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Electrochemical characterisation of a Zn/(PEO)₄ZnCl₂/Nb₂O₅ solid-state cell

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Abstract The (PEO)₄ZnCl₂ electrolyte (PEO, polyethylene oxide) was studied in view of its potential application in a solid-state rechargeable zinc cell. The electrochemical stability window was established, and decomposition voltage values between 3.19 (20 °C) and 1.44 V (150 °C) were estimated. Cyclic voltammetry studies using a Pt/ (PEO)₄ZnCl₂/Pt cell indicated reversibility of the Zn²⁺/Zn couple at the electrode/electrolyte interface. Laboratory cells Zn(-)/(PEO)₄ZnCl₂/Nb₂O₅(+) were assembled and studied at 55 °C, under various discharge current densities. Results of cell discharge profiles, capacity values, charge–discharge cycles and cell stabilities are reported.

Keywords Zinc polymer electrolytes · Electrochemical window · Zinc-niobium pentoxide cell · Solid-state batteries

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Introduction

Interest in polymer electrolytes is based on the potential technological applications of these materials, as solid electrolytes in solid electrochemical devices, such as highenergy batteries, supercapacitors, chemical sensors, fuel cells, electrochromic display devices and others [1-4]. Besides the general advantages associated to solid electrolytes-which include prevention of problems such as chemical and electrochemical instability and corrosion and gas emissions, which are typical in liquid electrolytes-the key issue resides in the enhancement of solid-state batteries' specific energy. Other advantages of these polymeric materials are suitable mechanical properties and ease of fabrication of thin films. The ability to support volume changes, ensuring proper permanent contact with the electrodes in the course of charge/discharge cycles, is considered particularly important in rechargeable batteries that use cathodes based on insertion compounds such as Nb2O5, TiS_2 or V_6O_{13} [5, 6].

The development of polymer electrolytes for lithium batteries has been one of the main areas of investigation over the past two decades [5, 7–24]. Comparatively, less attention has been given to polymer electrolytes based on cation multivalent salts, from divalent alkaline-earth [25–29] and transition metals [30–37] to trivalent rare-earth salts [38–40], which are easier to handle than alkaline metals.

Despite the fact that the zinc electrode potential is only -0.76 V vs. SHE, there are several characteristics associated with zinc-based devices, which make attractive the employment of zinc metal as an anode. (i) Metallic zinc is cheap because of the great availability of zinc natural

resources. (ii) Zinc has low toxicity and is very stable. It can be safely handled in oxygen and humid atmospheres with consequent minimal safety problems associated with zinc metal. (iii) Insertion compounds used for lithium ions may be used for Zn^{2+} as the ionic radii of Zn^{2+} and Li^+ are comparable in magnitude [41]. Moreover, zinc-based devices have volumetric energy density comparable with lithiumbased devices and also high gravimetric energy density.

Research and development on zinc-based batteries started with the invention of the Leclanché- and Daniel-type cells in the nineteenth century [42]. Since then, research, first on primary alkaline cells and later on secondary cells, has received attention [43, 44]. The technology of rechargeable alkaline manganese oxide/zinc batteries has progressed rapidly [45, 46], but these cells suffer from having a poor life cycle. Capacity loss and internal shorts are the main problems associated with zinc distribution and solubility of zinc electrode discharge product in alkaline media [47]. Zinc is still considered to be a good candidate for the fabrication of rechargeable solid-state batteries of low power use with some studies being developed [35–37, 48–53].

Dry, all-solid-state batteries including a zinc ion containing polymer electrolyte coupled with a zinc anode and an intercalation cathode can yield high energy densities. Ionic conductivity, cationic transference numbers and electrochemical stability of the polymer electrolyte are important electrochemical properties that must be determined for evaluation of the possibility of its use in such rechargeable cells.

In previous work, the authors have reported the ionic conductance and transport behaviour of the polyethylene oxide (PEO)-zinc chloride system [54-56]. The (PEO)₄ZnCl₂ electrolyte presented the highest conductivity values in the temperature range studied, from 2.50×10^{-7} S cm⁻¹ at 24 °C to 6.81×10^{-4} S cm⁻¹ at 145 °C. Cationic transference number (T_{+}) values from 0.22 to 0.47 were estimated for this composition, in the same temperature range, by the application of the ac Sorensen and Jacobsen method [57]. These values, showing a somewhat less contribution for the ionic conduction from the cations than from the anions, were confirmed by using the electrochemical technique introduced by Bruce and Vincent, a combination of complex impedance and potentiostatic polarisation measurements [58, 59]. For 55 °C, the estimated value was within the range 0.39-0.41 depending on the applied voltage of dc polarisation experiments [60]. In this paper, we extend the study by determining the electrochemical stability window and reversibility of the Zn^{2+}/Zn couple.

