



A novel anode material for solid state electrochemical generators involving protonic conductor electrolytes

L. Telli ^{a,*}, A. Merrouche ^a, A. Ghanem ^a, S. Walter ^b, A. Hadj Mebarek ^b

^a Laboratory of Inorganic Materials, M'sila University, 28000, Algeria

^b Groupe Sécurité et Ecologie Chimiques (GSEC), ENSCMu, 3 rue Alfred Werner, F-68093 Mulhouse Cedex, France

ARTICLE INFO

Article history:

Received 17 February 2010

Accepted 31 March 2010

Keywords:

All-solid state cell

Composite anode

Ammonium–zinc chloride double salt

H-montmorillonite

Protonic conductor

ABSTRACT

The aim of this work is to study a new composite material anode made of Zn + (NH₄)₂ZnCl₄ associated with a MnO₂ cathode for proton conductive solid state electrolyte (H-montmorillonite) electrochemical generators. The double salt (NH₄)₂ZnCl₄ has been prepared and characterized by X-ray diffraction and differential thermogravimetry.

The composition of the anode has been optimized. Generators using such an anode show a specific capacity of about 273 Ah kg⁻¹ with a high energy to mass ration of about 345 Wh kg⁻¹ when the relative humidity is at saturation level (RH = 100%) These characteristics depend strongly on both the hydration of the clay and of the double salt. The results of the electrochemical study of such generators as well as the physico-chemical characterization of the anode reaction induced compounds show clearly that the formation of a new phase takes place, and gave us the possibility of proposing a new anodic reaction.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Aqueous electrolyte based (H₂SO₄, KOH,...) electrical energy storage devices show interesting characteristics and are actually rather performing from a technico-economical point of view. As a consequence of the liquid state of the electrolyte, the electrical contact with the electrodes is good, resulting in the possibility of developing high power electrochemical generators. However, several limiting drawbacks are associated with such a kind of technique, more especially (a) the corrosion and passivation phenomena occurring at the electrodes, (b) the consumption of the solvent (electrolyte) during the charging procedure, (c) the restrained electrochemical stability domain related to aqueous electrolytes resulting in poor energy density of such devices and (d) the formation of gaseous phases due to secondary reactions which renders impossible the manufacturing of totally sealed cells. Many attempts have been done in order to solve these problems. Among them several trials aimed at replacing aqueous electrolytes by solid state ionic conductors, which possibly could solve most of the problems arising from liquid electrolytes. Thus, such “all solid” systems have several fundamental advantages and more especially (a) a larger potential stability range than their aqueous equivalents, (b) a lower corrosion rate due to a

negligible anionic transport number within the electrolyte, and (c) no corrosive liquid leakage.

Our present approach consists in using as electrode material some compounds allowing easy intercalation and de-intercalation of ions with low ionic radius and sufficient mobility in the solid state electrolyte (such as H⁺, Li⁺, Ag⁺,...) during the charging and discharging processes. Nevertheless, most of the published work has been done on lithium based generators mostly because of the availability of good Li⁺ solid state ionic conductors, and also because of the large electrochemical stability window [1,2] and the high energy density of lithium cells [3]. Despite of these obvious advantages, this kind of electrochemical generators presents some major drawbacks among which one must mention the difficult handling of lithium electrodes, their limited safety and their high economical cost [4].

Based on the fact that the radius of H is smaller than the radius of Li⁺, a significant progress has been made recently in the area of the development of new solid state electrolyte materials with a high protonic conductivity. Although they show a much smaller electrochemical stability than lithium cells, they can nevertheless be considered as a true economically interesting alternative, especially when high energy densities are not required [5,6]. Protonic conductors (MnO₂, PbO₂, V₂O₅, and V₆O₁₃) have already been used for the cathodic electrodes in aqueous storage cells. Such species can also be used in the presence of solid state electrolytes [4,7–17]. The problem consists in choosing an appropriate material for the anodic electrode. The negative anodic electrode must be capable of generation protons at a sufficiently

* Corresponding author.

E-mail address: laidtelli@yahoo.fr (L. Telli).

negative fixed potential. The first studied materials for such kind of applications were metallic hydrides [9,18–24]. Later, zinc-based composite electrodes have been studied in order to satisfy the mentioned conditions [4,6,7,13,15,16]. The system studied by [25] used $\text{Zn} + (\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2$ as anode material. In our system, we studied the possible changes induced by replacing the sulfate ions by chloride ions in the anode. The chloride based salt is more hygroscopic than the sulfate salt. Thus, since the water molecule plays an essential role in the electrical conductivity of the system, one could expect that replacing the sulfate by chloride would result in an interesting improvement of the properties of the cell at higher current densities.

In this work, one also expects the negative composite electrode based on $\text{Zn} + (\text{NH}_4)_2\text{ZnCl}_4$ to result in a good compatibility with the protonic conductive electrolyte and to enhance the overall skills of the generator.

2. Experimental

2.1. Synthesis of the ammonium–zinc chloride double salt $(\text{NH}_4)_2\text{ZnCl}_4$

The double salt $(\text{NH}_4)_2\text{ZnCl}_4$ has been prepared from a saturated solution containing zinc chloride ZnCl_2 (Prolabo) and ammonium chloride NH_4Cl (Prolabo) in a molar ratio 1:2. In the presence of a slight excess of ZnCl_2 slow evaporation at 30°C yields crystals of the double salt. Before using this salt for the composite anode, the crystals have been ground to an average grain size of about $10\ \mu\text{m}$.

