Short Communication

Zinc composite anode for batteries with solid electrolyte

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Abstract

A new negative composite anode for batteries with a solid electrolyte is studied. Using a complex of zinc ammonium chloride mixed with zinc metal powder, the advantage of the Zn/Zn^{2+} electrode ($e = -760$ mV) is kept while the energy density and the shelf-life of the battery are increased.

Introduction

The negative electrode of a battery generally consists of a given metal which is immersed in an electrolyte. The electrolyte may be aqueous, organic or solid. In the first category Zn, Pb, Cd, Fe and Al are used as negative electrodes [1]. In the second category pure Li, Ca and Li–Al alloys [1, 2] are generally used. The last decade had seen the birth of batteries using two types of solid ionic conductors as electrolyte, i.e. lithium and proton conductors [3–5]. For lithium systems pure Li or Li alloys are normally used; for proton systems problems of using and handling the hydrogen electrode occur (especially for civilian application). Hydrides were recently tried as negative electrodes for solid states systems [5, 6] with MnO_2, TiS_2, WO_3 and CoO_2 as cathodes. However, the maximum open voltage was only 1.250 V.

A new metallic composite anode associated with a solid-state electrolyte was reported by Guitton *et al.* [7]. The open-circuit voltage and the discharge characteristics observed were encouraging. But the best result was obtained when the Zn/PbO_2 battery was first charged with a constant current of 500 μA for 16 h before discharging. On the other hand, the use of two salts with high molecular weights ($ZnSO_4 \cdot 7H_2O = 287.54$ g, $Na_3PO_4 \cdot 12H_2O = 358.14$ g) is inconvenient with regard to the energy density of batteries.

It is well known that a composite system must be constructed as follows: metal/metal salt/intermediate salt, with zinc sulfate as the metal salt and sodium phosphate as the intermediate salt as reported by Guitton *et al.* [7].

In order to increase the capacity of the battery and to avoid the first charging step as seen before, we report here a new composition for a negative composite electrode.

Experimental

Electrochemical performance evaluation was carried out on a three layer button cell of 13 mm diameter and 5 mm height using the following composition:

- 300 mg of composite anode (100 mg of zinc powder and 200 mg of appropriate salts),
- 300 mg of proton conductor solid electrolyte (hexauranyl phosphate),
- 200 mg of composite cathode (80% PbO_2 or MnO_2 and 20% graphite) mixed with solid electrolyte.

The three layers were pressed together at 5 tonne/cm^2 in a pellet press. Zinc di-ammonium chloride was prepared by addition of the appropriate amount of ammonium chloride to a saturated solution of zinc chloride. The solution was then crystallized and dried at 60 °C. The so-called double salt is a mixture of $ZnCl_2$ and NH_4Cl in the molar ratio of 1:2. The solid electrolyte was synthesized according to the method described by Shelton and Howe [8]. The PbO_2 was an industrial product removed from a lead/acid battery plate. The manganese dioxide was the International Common Samples N.8 (ICS 8), obtained by chemical precipitation from manganese sulfate solution. All the other products were used as received (Merck quality). Electrical conductivity was measured by an impedance spectroscopy method between 10 MHz and 5 Hz using an HP 4192 A system.

Results and discussion

As noted before, the composite metallic anode needs the following conditions:
- presence of conjugated ion in order to keep the open voltage at that of the classical metal anode (ex: -760 mV for Zn/Zn^{2+}),
- reversible proton extraction from intermediate salt to solid electrolyte,
- reversible metal ion extraction from related salts.

This explains the choice of the $Zn/ZnSO_4/Na_3PO_4$ system by Guitton et al. [7]. In order to achieve this, the following mixtures were used in the present work:
- double salt/ammonium oxalate
- double salt/ammonium chloride
- double salt/oxalate acid
- prepared complex alone

The double salt is a zinc ammonium chloride (in molecular ratio of 1:2) which is used as a flux in the galvanizing process of steel, and it is also present in the corrosion of the zinc anode by the classical weak acid Leclanché electrolyte [9]. In the Leclanché electrolyte, the zinc anode is protected during storage by a zinc ammonium chloride layer [9] which is destroyed rapidly at the start of discharge. According to this behaviour we can suppose that its salts may have conducting properties.

In other words, it is well known that in high concentrated $ZnCl_2$ solution, the Zn^{2+} ion activity is very low with comparison to the anionic chloro–zinc complexes ($ZnCl_4^{2-}$, $ZnCl_3^{-}$ [10]. With regard to these two considerations, we prepared a zinc ammonium chloride by addition of the appropriate amount of NH_4Cl to 5.5 M $ZnCl_2$ solution. An X-ray diffraction of the product was carried out. The diffraction pattern was indexed as diammonium zinc chloride (A.S.T.M.02-155). The electrical conductivity is calculated from the intersection of the loop at low frequency with the real part impedance axis. The value obtained is 6.3×10^{-5} Ω cm^{-1} at 29 °C. This value is similar

to some proton conductors such as $SnO_2 \cdot nH_2O$; $Sb_2O_5 \cdot nH_2O$, H_3OClO_4 and some super proton conductors obtained from the alumino-silicate group [11–13].

Figure 1 shows the effect of the intermediate salt on the typical discharge curve under 200 μA load (*C*/20) with the double salt. The discharge was stopped when the voltage droped to 1.5 V. The highest initial voltage was observed when ammonium chloride was introduced while the longest discharge time was obtained with ammonium oxalate. The presence of solvated proton (as NH_4^+) seems to increase the efficiency more than observed with proton bonded in solid-state acid ($H_2C_2O_4 \cdot 2H_2O$). The analytical composition of the prepared diammonium zinc chloride suggests that this salt can be used as a single salt instead of a conjugated metal salt and the intermediate salt.

