

# A novel solid state battery based on a polymer proton conductor: poly(propargyl alcohol) doped with perchloric acid

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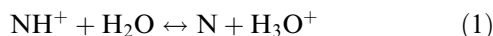
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A battery was constructed by including a polymer proton conductor, poly(propargyl alcohol) doped with perchloric acid, between electrodes of magnesium and gold. The characteristics of the cell, showing an open circuit voltage of 2.0–2.2 V, were studied as the function of the relative humidity. It was found that the system behaves as a fuel cell and that the discharge current of the battery is due to magnesium oxidation at the anode and proton reduction at the cathode.

## 1. Introduction

The importance of solid state batteries in everyday life and technology is demonstrated by the great number of recent papers in the literature. However, most of the contributions deal with lithium batteries, owing to their high power density, for example [1]. In this paper a solid state battery is described, based on the use of a polymer proton conductor.

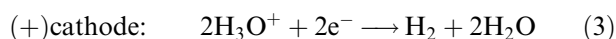
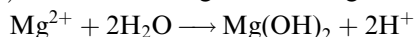
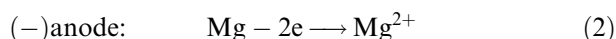
Previously, the charge transport mechanism was studied in proton conductors obtained by two different methods: that is, by acid-doping of polymers and by anodic oxidation of heterocyclic compounds. In particular, acid-doped poly(propargyl alcohol) [2] (Fig. 1(a)) for the first kind of material, and poly(thionaphtheneindole) [3], pTNI (Fig. 1(b)) for the second kind of material were investigated in the form of pressed powder pellets. In both cases the proton motion was found to be water assisted. A hypothesis was proposed by which water increases the dielectric constant, and therefore decreases ionic interaction in a thin layer of acid solution adherent to the solid polymer grains [2]. Proton mobility in these materials was then considered a surface process. In the case of pTNI, water [3] also promotes the equilibrium:



where  $\text{NH}^+$  is the protonated (Fig. 1(b)) and N the nonprotonated (Fig. 1(c)) form of pTNI. The equilibrium of Reaction 1 is responsible for proton conduction in pTNI which shows a behaviour very similar to that of acid-doped polymers.

Solid state batteries, assembled by including a pressed pellet of pTNI between two electrodes, one of

gold and another of zinc or magnesium, with open-circuit voltages of 0.9 and 2.1 V, respectively, were previously investigated [4]. The overall electrode reactions, using magnesium as negative pole, are



The battery can supply energy only when, after cell assembly, a white thin film of oxidized magnesium, acting as electronic insulator and ionic conductor, is formed, adherent to the magnesium electrode. The formation of this film, observed previously by impedance spectroscopy [4], reaches its maximum thickness 72 h after the cell assembly. The function of pTNI is that of proton source, water adsorbing agent and proton conducting spacer between the oxidized magnesium film and the gold electrode.

In this paper we report the properties of a battery obtained by substituting the acid-doped poly(propargyl alcohol) by pTNI as proton conductor between gold and magnesium electrodes. The possibility of constructing solid state batteries by assembling wafers in the form 'metal | proton conductor | gold' is discussed.

## 2. Experimental details

Poly(propargyl alcohol) (POHP) was prepared according to the method previously described [5]. Doping with  $\text{H}_2\text{SO}_4$  was carried out by immersion of POHP powder in a 1.64 M solution of acid in tetrahydrofuran (THF) for 4 h. Different doping levels were attained with  $\text{HClO}_4$  by immersion of POHP powder in THF acid solutions for 4 h, with  $\text{HClO}_4$

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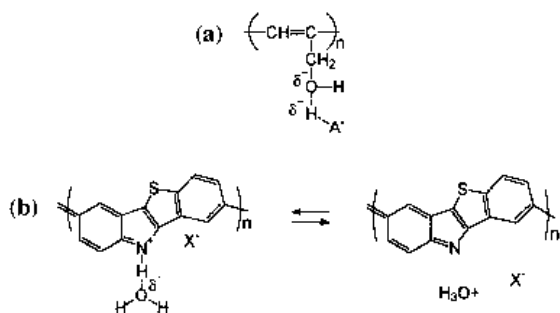


