

Short Communication

Is 'protode' a new name for composite anodes in solid-state protonic batteries?

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(Received July 16, 1993; in revised form September 4, 1993; accepted September 11, 1993)

Abstract

Solid-state protonic batteries need a proton-generating negative electrode. In order to realize a compromise between high cell voltage and proton supplying, a new kind of anode was recently introduced. Analysing the behaviour of such a negative electrode, it is proposed to label it as 'protode'.

Among the basic components of a battery, the negative electrode is a condensed phase with the properties of electronic conduction together with an ionic conductor (liquid, solid or melting salt).

By IUPAC convention, this negative electrode is the place of the oxidation reaction. A solvated metal ion is formed according to:

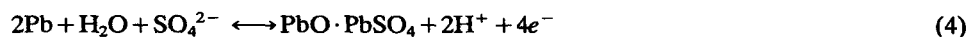


In particular, negative electrodes for aqueous batteries consist generally of a given metal immersed in an electrolyte. In aqueous electrolytes, zinc, cadmium, lead, iron and aluminium [1] are used as negative electrodes with a global reaction according to the above-mentioned reaction. Solubility of the anodic product M^{n+} leading to an electrode of the second kind determines the rechargeability of the negative electrode.

In the lead/acid battery rechargeability of the anode occurs via:



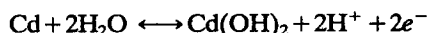
All the reactions that can occur on a lead anode are [2]:



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We can see that the anodic oxidation of lead takes place with proton supplying. The same situation occurs with the negative electrode of the nickel/cadmium battery:



and with the iron-negative electrode which was used in Fe/NiOOH and Fe/air batteries [3]. For the former anode, it has been shown that the discharge reaction occurs via dissolved forms and proton generation according to Flerov *et al.* [3] and was supported by Armstrong [4] as:



Attempts to use aluminium as a negative electrode in batteries using neutral or alkaline electrolytes were also reported [5, 6] with the main anodic reaction as:



In primary systems soluble anodic products lead to an electrode of the first kind. For example, with a zinc anode the reactions are:

(i) Leclanché 'weak acid' electrolyte [7, 8]



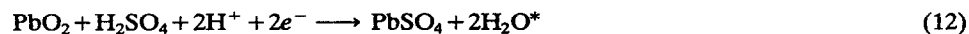
(ii) Leclanché alkaline electrolyte [9]



A comparison between the above-mentioned reactions shows that anodic dissolution is accompanied by the production of protons. On the discharge step, the anode supplies a proton to the electrolyte; this proton can be cathodically inserted into insertion compounds according to:



With the lead, zinc and cadmium anodes described above, the main cathodic materials are MnO_2 , PbO_2 and NiOOH with the reduction reactions as:



In solid-state protonic batteries, the electrolyte is stable and the protons supplied by the anode are transferred via the ionic phase and are inserted cathodically. These protons can be produced by the H_2/Pt electrode, but the low voltage of this electrode and the problems of handling and using hydrogen has led to the development of a new negative electrode. First attempts to solve this problem used hydride systems such as TiNiH_x [12] and multicomponent alloys as hydrogen storage. Extensive development of AB_2 and AB_5 systems have been carried out [13–16]. But even though rechargeable systems were reported and Ni/metal hydride batteries are now in the market, there

*While PbO_2 is not considered as a true insertion material as recently demonstrate [10, 11], the positive electrode of lead/acid battery catches protons as other protonic cathodic materials.

is a major inconvenience of this system in that its potential is low. In order to realize a compromise between proton supplying and higher potential, a new composite negative electrode for a solid-state protonic battery was reported for the first time by Guitton and coworkers [17, 18]. The most important improvement is that exchange occurs between metallic cation and the protonic phase. Such a composite electrode with configuration reported in Fig. 1 acts as a proton-producing electrode according to:

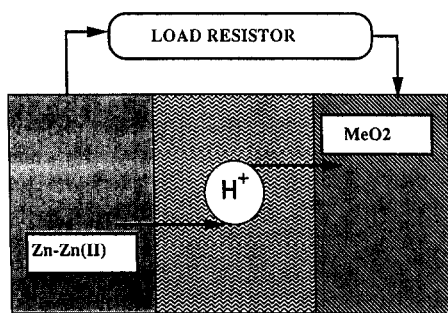


where IIS is the initial intermediate salt, and NIS the new intermediate salt after zinc/proton exchange. In the first composition, hydrated sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) was used as zinc insertion matrix [16]. The potential of the Zn/Zn^{2+} couple was obtained by adding $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. An advantage of this configuration was the important voltage gain induced by Zn/Zn^{2+} . Complete cell using hexauranyl phosphate acid as a solid-state protonic electrolyte and MnO_2 or PbO_2 as a cathode was reported [17, 19]. The open-circuit voltage and the discharge characteristics were encouraging. But the best results were obtained when the PbO_2/Zn cell was previously charged at constant current for 16 h. As PbO_2 is already in the charged state, this charge was probably used in order to initiate the zinc insertion into the initial intermediate salt. A new configuration was recently reported using $(\text{NH}_4)_2\text{ZnCl}_4$ [19] as initial intermediate salt. Either with $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ or with $(\text{NH}_4)_2\text{ZnCl}_4$, the anodic process produces zinc ion introduced into the intermediate salt which supplies protons. Along the line of the classical nomenclature of electrodes it is possible to consider this composite proton-producing electrode as a 'protode'. We reported this word for the first time in a study related to all solid-state battery with exchanged montmorillonite as electrolyte and 'protode' as the negative electrode [20]. A configuration of a solid-state protonic battery can be now formulated with 'protode' according to:

<source>/protonic conductor/<host> 'protode'/electrolyte/cathode

and related multilayered cell is reported on Fig. 1.

As the major problems of rechargeable protonic primary cells are connected to the anode, this concept may offer a very interesting avenue for research on composite anodes. For example, a second opportunity can be given to aluminium anodes which present a high theoretical density energy (8.4 kWh kg^{-1} for Al versus 1.4 kWh kg^{-1}



"Protode" Electrolyte cathode

Fig. 1. Solid-state cell configuration.

for Zn). This can also help to solve major problems arising in aqueous systems such as high anodic corrosion rate and/or passivating oxide layer growth (depending on the pH of the electrolyte). Association of a 'protode' with a solid-state protonic electrolyte was tested in complete cells with acceptable performances [17–21]. In the first configuration 'protode' was tested with MnO_2 and PbO_2 as positive electrode and hexauranyl phosphate acid (HUP) as electrolyte. In the other configuration, the inorganic protonic electrolyte was substituted by H_3PO_4 -doped poly(vinyl alcohol) [21]. In all cases operation of proton conductors in the solid state will require the use of thin-layer technology in similarly to the lithium systems introduced by Armand [22, 23]. In this case, the lithium anode can also be called 'lithode'.

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