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Electrochemical and kinetic behavior of the $\text{MnO}_x/\text{C}-\beta\text{-PbO}_2$ electrode

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Abstract The $\text{MnO}_x/\text{C}-\beta\text{-PbO}_2$ electrode was obtained by admixture of $\beta\text{-PbO}_2$ to MnO_x/C . Slow scan voltammetry shows a double reduction peak which is discussed. Galvanostatic intermittent titration technique curves are also used and the value of the proton diffusion coefficient, $D(\text{H}^+)$, is determined. All studies are made in 2 M KOH.

Keywords Galvanostatic intermittent titration technique · Lead dioxide · Manganese dioxide · Proton diffusion · Slow scan voltammetry

Introduction

The high positive electrode potential, low molecular weight, inexpensive reactants and ambient temperature of operation, among other properties, make MnO_2 a good material for primary batteries. However, the highly irreversible behaviour of MnO_2 batteries limits the life of MnO_2/Zn alkaline batteries. Accumulation of hausmanite is believed to be responsible for the irreversible behaviour of deeply discharged conventional MnO_2 electrodes [1].

The possible application of MnO_2 oxides in secondary alkaline cells is based on the fact that MnO_2 has an open structure which can be maintained through redox cycles, thus inhibiting the great volumetric changes which cause the decrease of rechargeability [2].

It has been reported [3, 4] that synthetic bismuth and lead birnessite electrodes behave reversibly even when fully discharged to Mn^{2+} species. The aim of this work

is to study the poorly crystalline modified MnO_x/C electrode by admixture of $\beta\text{-PbO}_2$.

Experimental

Preparation of the $\text{MnO}_x/\text{C}-\beta\text{-PbO}_2$ composite electrode

The composite electrode contained: (1) manganese dioxide, MnO_x/C , prepared according to a published procedure [5], (2) $\beta\text{-PbO}_2$ as an admixture and (3) graphite (G) as an electronic binder. The proportions were the following: $\text{MnO}_x/\text{C}-\beta\text{-PbO}_2:\text{G} = 1:50$ and $\text{Pb}:\text{Mn} = 3:10$. We obtained in this way a composite electrode with 0.1–0.2 mg of active material.

$\beta\text{-PbO}_2$ was prepared by electroformation of cured battery plates (with grids cast from a 5% Sb–Pb alloy) in acidic solution according to the method described [6]. After washing in running water for several hours to remove excess H_2SO_4 from the $\beta\text{-PbO}_2$ plates, the plates were dried overnight at 110 °C. Then the active mass was removed from the grid, homogenized in a mortar and saved for subsequent analyses. $\beta\text{-PbO}_2$ was characterized by X-ray powder diffraction using Cu K_α radiation.

Investigation techniques

Electrochemical measurements were carried out in a three-electrode cell: the counter electrode was a platinum wire, the reference one was Hg/HgO and the working electrode was the $\text{MnO}_x/\text{C}-\beta\text{-PbO}_2$ composite electrode; the supporting electrolyte was a 2 M KOH solution.

Slow scan voltammetry and galvanostatic charge–discharge were performed and potential–time curves were recorded. A potentiostat-galvanostat (PJT-16-0.6), a recorder (SEFRAM 164) and an Enregistrator (Tacussel) were used.

Results and discussion

First proton insertion with the galvanostatic intermittent titration technique

At the early step of insertion the curves corresponding to the open circuit voltage (OCV) present a plateau at 820 mV. This means that for low values of x (proton content) we observe a plateau. The difference between

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the OCV and the voltage under current is not negligible, about 800 mV.

In Fig. 1 are shown the first insertion galvanostatic intermittent titration technique (GITT) curves for $MnO_x/C-\beta-PbO_2$. The x -axis corresponds to the proton content calculated with the experimental mass. The open circles are the voltage values reached at the end of each time of proton insertion ($t = 5, 10, 15, 20$ min) increment just before turning the current off, whereas the dots are the voltage values reached after the following 15 min relaxation (OCV).

First proton insertion with slow scan voltammetry

In Fig. 2 is shown the first insertion voltammogram for $MnO_x/C-\beta-PbO_2$. Two principal cathodic peaks are observed. The first one is at $E = -240$ mV and the second at $E = -640$ mV. Moreover, it appears that the former one is double, a shoulder on the curve at $E = -160$ mV. This could be explained by the existence of two steps in the reduction process of MnO_2 to $MnOOH$ [7, 8, 9, 10]. With the carbon paste technique, two cathodic peaks (-160 mV and -240 mV) appear when we used the corresponding proportion for $MnO_x/C-\beta-PbO_2:graphite = 1:50$. One can observe the appearance of the first peak which is, according published data [10, 11, 12, 13, 14, 15], the expression of the occupation of the A sites. According to Rippert et al. [16], the first peak corresponds to the proton insertion which is realized by the intermediary of the pyramidal sp^3 oxygen of the Mn oxide and the second peak (-240 mV) corresponds to the occupation of the B sites and the proton insertion is the result of the action of the planar sp^2 oxygen. In Fig. 3 a smooth potential decrease in the first 90 min is seen; it remains as a plateau for 150 min. The