Fig. 1. (a) Acid doped poly(propargyl alcohol), (b) protonated form and (c) nonprotonated of poly(thionaphtheneindole). The protonated and nonprotonated form of poly(thionaphtheneindole) are involved in acid-base equilibrium with the water adsorbed by the polymer.

concentrations ranging between 0.375 to 1.66 M. The doping level was measured by the weight difference between the doped and non doped polymer. The acid-doped polymer was pressed at  $10^9$  Pa in compact pellets of 5 mm diameter and about 2 mm thickness.

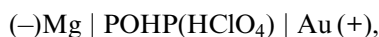
The battery was easily assembled by including the pellet between two disc electrodes having the same diameter as the polymer pellets, one of which being magnesium or zinc plate 1 mm thick and the other gold plate 0.8 mm thick. The electrical characteristics of this assembly, as a function of the per cent of relative humidity (RH%), were tested in a home made cell equipped with a commercial humidity sensor. Different relative humidities were obtained by bubbling dry argon in water. The impedance measurements were made by a Solartron 1255 FRA apparatus. The charge and discharge characteristics of the battery, at constant current, were carried out with an AMEL 545 galvanostat-electrometer connected to a computer through a Keithley 2000 multimeter.

All measurements were carried out at room temperature (22 °C).

### 3. Results and discussion

Pressed pellets of  $\text{H}_2\text{SO}_4$ -doped POHP, included between electrodes of gold and magnesium, give rise, in the presence of high relative humidity, to a battery which increases its open circuit voltage up to 2 V. However, this system is not able to supply energy at very low currents (nA).

Following the hypothesis that the difference between the performance of this system and of the corresponding battery based on pTNI is due to the kind of acid, POHP was doped with  $\text{HClO}_4$ , the same acid active in pTNI battery. The system:



gradually reaches a voltage of 2.0–2.2 V in about 1 h; during this time a white film of a nonidentified species of oxidized magnesium (probably magnesium hydroxide/magnesium perchlorate) is formed, adherent to the magnesium electrode. The formation time of the oxidized Mg film is, in this case, shorter than in pTNI-based cell; this is due to the higher acidity of

acid-doped POHP than that of oxidized pTNI. The cell is now able to supply current with characteristics, constant in the time, which depend on the doping level and on current density.

The electrical properties of systems based on pellets with different doping levels were studied as a function of percentage RH by charge–discharge and impedance measurements. The voltage of a battery during the discharge is given by

$$V_D = V_{\text{ocv}} - V_{\text{ct}} - V_d - iR \quad (4)$$

where  $V_D$  is the voltage of the battery during the discharge,  $V_{\text{ocv}}$  is the thermodynamic (open circuit) voltage,  $V_{\text{ct}}$  and  $V_d$  are the voltage drops due to the charge transfer and to the diffusion processes at the electrodes, respectively, and  $iR$  is the potential drop which arises from the impedance of the various components of the battery, mainly from the impedance of the doped polymer pellet.

Charge and discharge curves (at very small currents,  $5 \mu\text{A cm}^{-2}$ , to decrease the contribution of  $V_{\text{ct}}$  and  $V_d$ ) were recorded as a function of the percentage RH on batteries  $\text{Mg} \mid \text{POHP}(\text{HClO}_4) \mid \text{Au}$  obtained by using polymers with different doping levels. The results of some of these experiments are reported in Figs 2 and 3. In Fig. 4 the discharge voltage, at  $5 \mu\text{A cm}^{-2}$ , is reported as a function of relative humidity. The plot shows a sigmoidal-shaped trend, the same trend as that previously found for the proton conductivity of the doped polymer as a function of percentage RH [2]. It is also observed that the charge and discharge curves are symmetrical. Both charge and discharge curves, at high humidity values converge to a voltage 0.34 V higher (lower) than that of the open circuit voltage. This minimum voltage drop is due to diffusion processes at the electrodes.