The solid electrolyte is a protonated montmorillonite obtained as described in [25] and [26]. The conductivity of this H-montmorillonite increases from 10^{-7} to 2.2×10^{-3} as the relative humidity (RH) increases from 0.2 to 0.9 [27,28]. Therefore, the H-montmorillonite samples were settled in a glass vessel to fix their conductivity at the chosen value. Settling has been carried out in an atmosphere within which the RH could be set to fixed values over a wide range from 0.2 to 0.9 by means of various saturated salt solutions in the presence of an excess of solid salts.

2.2. Characterization of $(\text{NH}_4)_2\text{ZnCl}_4$ by X-ray diffraction and thermal analysis

The characterization has been made by means of powder diffraction patterns as obtained on hand of a PHILIPS PW 1800 diffractometer. The used wavelength has been set at $\lambda = 1.5418\ \text{\AA}$ by using the $\text{K}\alpha$ line of a copper anticathode for 2θ ranging from 1 to 7° .

The observed diffraction pattern (Fig. 1) is in good agreement with the theoretical pattern as given by (JCPDS 12-0304), confirming the obtained product is the expected one, without any detectable impurity.

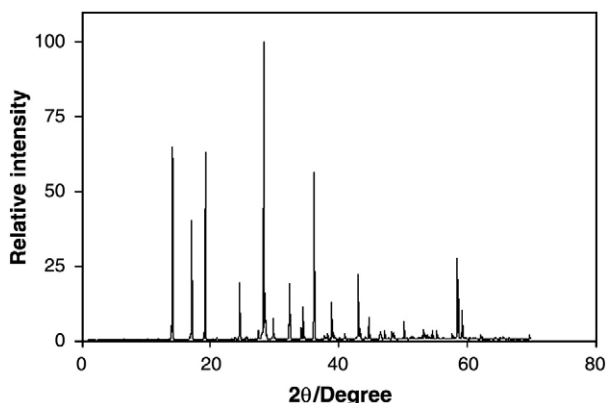


Fig. 1. Powder X-ray diffraction pattern of the double salt $(\text{NH}_4)_2\text{ZnCl}_4$.

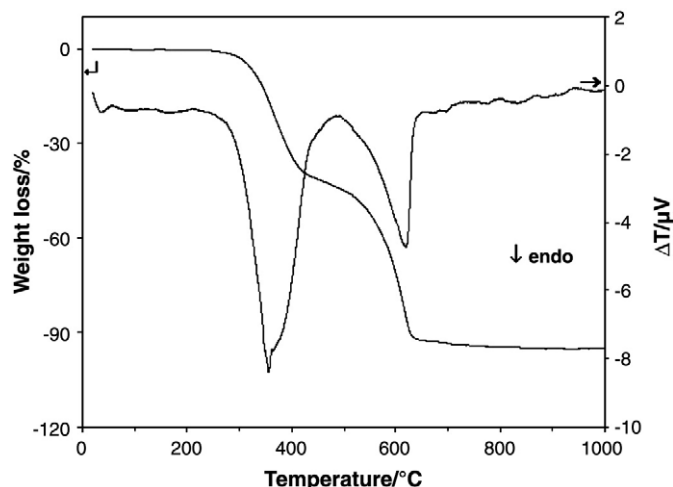


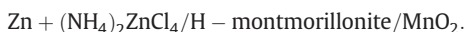
Fig. 2. TGA and DSC of $(\text{NH}_4)_2\text{ZnCl}_4$ under inert (N_2) at $5^\circ\text{C}\ \text{min}^{-1}$ heating rate.

Thermal analysis characterizations have been carried out by means of a SETARAM TG-DTA 16 device over temperatures ranging from 20°C to 900°C under nitrogen (inert) atmosphere, with a temperature increasing rate of $5^\circ\text{C}\ \text{min}^{-1}$.

Fig. 2 shows that there is no observable weight loss at an ambient temperature. That means that this material is thermally stable at least from room temperature up to more than 200°C . At temperatures higher than 250°C one observes a loss of weight. The weight loss involves two steps: the first one, between 300°C and 400°C , is related with a strong endothermic phenomenon shown by the corresponding TGA signal. It can be attributed to the decomposition of the double salt, yielding zinc chloride ZnCl_2 . A second step takes place between 450°C and 800°C . Its endothermic signal is smaller than the previous one and corresponds to the evaporation of the remaining zinc chloride ZnCl_2 according to data given by [29] and [30].

2.3. Generator assembly

The galvanic system used in this work consisted in following elements:



The mounting of such a generator has been done by assembling by means of a hydraulic press ($800\ \text{MPa}\ \text{cm}^{-2}$) three layers of the different components (cathode, electrolyte, and anode) as a unique solid system in a cylindrical one-end opened stainless steel container. The internal diameter is $13\ \text{mm}$. The bottom and top disks used during pressing the materials will give the cell electrode ends flat surfaces allowing thus a good electrical contact.

The electrolyte is made of $300\ \text{mg}$ of protonated montmorillonite (from Maghnia, Algeria).

The cathodic electrode is made of $300\ \text{mg}$ chemically prepared Faradiser type γ -manganese dioxide MnO_2 .

The anodic working electrode contains $50\ \text{mg}$ of a mixture of metallic zinc and zinc–ammonium chloride (double salt). This small amount of cathodic material is used in order to avoid any limitation of the cell properties due to the cathodic or to the electrolyte material.

3. Results and discussion

Electrochemical measurements have been done with a RADIOMETER PGP 201 type galvanostat and have been recorded through a BBC GOREZ METRAWATT SE 120 recorder.

Download English Version:

<https://daneshyari.com/en/article/1297710>

Download Persian Version:

<https://daneshyari.com/article/1297710>

[Daneshyari.com](https://daneshyari.com)