Fig. 1 GITT curves of the $MnO_x/C-\beta-PbO_2$ composite electrode

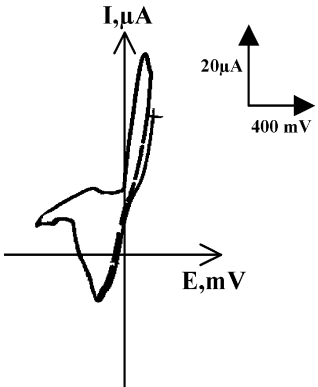
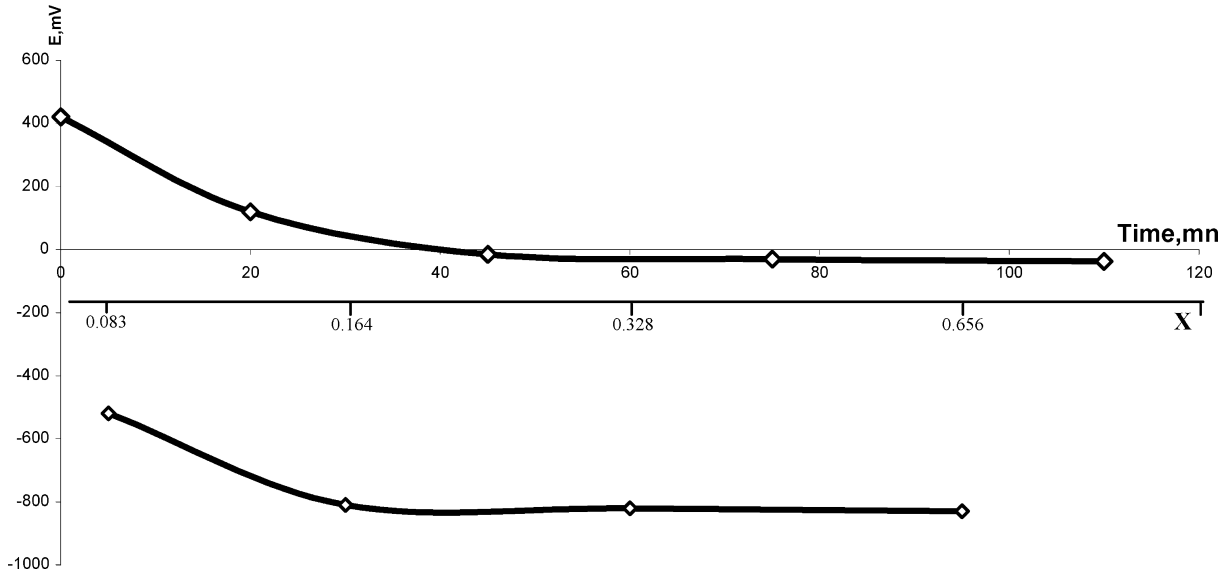


Fig. 2 Voltammogram for the first proton insertion recorded at 0.5 mV/s for the $MnO_x/C-\beta-PbO_2$ composite electrode in 2 M KOH vs. Hg/HgO

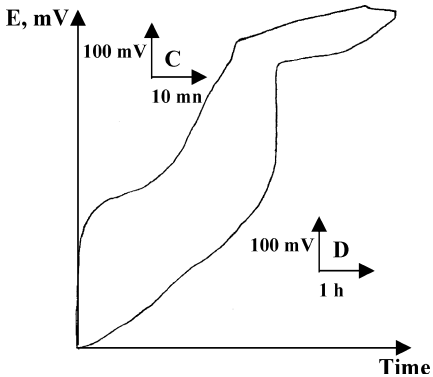


Fig. 3 Charge-discharge curve for the $MnO_x/C-\beta-PbO_2$ composite electrode in 2 M KOH vs. Hg/HgO; $I_c = -0.18$ mA, $I_d = 30$ μ A

third step of the discharge is characterized by an abrupt decrease of the potential to the value $E = -600$ mV; this again shows a smooth decrease until the final value of $E = 0$ mV.

The diffusion coefficient, $D(\text{H}^+)$, was determined by GITT and is equal to $1.45 \times 10^{-9} \text{ cm}^2/\text{s}$.

Conclusion

From slow scan voltammetry, proton insertion in $\text{MnO}_x/\text{C}-\beta\text{-PbO}_2$ has been shown to occur in two steps. The first one is double ($E = -160 \text{ mV}$ and -240 mV) which is the expression of the action of pyramidal sp^3 oxygen and planar sp^2 oxygen. The value of the diffusion coefficient in the $\text{MnO}_x/\text{C}-\beta\text{-PbO}_2$ composite electrode was determined by GITT and is $D(\text{H}^+) = 1.45 \times 10^{-9} \text{ cm}^2/\text{s}$.

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