The behaviour of an all-solid-state cell, assembled with a zinc anode, a composite oxide as the insertion cathode, Nb_2O_5 _{comp.} and a (PEO)₄ZnCl₂ film as the polymer electrolyte is described. Stability and performance of Zn/ (PEO)₄ZnCl₂/Nb₂O₅ _{comp.} cells were briefly examined to

evaluate the applicability of the polymer electrolyte to solidstate rechargeable zinc batteries for low power applications.

Experimental

Preparation of polymer electrolyte film

The standard solution casting technique was employed to prepare the polymer electrolyte film under study, (PEO)₄ZnCl₂. Appropriate amounts of powdered ZnCl₂ (BDH 98%, Poole, England) and PEO (Aldrich, MW 5×10^6 , Steinheim, Germany), required for an ether oxygen-to-Zn ratio of 4:1, were dissolved in acetonitrile (Aldrich 99.9%, Steinheim, Germany)/methanol (Merck 99.8%, Darmstadt, Germany) mixture and allowed to stir until complete dissolution. The obtained viscous solution was cast in glass Petri dishes, and the solvent was allowed to evaporate at room temperature in a desiccator over molecular sieves. The resulting membranes were found to have thicknesses in the range of 50–70 µm.

Preparation of niobium oxide composite cathode

The niobium oxide composite cathodes, Nb₂O_{5 comp.}, were prepared by a method similar to that used for polymer electrolyte films preparation. The constituent compounds mass ratio of the used composite was: Nb₂O₅ (65%):graphite (25%):(PEO)₄ZnCl₂ (10%). The pure oxide and the graphite (synthetic, particle size <20 μ m, Aldrich, Germany) were added to the (PEO)₄ZnCl₂ electrolyte solution leaving it under agitation until a homogenous solution was obtained. The mixture, with a solids percentage of 10% (*w*/*v*), was poured into glass cylinders placed on top of one nickel foil, and the solvent was allowed to evaporate slowly, in a desiccator containing molecular sieves.

Cell assembly and electrical measurements

Electrolyte characterisation

The electrolyte films prepared were compressed and sandwiched between two Pt electrodes. Unidirectional voltammetry at a scan rate of 5 mV s⁻¹ was applied to assembled symmetrical cells Pt/(PEO)₄ZnCl₂/Pt, the electrolyte decomposition voltages being determined at temperatures of 20 °C, 55 °C, 97 °C and 150 °C. The electrochemical stability range of the (PEO)₄ZnCl₂ electrolyte and the reversibility of the Zn²⁺/Zn redox couple were investigated with a threeelectrode configuration, adding a Ni foil that worked as a pseudo-reference electrolyte film. The voltammograms were recorded using a potentiostat/galvanostat (Solartron, model 1286, Farnborough, England), and the measurements were performed on the assembled cells in an oven, which enabled the control of the temperature within ± 1 °C. The temperature inside the cell was measured using a T-type thermocouple.

Cell testing

The characteristics and performance of the Zn/(PEO)₄ZnCl₂/Nb₂O_{5 comp.} cell, at 55 °C, were investigated by galvanostatic charge/discharge cycling curves, typically under 10 μ A cm⁻². The potentiostatic polarisation technique was also used for the charge of some cell samples, with the application of a constant voltage value of 1.2 V for 30 min.

For the evaluation of the cell self-discharge, open circuit potential was monitored over time with a data acquisition system DataLogger from Solartron, model 3531D, Slough, England.

Results and discussion

Electrolyte characterisation

An important parameter for the characterisation of a polymer electrolyte is its electrochemical stability domain, to both the reduction and the oxidation processes occurring at the electrodes, over a wide potential window, particularly if the desirable applications are electrochemical energy power sources. In this work, the maximum working voltages, also known as decomposition voltage values (V_D), of the (PEO)₄ZnCl₂ as a polymer electrolyte for a secondary battery, were determined at four different temperatures, by unidirectional voltammetry in a sandwich-type cell with symmetrical Pt electrodes. The voltage was swept from the open circuit potential of the cell towards higher values. The V_D values, ranging from 3.19 (20 °C) to 1.44 V (150 °C), were obtained from the extrapolation to the origin of the linear regions of the potentiodynamic curves (Fig. 1), where the current density increased with an appreciable rate. V_D values decrease with temperature (see Table inserted in Fig. 1). The stability of the electrolyte is higher than 2 V for temperatures lower than 150 °C.