The frequency response analysis of the battery gives Nyquist plots as shown in Fig. 5. The equivalent circuit of the battery is also depicted in Fig. 5, in accord with previous studies [6]: the semicircles inherent to the impedance of the polymer pellet at

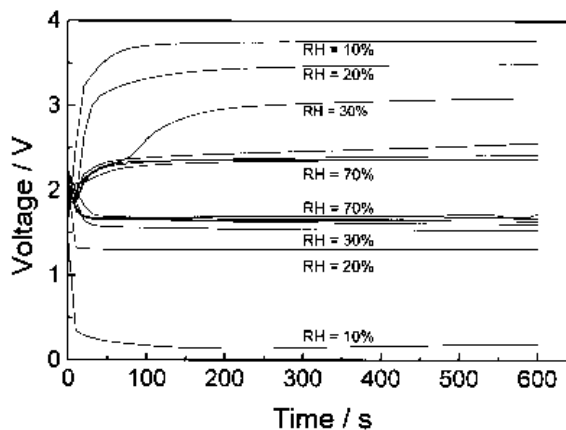


Fig. 2. Discharge and charge characteristics at  $5 \mu\text{A cm}^{-2}$  of a cell (see inset of Fig. 3) assembled by including a pressed pellet (1 mm thick) of perchloric acid-doped poly(propargyl alcohol) between gold and magnesium electrodes, of 0.5 cm diameter. Doping level of the polymer: 52% (weight of acid/weight of polymer) or 0.3 (acid molecules  $\times$  monomer unit).

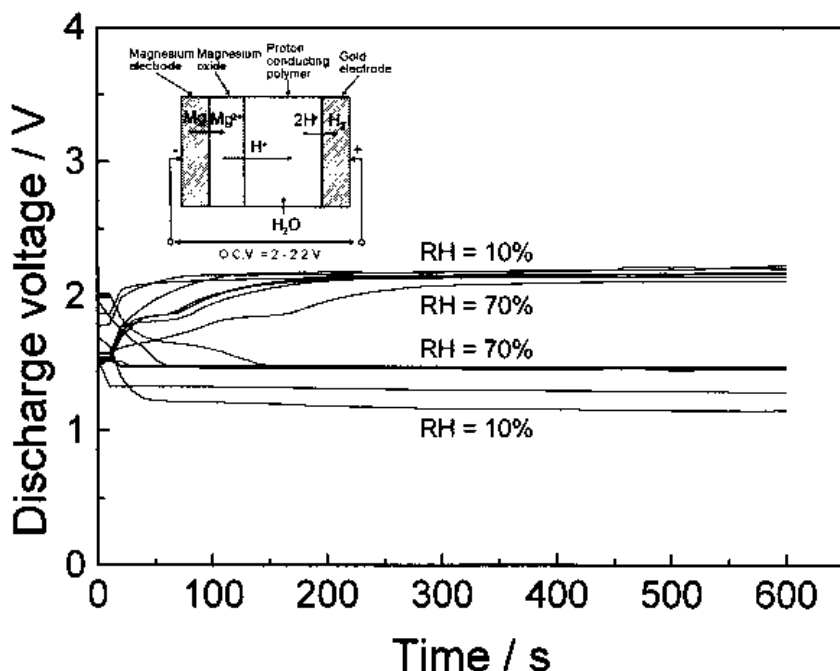


Fig. 3. Discharge and charge curves at  $5 \mu\text{A cm}^{-2}$  of a cell with the same characteristics as that of Fig. 2. In this experiment a polymer was used with a doping level of 89% (weight of acid/weight of polymer) or 0.5 (acid molecules  $\times$  monomer unit). Inset: scheme of the cell.

higher frequencies, strongly dependent on the percentage RH, and of the more resistive interface, at lower frequencies, are apparent. At the lowest frequencies, a straight line, probably Warburg impedance, is also evident. The reciprocal of the pellet resistivity, which is very similar to that found in a previous study [3] for the same acid-doped polymer, plotted in logarithmic scale as a function of percentage RH, gives a good straight line (Fig. 6). This is an indication that the change in the charge (discharge) potentials with percentage RH is due to a parallel variation of the impedance of the polymer pellet.

