Characterization of a new rechargeable Zn/PVA-KOH/Bi$_2$O$_3$ battery: structural changes of the Bi$_2$O$_3$ electrode

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Calculation of the Battery parameters

The calculation of the theoretical specific capacity has been carried out considering that a mol of Bi$_2$O$_3$ contains 2 Bi$^{3+}$ cations, which are theoretically reduced to metallic Bi, following the reaction:

$$2 \text{Bi}^{3+} + 6\text{e}^- \rightarrow 2 \text{Bi}^0$$  \hspace{1cm} (S1)

Furthermore, the specific capacity can be calculated following the equation S2 and considering the participation of 6 e$^-$/mol Bi$_2$O$_3$.

$$\text{Theoretical Specific Capacity} = \frac{n \times F}{M} \times \frac{1}{3600} \text{ s} = 345.11 \text{ mAh g}^{-1}$$  \hspace{1cm} (S2)

Where $n$ is the e$^-$ number transferred in the redox reaction, $F$ is the Faraday constant and $M$ is the molar mass of the Bi$_2$O$_3$ (465.96 g/mol). Thus, considering that 6 e$^-$ are consumed in reaction S1, the theoretical specific capacity of Bi$_2$O$_3$ is 345.11 mAh$^{-1}$.

From here, the specific capacity efficiency can be calculated with:

$$\text{Specific Capacity Efficiency} = \frac{\text{Experimental Specific Capacity}}{\text{Theoretical Specific Capacity}} \times 100$$  \hspace{1cm} (S3)

Besides, Coulombic and Energy Efficiencies are calculated by the following expressions

$$\text{Coulombic Efficiency} = \frac{\text{Total Capacity}_{\text{discharge}}}{\text{Total Capacity}_{\text{charge}}} \times 100$$  \hspace{1cm} (S4)

$$\text{Energy Efficiency} = \frac{\text{Total Energy}_{\text{discharge}}}{\text{Total Energy}_{\text{charge}}} \times 100$$  \hspace{1cm} (S5)
Cyclic Voltammetry

With the aim to investigate the reversibility of the Bi$_2$O$_3$ material, a primary CV study in 0.1 M KOH solution have been carried out. Figure S1 shows 20 consecutive cycles confirming the reversibility of the Bi$_2$O$_3$/Bi redox process. Besides, increase of intensity peaks indicates the increment of the Bi$_2$O$_3$ activity with the cycling. This result agrees with the previously reported articles$^{1-4}$, which are recommended to the readers interested in the CV analysis of the Bi$_2$O$_3$ material.

**Figure S1.** Consecutive Cyclic Voltammograms of Bi$_2$O$_3$ in 0.1M KOH. Arrows indicate the increase of intensity peaks with the cycling. $V= 20$ mV/s

**Coulombic Efficiency with the cycles**

Figure S2 shows the coulombic efficiency for the 190 cycles carried out to a two Zn/PVA-KOH/Bi$_2$O$_3$ cells connected in series. Values of 100% were obtained for the initial 130 cycles and it maintains values higher than 90% for more than 180 cycles.
**Figure S2.** Coulombic Efficiency vs. cycle number for a connected in series two-batteries pack.
**SEM images of Bi₂O₃ electrodes**

Figure S3 and S4 show the SEM images of the pristine and soaked in KOH Bi₂O₃ electrodes, respectively. A clear surface change is observed when the Bi₂O₃ electrode is immersed in a KOH solution.

**Figure S3.** SEM image of the pristine Bi₂O₃ supported in Ni foam.
Figure S4. SEM image of the Bi$_2$O$_3$ supported in Ni foam and soaked in KOH solution.
XPS measurements

<table>
<thead>
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<th>Sample</th>
<th>Binding energy 4f7/2 (eV)</th>
<th>FWHM 4f7/2 (eV)</th>
<th>Area 4f7/2 (%)</th>
<th>Error (%)</th>
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<td>2.5</td>
<td>50.4</td>
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</table>

Table S1. Binding energies, areas and FWHM for Gaussian fits of XP Bi 4f7/2 spectra
Figure S5. K 3p, Bi 5d and K3s XP spectra for the discharged electrode (blue line) and recharged electrode (black line).
Figure S6. K 2s XP spectra for the discharged electrode (blue line) and recharged electrode (black line).
Figure S7. Zn 2p XP spectra for the discharged electrode (blue line) and recharged electrode (black line).
Conductivity measurements of Bi$_2$O$_3$ electrodes.

It is well known that Bi$_2$O$_3$ has a limited electric conductivity, as other metal oxide materials, which makes difficult the applicability of these materials in storage energy systems. A successful method to enhance the charge transfer of Bi$_2$O$_3$ electrodes is to perform its synthesis adding graphene, mesoporous carbon or other conductive nanomaterials$^5$.

As an alternative to solve the low conductivity of Bi$_2$O$_3$ material, we have prepared the Bi$_2$O$_3$ electrodes depositing it in Nickel metallic foams or meshes. Figure S8 shows the I-V curves obtained for pure Bi$_2$O$_3$, Bi metal and the electrodes prepared depositing Bi$_2$O$_3$ inside Ni foam and Ni mesh. From the slope of these curves we can obtain the resistivity values for each sample, which are displayed in Table S2. As can be seen, when Bi$_2$O$_3$ is deposited on Ni, the resistivity values obtained diminish with respect to pure Bi$_2$O$_3$. These conductivity increments are enough to permit using the Bi$_2$O$_3$ as active material of the positive electrode in the Zn/PVA-KOH/Bi$_2$O$_3$ battery. The agreement between the Bi metal resistivity value obtained in this article and that published previously$^6$, confirms the accuracy of our measurements.
**Figure S8.** I-V curves obtained for pure Bi$_2$O$_3$, Bi metal and the electrodes prepared depositing Bi$_2$O$_3$ inside Ni foam and Ni mesh.

**Table S2.** Resistivity values (Ω·m) obtained for pure Bi$_2$O$_3$, Bi metal and the electrodes prepared depositing Bi$_2$O$_3$ inside Ni foam and Ni mesh.

<table>
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<tr>
<th>Material</th>
<th>$\rho$ (Ωm)</th>
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<td>Bi$_2$O$_3$</td>
<td>$1,97 \cdot 10^7$</td>
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<tr>
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<td>$2,23 \cdot 10^7$</td>
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<td>Bi$_2$O$_3$ + Ni foam</td>
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<td>$6,06 \cdot 10^5$</td>
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<td>Bi metal</td>
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References


