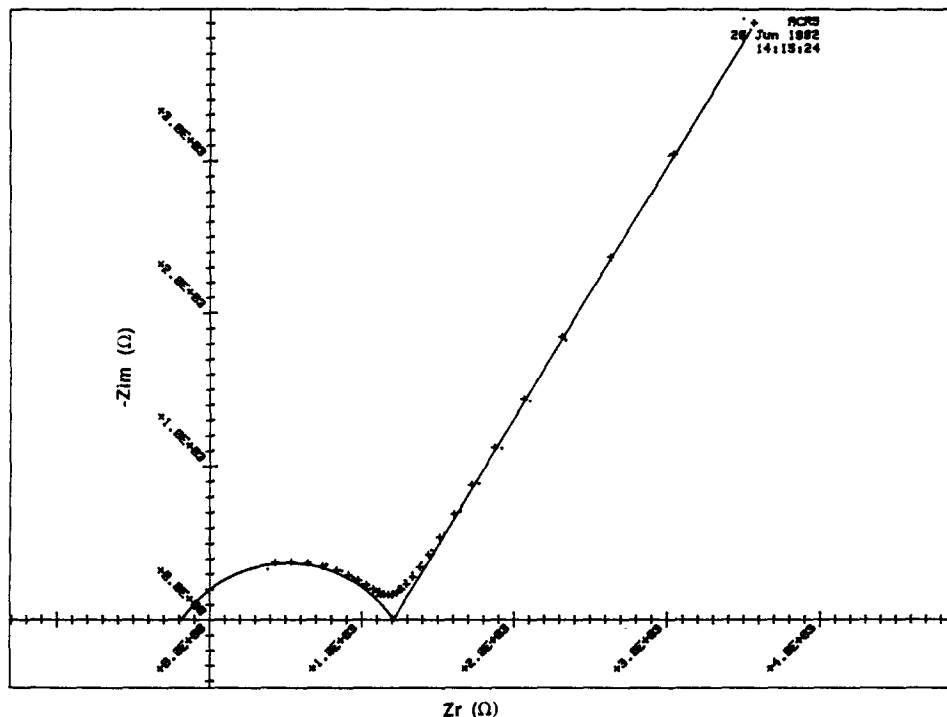


Fig. 2. Complex impedance plot explained as Nyquist representation.

TABLE 1

Conductivities of various films

Doping agent	Conductivity at room temperature ($\Omega^{-1} \text{ cm}^{-1}$) $\times 10^{-5}$	Observation on film
H ₃ PO ₄	3	Clear
HCl	0.5	Clear
H ₂ SO ₄	10	Black and degraded
HI	0.02	Dark after few days
Tetrabutylammonium iodide	0.016	Dark after few days

Infrared spectra of films obtained with various doping agents

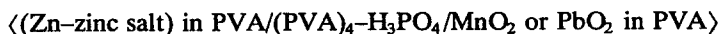
The typical bands of undoped polymers at 2940 and 600 cm^{-1} were present in the spectra of all doped polymers except those H₂SO₄-doped. This can be related as before, to a degradation of H₂SO₄-doped polymer where the HSO₄ band is also observed at 1200 cm^{-1} . The clear iodide-doped films change gradually in air to dark films. This suggests that iodide is oxidized in iodine since this change is not observed with other polymers.

Investigation of batteries

$(\text{PVA})_n\text{-H}_3\text{PO}_4$ and $(\text{PVA})_n\text{-N}(\text{C}_4\text{H}_9)_4\text{I}$ were used as solid electrolytes (where n in $(\text{PVA})_n$ represents the molar ratio between the molecular weights of PVA and the doping agent). Owing to the fact that polymers can act as storage media for halogen electrodes, as reported by Mengoli *et al.* [21], we have used a solid configuration with PVA as storage host for the iodine system:



In order to produce a protonic configuration identical to a lithium-conducting system constructed by Wintergall *et al.* [15] with MnO_2 and poly(vinyl acetate), a following cell was studied:



