

## The Electrochemical Performance of $\delta$ -MnO<sub>2</sub> Cathode Material for Aqueous Zinc-Ion Batteries: the Role of Current Collector

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Electrochemical properties of  $\delta$ -MnO<sub>2</sub>-based cathode materials for zinc-ion batteries were studied using various current collectors (stainless steel mesh, carbon paper and titan foil). Among the investigated materials the stainless steel current collector was the most inconvenient for oxide-based electrode materials which was confirmed by galvanostatic charge/discharge measurements and cyclic voltammetry. This phenomenon might be explained by side reactions of electrolyte decomposition and corrosion of steel.

### Introduction

Novel types of energy storage systems are rapidly developed in last decades. Among them, aqueous zinc-ion batteries (AZIBs) have attracted special research attention owing to low cost, high specific capacity of zinc anode (820 mAh·g<sup>-1</sup>), environmental friendliness and safety (1). Many types of cathode materials for AZIBs have been recently investigated (2), among them different types of manganese dioxide MnO<sub>2</sub> are on the top of the study because of its numerous advantages such as environmental friendliness, low cost, abundance, remarkable theoretical capacity (308 mAh·g<sup>-1</sup>) and relative high voltage of redox transformation (1.3 – 1.5 V vs. Zn/Zn<sup>2+</sup>) (3). Among different types of MnO<sub>2</sub> crystal lattice, layered-type MnO<sub>2</sub> (or  $\delta$ -MnO<sub>2</sub>) is promising candidate because of its structure facilitate to reversible process of zinc ion intercalation.

Nevertheless, the main drawbacks of MnO<sub>2</sub> as cathode material for ZIBs are low electronic conductivity of the oxide and manganese dissolution during charge/discharge processes. Addition of Mn<sup>2+</sup>-containing salt helps improving cycling stability by suppressing the dissolution of MnO<sub>x</sub> layer (4). To increase the electronic conductivity, various types of carbon coatings or graphene can be applied.

In accord with reported data different types of current collector were applied for  $\delta$ -MnO<sub>2</sub>-based cathodes: stainless steel mesh or grid, various forms of carbon paper or clothes and titan foil. As it was demonstrated previously for electrode materials for lithium-ion batteries, the nature of current collector can affect on the electrochemical performance of  $\delta$ -MnO<sub>2</sub> cathodes. In the case of AZIBs with aqueous electrolytes also can be supposed that the nature of current collector material can greatly effect on the electrode processes.

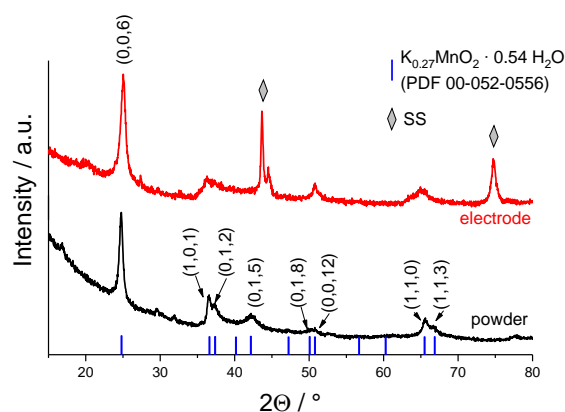
### Experimental Details

$\delta$ -MnO<sub>2</sub> was synthesized hydrothermally as it was ascribed in (5). The 0.001 M MnSO<sub>4</sub> aqueous solution was mixed with 0.006 M KMnO<sub>4</sub> aqueous solution under stirring for 30 min, then the solution obtained was transferred in the Teflon autoclave and heated up to 160 °C for 12 h. The product obtained were washed by deionized water for five times and dried under vacuum at 55 °C. The black powder was tested by X-ray diffraction (Cu K<sub>α</sub> radiation).

$\delta$ -MnO<sub>2</sub> electrodes were prepared by mechanically mixing of electroactive grains with carbon black and polyvinylidene fluoride (PVDF) in the ratio 70 wt% of  $\delta$ -MnO<sub>2</sub>, 20 wt% of carbon and 10 wt% of PVDF. The resulting viscous slurry was cast on the stainless steel grid, carbon paper and titan foil (blade gap height – 150  $\mu$ m), dried under vacuum at 60 °C for 12 h. Mass loading of the electrodes was near 5 mg·cm<sup>-2</sup>, 2 mg·cm<sup>-2</sup> and 1 mg·cm<sup>-2</sup> for electrodes on steel, carbon paper and Ti. Electrodes were assembled in CR2032 coin cells vs. Zn anode, Whatman glass fiber soaked in aqueous solution 2 M ZnSO<sub>4</sub> / 0.1 M MnSO<sub>4</sub> was used as separator. Electrochemical tests were performed by galvanostatic charge/discharge (current 0.3 A·g<sup>-1</sup>), cyclic voltammetry (CV) at a scan rate of 0.1 mV·s<sup>-1</sup> in the potential range 1.0 – 1.8 V vs. Zn/Zn<sup>2+</sup> and electrochemical impedance spectroscopy.