In order to investigate which are the processes that limit the electrochemical stability of the (PEO)₄ZnCl₂ electrolyte, cyclic voltammetry measurements using a threeelectrode cell were performed. The limiting reduction and oxidation potentials were taken at the onset of the peaks. Figure 2 displays the potential-current density curve obtained for the Pt/(PEO)₄ZnCl₂/Pt cell at 55 °C, using Ni as a pseudo-reference electrode. The figure also shows the redox reactions associated with each peak. Regarding the active species in the electrolyte and the peaks resulting from the voltammogram, it can be seen that the electrolyte is cathodically limited by Zn deposition, observed at -0.74 V vs. Ni, and anodically limited by chloride ion oxidation at +0.60 V vs. Ni. The potential gap between the cathodic and anodic limits is then 1.34 V (vs. Ni) with partial redox potentials measured as discharge potentials.



Fig. 1 Unidirectional voltammetry (scan rate, 5 mV s⁻¹) for the (PEO)₄ZnCl₂ electrolyte between Pt electrodes at 20 °C, 55 °C, 97 °C and 150 °C. Inserted is a table with the V_D value obtained for each of the temperatures studied



Fig. 2 Cyclic voltammogram of Pt/(PEO)₄ZnCl₂/Pt cell at 55 °C. Ni, reference electrode; scan rate, 5 mV s⁻¹



Fig. 3 Schematic diagram of the laboratory solid-state cell

This gap value is expected to differ from the value of 2.12 V (vs. NHE) which is referred in the literature as the gap for the standard electrode potentials for the above reactions in water at equilibrium/standard conditions. The volatility of gaseous chlorine justifies the almost total disappearance of the reduction peak of this compound. Additionally, the anodic peak at +0.50 V which is displaced with increasing temperature to lower potential values, may be associated with the electrochemical oxidation of water molecules, present as traces in the electrolyte.

The mobility of both the cation and the anion in the $(PEO)_4ZnCl_2$ electrolyte confirmed the T_+ results (mixed ionic conduction) that were obtained in the authors' previous work [55, 60].

The electrochemical equilibrium established between Zn^{2+} ions in the polymer electrolyte and zinc metal at the electrode/ electrolyte interface has also been observed in other Zn systems: in a gel-polymer electrolyte based on polyacrylonitrile (PAN), propylene carbonate, ethylene carbonate and ZnX₂ (*X*=CF₃SO₃) [35, 61], in (PEO)₁₆[0.05ZnBr₂+ 0.95LiBr] [62], in the gel-polymer electrolyte systems based on PAN, dimethylsulphoxide and salts ZnX₂ (*X*=Cl and CF₃SO₃) with and without KCl [49] and in (PEO)₉ZnX₂ (*X*= Cl and CF₃SO₃) [63].

Cell testing

For application in rechargeable zinc batteries using $(PEO)_4ZnCl_2$ electrolyte, a conductivity value of 2.27×10^{-4} S cm⁻¹ [54] was considered an adequate value at 55 °C [19, 26, 61, 64, 65]. Moreover, at the same temperature, the polymer electrolyte exhibits a reasonable cationic transference number (0.44 ± 0.05) [60], decomposition voltage of 2.60 V and the ability of Zn to dissolve into the polymer electrolyte and to electrodeposit at the electrode surface. These characteristics stimulated our interest on the applicability of this electrolyte in a galvanic cell and on the study of its performance.

The Zn/Nb_2O_5 _{comp.} cells were assembled (Fig. 3), using (PEO)₄ $ZnCl_2$ as electrolyte, and allowed to equilibrate at 55 °C for about 1 h before they were subjected to different

tests. During this period, the cell voltage remained constant in the range of 1.0-1.1 V.

The discharge behaviour of the cells is illustrated in Fig. 4 for a galvanostatic discharge at a current density of 10 μ A cm⁻², until a cut off voltage of 0.2 V. On applying current, the cell voltage instantaneously dropped from the open circuit voltage to a lower value due to the cell internal resistance. After this initial drop, a gradual decrease of the circuit voltage is shown. This was assigned to the decrease of the Nb₂O_{5 comp.} electrode potential as it reacts with zinc. Also, the contribution of a possible anodic potential increase cannot be discarded. At the end of the discharge, the observed deviation on the curve may be due to the concentration polarisation related with a decrease of the cathode acceptor sites or of the zinc mobile cations at the electrolyte/oxide interface. After interrupting the current, the cell voltage gradually recovered and finally reached a new stationary value (not shown).