The above results can be explained in terms of Reactions 2 and 3 and the same function of the proton conductor previously hypothesized for the battery based on pTNI. One of the problems not yet solved, inherent to the complete understanding of the battery, is the nature of the oxidized magnesium; this compound, arising from the reaction of water and

acid contained in the polymer and magnesium electrode, forms a white film adherent to the magnesium after the battery assembly. The build-up of this layer, probably a good proton conductor and electron insulator owing to the complete absence of self discharge of the battery, is of utmost importance in the formation of the cell. It is probable that sulfuric acid and perchloric acid doped polymers lead to systems with different performances because different species of oxidized magnesium are formed in the two cases. Investigations in this direction are in progress.

The polymer proton conductor has several functions: it acts as proton sink, water adsorbing agent and proton-conducting spacer between the oxidized magnesium and the gold electrode.

The electrode reactions related to the battery charge are not completely understood. The anodic reaction is probably water oxidation, leading to  $\text{H}^+$  and oxygen production; at the cathode, proton re-

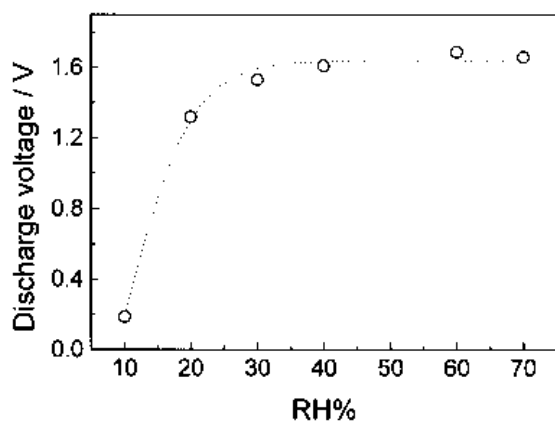


Fig. 4. Discharge voltage as a function of RH%, drawing from the experiment of Fig. 2.

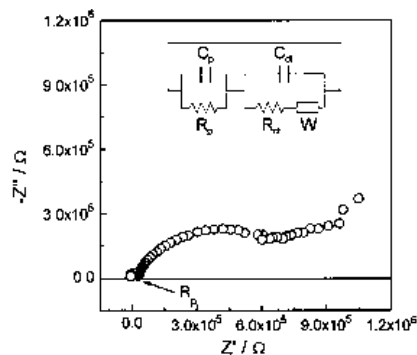


Fig. 5. Nyquist plot inherent to the cell of Fig 2 at RH = 10%; frequency range 0.1–500000 Hz, sinusoidal voltage: 10 mV, bias 0 V. Inset: equivalent circuit;  $R_p$  and  $C_p$  are the capacitance and the resistance of the polymer pellet,  $R_{ct}$  is the charge transfer resistance,  $C_{dl}$  the double layer capacitance and  $W$  the Warburg impedance.

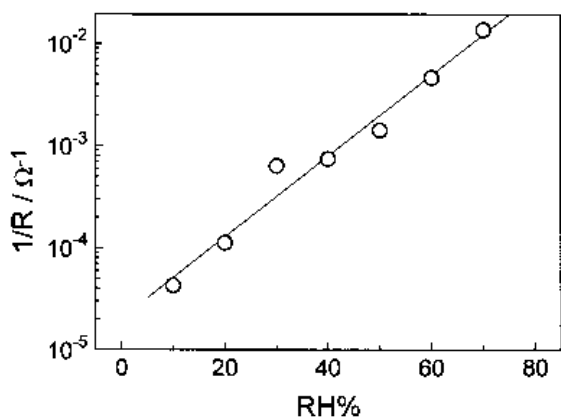
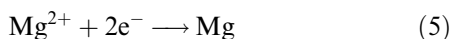