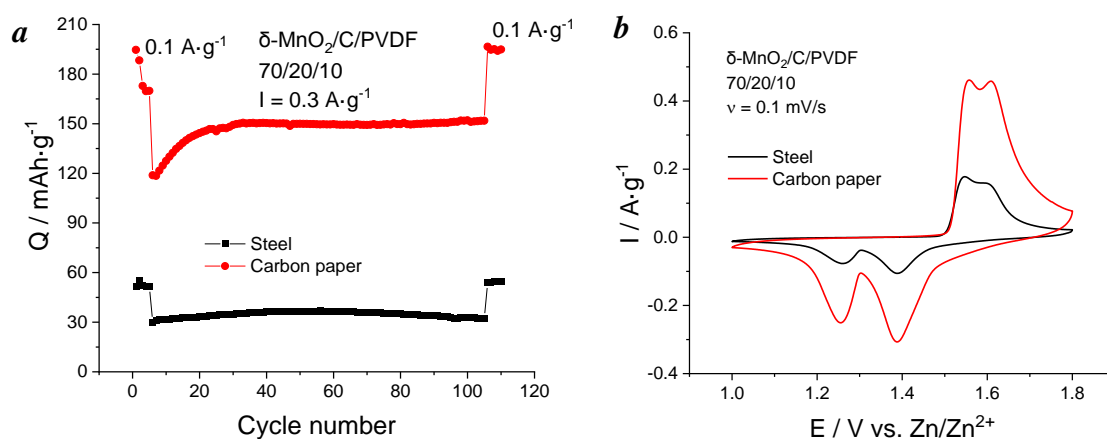
## Results and Discussion

X-ray diffraction patterns of powder synthesized and electrode material are shown on Fig. 1. The MnO<sub>2</sub> pattern demonstrated a high-intensive peak at 24.77 ° and several coupled peaks which are usually observed for layered-type material. Thus, it confirmed that layered manganese dioxide MnO<sub>2</sub> with molecular formula K<sub>0.27</sub>MnO<sub>2</sub> · 0.54 H<sub>2</sub>O. The same peaks are observed for electrode material which allow us to conclude that no crystal lattice changes are not occurred.



**Figure 1.** XRD patterns of  $\delta$ -MnO<sub>2</sub> powder and electrode material on stainless steel.

Fig. 2,a shows electrochemical performance of  $\delta$ -MnO<sub>2</sub> cathodes vs. Zn anode on two types of current collector: steel and carbon paper, at a current density 0.3 A·g<sup>-1</sup>. It is clearly seen that electrode cast on the carbon paper demonstrated a five-times higher specific capacity values at selected current (near 150 mAh·g<sup>-1</sup>) while electrode material on stainless steel shows only 30 – 40 mAh·g<sup>-1</sup>. In both cases during initial 20 – 25 cycles increasing of specific capacity is observed which correlated with MnO<sub>x</sub> electroactive layer formation, and then the maximum value is stabilized.



**Figure 2.** a) Cycling stability of  $\delta\text{-MnO}_2$  electrodes on carbon paper and stainless steel at  $0.3 \text{ A}\cdot\text{g}^{-1}$ ; b) cyclic voltammograms of  $\delta\text{-MnO}_2$  electrodes after 100 charge/discharge cycles.

On the cyclic voltammograms of the cells after charge/discharge tests two pairs of peaks are determined. The first pair is connected with zinc intercalation/deintercalation and insoluble salt layer formation and the second one is assigned to proton intercalation. For the  $\delta\text{-MnO}_2$  electrode cast on carbon paper specific current density values were in three times higher than for electrode with steel current collector.

Thus, these results demonstrated that application of stainless steel as current collector is irrelevant than carbon paper or titan foil. This can be associated with corrosion processes on steel and electrolyte decomposition at high anodic potentials.

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