As the cell voltage continuously decreases without attaining any constant value, it is suggested that the discharge product is the result of a topochemical insertion [66]. The formation of a ternary compound of variable composition $Zn_xNb_2O_5$ is considered. During discharge, the following reactions are assumed as taking place on each of the electrodes:

$$xZn \rightarrow xZn^{2+} + 2xe^{-}$$
 in anode (1)



Fig. 4 Galvanostatic discharge curve of a Zn/Nb_2O_5 cell at 10 $\mu A\ cm^{-2}$

and

$$xZn^{2+} + Nb_2O_5 + 2xe^- \rightarrow Zn_xNb_2O_5$$
 in cathode (2)

The zinc is dissolved in the anode; the Zn^{2+} cations are transported through the polymer electrolyte up to the cathode, where they are incorporated into the oxide structure. The electroneutrality is maintained due to the reduction of niobium oxide (Nb⁵⁺ to Nb⁴⁺), which has been demonstrated by the Electron Spectroscopy for Chemical Analysis technique [67]. The discharge product composition value, x, follows Faraday's law during the entire time period of the discharge. The total molar number of Zn^{2+} ions that was inserted per mole of niobium pentoxide was estimated at 0.13. This low cathode utilisation value may be based mainly on diffusion problems that reach the maximum limit at this insertion level. This limitation is also found in a secondary Zn/V₆O₁₃ battery study, where it was shown that the zinc chemical diffusion coefficient in the Zn_xV₆O₁₃ cathode decreased to zero when the intercalated zinc composition was only 0.4 [68]. The results obtained in that work indicated that the presence of intercalated Zn²⁺ retards the ingress of further intercalating Zn^{2+} ions. Other system studies have shown equally low Zn^{2+} insertion levels in the respective cathodes [48, 52, 69], with x values similar to those estimated in the present study.

To evaluate the battery rate capability, several galvanostatic discharges were carried out, from 3 to 200 μ A cm⁻², with a cut off voltage of 0.2 V. Figure 5 shows the obtained results as a function of discharge capacity, to better compare the efficiency of different discharge regimes. Between 3 and 100 μ A cm⁻², the discharge capacity values obtained (*Q*) decreased about 29% with current density (from 30.7 to 21.8 mAh g_{oxide}⁻¹).

For the discharge at 200 μ A cm⁻², the *Q* value decayed to 1.6 mAh g_{oxide}⁻¹. The large contribution of the concentration polarisation effect is thought to be responsible for the remarkable decrease of the discharge capacity. This can be associated to Zn²⁺ ions' lower diffusion rates, both at the



Fig. 6 Discharge/charge behaviour of the $Zn/(PEO)_4ZnCl_2/Nb_2O_5$ cell at 55 °C. *C1* to *C6*, potentiostatic charges at 1.2 V. *D1* to *D6*, discharges with a depth of discharge of 25% at 10 μ A cm⁻². *D7* is the seventh discharge after the six cycles. The continuous discharge of another cell sample is also included

electrode/electrolyte interface and within the oxide, causing a sharp decline of the discharge curve which reaches the cut off voltage sooner than in the case of lower current densities.

Since investigations on rechargeable Zn batteries are more interesting, an attempt was made to examine the rechargeability of the Zn/Nb₂O₅ cell. During galvanostatic charge–discharge cycling (at 10 μ A cm⁻²), the cell was charged with the same amount of charge that was withdrawn during the previous discharge (graph not shown). The cell tested discharged for about 46 h and delivered a specific discharge capacity of 30.6 mAh g_{oxide}⁻¹ for the active Nb₂O₅ material in the composite cathode. It was possible to recharge this cell, but a high polarisation was observed (increase of cell internal resistance). At the end of the charge process, the cell voltage values attained were near the (PEO)₄ZnCl₂ electrolyte decomposition voltage, as estimated in this work for 55 °C (2.60 V). The capacity retention of the cell was observed to be very poor. After the second cycle, the cell was not able to retain its charge.