Fig. 6. Conductance in logarithmic scale as a function of RH% inherent to a perchloric acid-doped poly(propargyl alcohol) pellet; doping level of the polymer: 52% (weight of acid/weight of polymer) or 0.3 (acid molecules  $\times$  monomer unit). The resistance of the polymer pellet was obtained by the frequency response analysis.

duction or, alternatively, the reduction of magnesium leading to hydrogen gas evolution (Reactions 5 and 6) can occur, depending on the relative concentrations of water, acid and oxidized magnesium species.



The charge and discharge curves are symmetrical and this accords with the reversibility of the battery reactions. However, from the above considerations, it can be inferred that the working life of the battery depends on the Mg consumption and the assembly works as a fuel cell.

If the discharge curves of Fig. 2 are considered, it is evident that the battery is efficient only at high relative humidity. In Fig. 7 a discharge curve at 65% of RH at a constant current density of  $150 \mu\text{A cm}^{-2}$  is reported. The characteristics of the battery can be described as follows:

- (a) *Capacity*: The theoretical capacity is related, through Equation 2, to the weight of the mag-

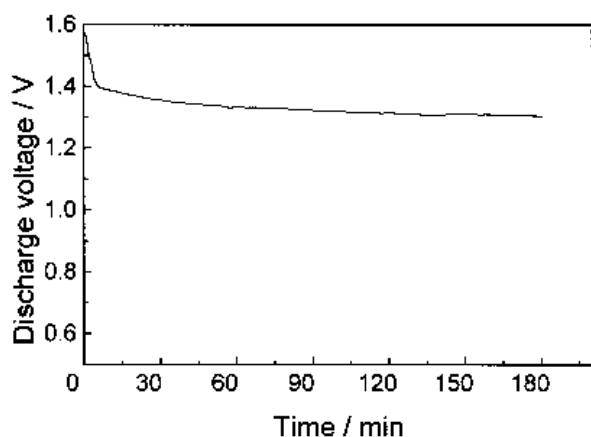


Fig. 7. Discharge curve at  $150 \mu\text{A cm}^{-2}$  of a cell assembled by including a pressed pellet (1 mm thick, 0.5 mm diameter) of perchloric acid-doped POHP between gold and magnesium electrodes, of 0.5 cm diameter. Doping level of the polymer: 89% (weight of acid/weight of polymer) or 0.5 (acid molecules  $\times$  monomer unit).

nesium electrode, which is the fuel. The real capacity was not tested. The same considerations are valid for the energy and energy density which are related to magnesium consumption. Moreover, most of the battery weight is due to the gold electrode (more than 90%) this can be reduced in a well-designed cell.

- (b) *Power*: In Fig. 8 the power-current density plots for two different percentage RHs are shown. At the higher percentage RH higher power and currents can be reached. At  $300 \mu\text{A cm}^{-2}$ , a stable voltage of 1.11 V was recorded at RH = 60%. If the weight of the gold electrode is not considered, high specific powers (up to  $180 \text{ W kg}^{-1}$ ) can be calculated. However, it is possible that, with a more appropriate assembly, the performances may be further improved.

As previously in the case of the cell based on pTNI as proton conductor, zinc was substituted for magnesium at the negative pole and an open circuit voltage of 1.15 V instead 2.1–2.2 V was reached; this is in accord with the difference in the redox potentials of the two metals, and further strengthens the hypothesized mechanism of the cell electrode reactions. By using Zn as a negative pole, the power is much lower (Fig. 9) than that obtained using a magnesium electrode.

The charge (discharge) characteristics of the battery as a function of humidity suggest the possibility of its utilization for humidity sensors. For this purpose the plot of Fig. 6 can be considered. It is evident that, in principle, it would be possible to assembly potentiometric sensors based on the battery '(-) Mg | POHP(HClO<sub>4</sub>) | Au (+)', or, more generally, on systems '(-) metal | proton conductor | Au (+)'. Preliminary results indicate that this is possible, but the response time as a potentiometric humidity sensor is not good (minutes). However, as the response time depends strongly on the geometrical layout of the sensor, it is possible that it can be further improved.