As the PVA is used both in the anode and the cathode, the cell resembles a lead/acid battery where the active PbO_2 and sponge lead are supported by a lead grid. The use of PVA both in the anode and cathode leads to acceptable mechanical performances of batteries (especially for assembling technology). The open voltage of the zinc/iodine battery reaches 1.32 V after 30 min while the open circuit of Zn/MnO_2 and Zn/PbO_2 increases quickly to 1.87 and 2.08 V, respectively. In Figs. 3 and 4, discharge/charge curves obtained with constant current at $20 \mu\text{A cm}^{-2}$ are reported. Acceptable performances were obtained both with PbO_2 (Fig. 4(a)) and MnO_2 (Fig. 4(b)). For the PbO_2 system, after the charge step, a higher open-circuit voltage than the last value when the discharge was stopped is observed. Since the rechargeability of PbO_2 is well known, this result indicated the ability of the zinc composite anode to be recharged*. The behaviour of PbO_2 in solid-state protonic electrolyte has been studied by Chelali [36], and identification of the discharge product of PbO_2 in protonic battery has been reported elsewhere [37].

In the first step of the MnO_2 reduction, the potential increases quickly to a value higher than the open-circuit voltage of the cell. At the end of charge, the potential

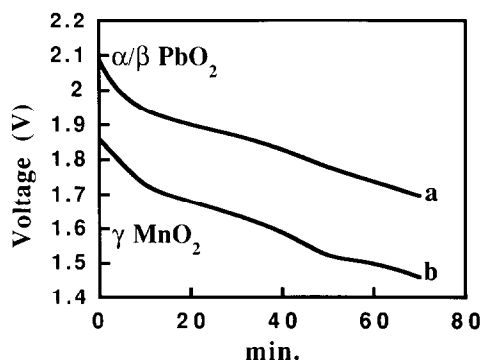


Fig. 3. Discharge curve of protonic chain under $20 \mu\text{A cm}^{-2}$: (a) $\alpha/\beta\text{-PbO}_2$ cathode, and (b) $\gamma\text{-MnO}_2$ cathode.

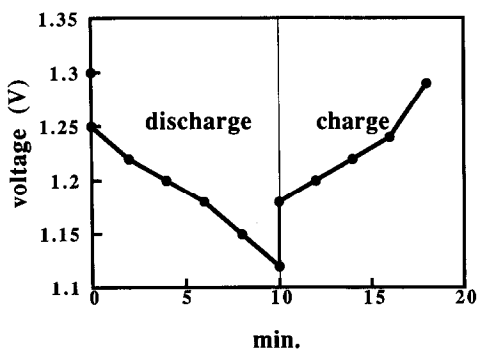


Fig. 4. Discharge curve of iodide chain under $20 \mu\text{A cm}^{-2}$; $\text{Zn}/\text{PVA}(\text{I}^-/\text{I}_2)$ cell.

*The responses of MnO_2 and PbO_2 electrodes were in agreement with previous observations on Zn/MnO_2 and Zn/PbO_2 cells with other protonic solid electrolyte [33–35] electrodes.

decreases quickly to a value less than that when the current is cut after a discharge (Fig. 3(a)). Reduction of MnO_2 takes place according to:



Although the rechargeability of MnO_2 electrode is recognized [33, 38] when the capacity drawn does not exceed one electron equivalent, no charging ability was observed in our experiment with this oxide. This can be attributed to a cathodic formulation and particularly the amount of carbon (in thin-layer technology, formulation must be calculated using a volumetric composition).

However, in all cases, the discharge curves look acceptable flat indicating that no considerable polarization concentration occurs when the active ions diffuse. No loss of electrolyte by evaporation being possible with the solid electrolyte, the open-circuit voltages of zinc dioxide systems are quite stable during storage at room temperature. We can also take account that degradation of the anode by corrosion is little. But the iodine system is air sensitive, which leads to a loss of capacity during storage.

Conclusions

The thin-layer concept introduced by Armand [11] for lithium systems using the attractive properties of conducting polymers leads to a very interesting way to manufacture all solid batteries. Deeper discharge can be drained from electroactive material than usually can be obtained from thick-film protonic systems. The principal advantage of avoiding evaporation and leakage of electrolyte, corrosion and degradation of electrodes (in classical liquid electrolytes) is complemented by the good mechanical properties of polymers. But the self-discharge of the iodine battery precludes application before introducing appropriate solutions for stabilization.

For the protonic cell, as PVA is thermally stable in higher temperature region than HUP, its protonic conductivity must be increased. This increase of ionic conduction can lead to a thin solid battery for special applications working in intermittent short sequences.

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