Fig. 5 Discharge capacities of $\rm Zn/Nb_2O_5$ cells at several current densities



Fig. 7 Effect of time on the open circuit voltage of a Zn/Nb_2O_5 cell at 55 $^{\circ}\mathrm{C}$

galvanostatic/potentiostatic cycles. An improvement on the cell charge retention was in fact observed for less deep discharges, leading to cell capacities of the order of 40 mAh g_{oxide}⁻¹. The effect of imposing six galvanostatic discharge (each at 10 μ A cm⁻² with a depth of discharge of 25%)/potentiostatic charge (each at 1.2 V for 30 min) cycles to a Zn/Nb₂O₅ cell at 55 °C is displayed in Fig. 6. This figure also includes (grey line) a curve for the cell submitted to a continuous discharge at 10 μ A cm⁻². The accumulated discharge capacity up to the seventh discharge is 34% higher than the discharge capacity of only one continuous discharge. This indicates that the amount of Zn^{2+} cations inserted in the cathode increases with shallower discharges. In this case, the final product obtained in the insertion cathode is Zn_{0.21}Nb₂O₅. One possible explanation for the lower cathode utilisation, when the cell is discharged continuously up to 0.2 V, could be associated to the development of a concentration polarisation. This suggests that a redistribution of Zn²⁺ ions might not occur at a sufficiently high rate at the reaction front. On the same account, after each partial discharge, there is a period of relaxation of the concentration gradient, giving place to a more uniform zinc concentration throughout the surface and bulk of the positive electrode.

The number of discharges, attained with a reasonable average discharge voltage, increased for even less deep discharges, namely with a depth of discharge of 2.5%. At least, eleven discharges with an accumulated capacity of 6.4 mAh g_{oxide}^{-1} were obtained.

Results indicated that shallower discharges resulted in a longer cycle life, with a less marked decrease in cell capacity at constant voltage. This might be due to a decrease of the contact loss effect between electrode particles (internal resistance increase), as the volume changes become less relevant. Moreover, the concentration polarisation is considered to be also lower for low insertion levels.

The charge retention decay with the number of discharge-charge cycles, for equal depth of discharge values and for equal discharge regimes (current density magnitudes), may be related with a combination of several effects that include the deterioration of interfacial contacts of both the electrodes with the cell polymer electrolyte, the electronic isolation of oxide particles inside the insertion electrode and also the concentration overvoltage effect that increases from cycle to cycle.

Other polymeric systems, based on the insertion of Zn^{2+} ions in battery cathodes with zinc anodes, demonstrated a similar behaviour to those found in the present work [35, 52, 61, 68, 70, 71].

Finally, to verify the battery stability and monitor the self-discharge effects, open circuit voltage measurements ($V_{\rm oc}$) were undertaken for long periods of time (*t*). Figure 7 displays $V_{\rm oc}$ vs. *t* for a Zn/Nb₂O₅ cell, maintained at 55 °C

during 339 days. The V_{oc} value decreased at a higher rate from 1.10 to about 0.80 V during the first 160 days, corresponding to a decay of around 1.9 mV day⁻¹. Afterwards, V_{oc} decreased down to 0.75 V more slowly. Taking into account the decay rate of 0.3 mV day⁻¹ of V_{oc} between these last two potential values (0.80–0.75 V), a lifetime of 4.9 years for this cell was addressed, if maintained at 55 °C.

Conclusions

The (PEO)₄ZnCl₂ electrolyte displayed an ionic conductivity of 2.27×10^{-4} S cm⁻¹ and a cationic transference number value of 0.44 ± 0.05 at 55 °C, according to the authors' own work [54, 60]. These results have been complimented with the electrochemical stability domain characterisation of the polymer electrolyte which rendered a decomposition voltage value of 2.60 V at the same temperature and also provided evidence of the existence of electrochemical reversibility between zinc metal at the electrode/electrolyte interface and Zn²⁺ ions within the electrolyte.

The cell rate capability was evaluated and, using discharge current densities between 3 and 100 μ A cm⁻², the same order of magnitude for discharge capacity values was observed. For a discharge at 200 μ A cm⁻², the discharge capacity value decayed considerably, assigned to a large contribution of the concentration polarisation effect, namely to a decrease of Zn²⁺ ion diffusion rates. A specific capacity discharge value of 30.6 mAh g_{oxide}⁻¹ was obtained for a galvanostatic discharge at 10 μ A cm⁻² on a Zn/(PEO)₄ZnCl₂/Nb₂O_{5 comp.} cell. The influence of depth of discharge on cycling was investigated to some extent, and it was observed that larger life cycles are obtained for less deep discharges. Lifetime evaluation for the studied cell was 4.9 years, if maintained at 55 °C, under non-operating conditions.

Further work is required concerning the optimisation of the Zn/Nb_2O_5 cell in order to improve its performance capability. The modification of the composite oxide is suggested to increase its charge retention. Evaluation of the effect of particle porosity and active area for the transfer of Zn^{2+} ions are also needed.

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