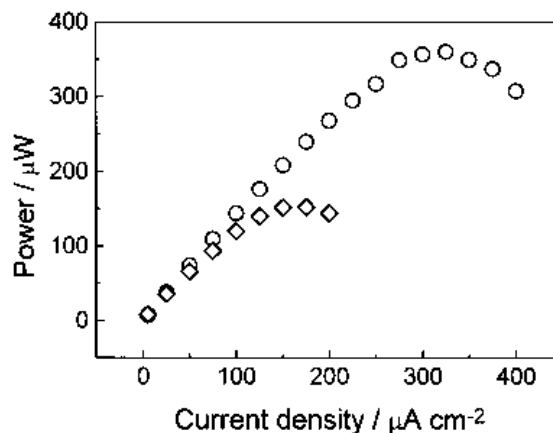


Fig. 8. Power as a function of the current density inherent to a cell assembled by including a pressed pellet (1 mm thick) of perchloric acid-doped POHP between gold and magnesium electrodes of 0.5 cm diameter. Doping level of the polymer: 89% (weight of acid/weight of polymer) or 0.5 (acid molecules  $\times$  monomer unit). Circles: cell kept at RH = 60%, squares: cell kept at RH = 50%.

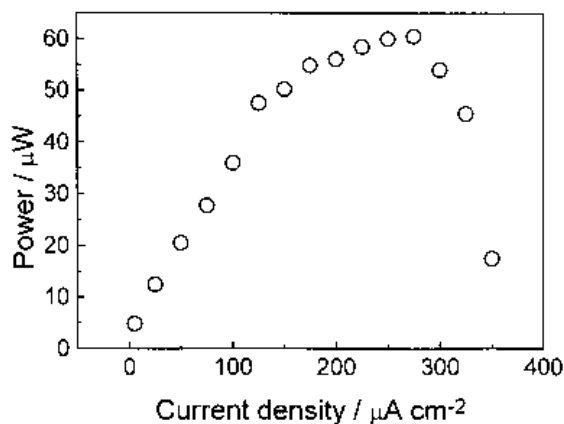


Fig. 9. Power as a function of the current density inherent to a cell assembled by including a pressed pellet (1 mm thick) of perchloric acid-doped POHP between gold and zinc electrodes of 0.5 cm diameter. Doping level of the polymer: 89% (weight of acid/weight of polymer) or 0.5 (acid molecules  $\times$  monomer unit). RH = 60%.

#### 4. Conclusions

The results of these studies indicate the possibility of the use of the system '(-) Mg | POHP(HClO<sub>4</sub>) | Au (+)' as a solid state battery. It was previously shown that a similar cell can be constructed by utilizing the pTNI, a proton conducting polymer produced by electrochemical oxidation of thionaphtheneindole. Therefore, the cell studied in this paper can be viewed as a particular case of the more general assembly '(-) metal | proton conductor | Au (+)', of which the open circuit voltage depends on the material used and, particularly, on the metal employed as negative pole. This can open a number of possibilities for future applications in battery construction.

The electrode reactions during battery discharge are the magnesium oxidation to magnesium perchlorate/magnesium hydroxide at the negative pole

and proton reduction at the positive pole. Even though the charge and discharge curves of the cell reported in this paper suggest the reversibility of the electrode reactions, this is not in accord with the fuel cell characteristics of the assembly. As the impedance of HClO<sub>4</sub>-doped POHP depends on percentage RH, the characteristics of the battery are acceptable only at high humidity values (>60%, see Fig. 2). However, the optimum performances of solid state systems '(-) metal | proton conductor | Au (+)' have not yet been investigated and work must be done to determine their application.

The same systems can, in principle, be used as potentiometric humidity sensors; some preliminary positive results in this field were obtained and further work is in progress.

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