In Fig. 2 the discharge of the cell prepared with this salt is compared to the previous composition. We can see that the shelf-life of the cell is higher than the best result obtained with the classical formulation using two salts. This result was obtained either with PbO_2 (Fig. 2(a)) or with MnO_2 as cathode (Fig. 2(b)). The advantage of using the single salt is the increase of the shelf-life of the cell and the energy density as reported in Table 1. It is evident that this modification of performance is induced by the presence of the ammonium ion. The conductivity of NH_4Cl in the solid state was studied by Fuller and Wallen [14]. Doping NH_4Cl with divalent ion leads to a drop in activation energy from 29 to 3.5 kcal/mol. Assuming that the determined conductivity is ionic, a mechanism similar to that described by Fuller and Wallen [14] can be suggested in terms of:

• switch of a proton from NH_4^+ to an anionic site
• migration
• reverse switching of the proton back to NH_4^+

On the other hand the size of the $ZnCl_4^{2-}$ anion leads to a decrease in the anionic transport number. This decrease of anionic conduction is at the origin of the advantage in using a large complex ion in the proton conductivity (such as $UO_2PO_4^-$, $H_2PO_4^-$, AsO_4^{3-}) [15, 16]. So, the potassium dihydrogen phosphate group (called KDP ferroelectric family) can be used as potential material with the addition of a conjugated metallic ion. Work on such compounds is in progress.
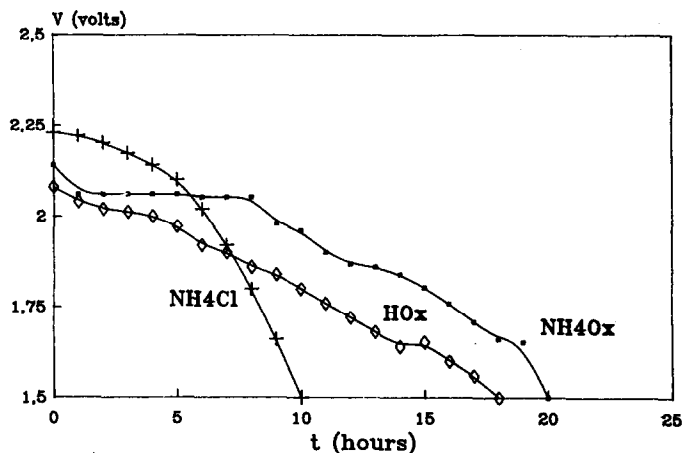

Fig. 1. Effect of the second salt on galvanostatic discharge of composite anode with zinc double salt under a load of 200 μA; lead dioxide is used as cathode.

Volts

(a)

Volts

(b)

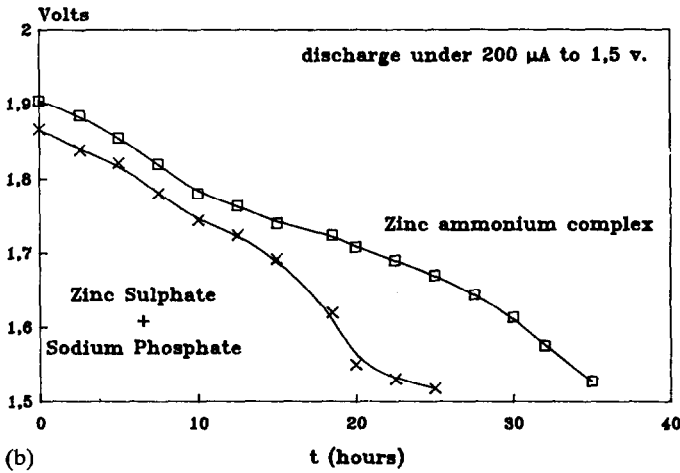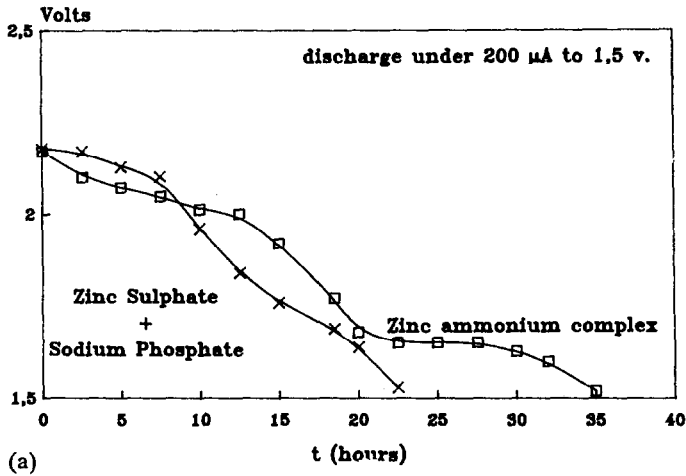Fig. 2. Galvanostatic discharge curves for complete cell with zinc ammonium complex as unique salt in composite anode under 200 μA: (a) PbO$_2$ as cathode; (b) MnO$_2$ as cathode.

TABLE 1

Characteristics of studied batteries

Cell	C (mA h)	E_m (W h/kg)	E_v (W h/dm^3)
PbO$_2$/zinc sulfate, sodium phosphate	4.5	6.8	18.5
PbO$_2$/zinc ammonium complex	7	15.4	28.8
MnO$_2$/zinc sulfate, sodium phosphate	5.5	6.4	19.2
MnO$_2$/zinc ammonium complex	7.2	13.1	24.8

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