Characterization of a new rechargeable Zn/PVA-KOH/Bi_2O_3 battery: structural changes of the Bi_2O_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_2O_3 contains 2 Bi^{3+} cations, which are theoretically reduced to metallic Bi, following the reaction:

$2\ Bi^{3+} + 6e^{-} \rightarrow 2\ Bi^{o}$ (S1)

Furthermore, the specific capacity can be calculated following the equation S2 and considering the participation of 6 e^{-} /mol Bi_2O_3.

$$Theoretical\ Specific\ Capacity = \frac{n \times F}{M} \times \frac{1h}{3600\ s} = 345.11\ mAhg^{-1} \quad (S2)$$

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_2O_3 (465,96 g/mol). Thus, considering that 6 e^{-} are consumed in reaction S1, the theoretical specific capacity of Bi_2O_3 is 345.11 $mAhg^{-1}$. From here, the specific capacity efficiency can be calculated with:

$$Specific\ Capacity\ Efficiency = \frac{Experimental\ Specific\ Capacity}{Theoretical\ Specific\ Capacity} \times 100 \quad (S3)$$

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

$$Coulombic\ Efficiency = \frac{Total\ Capacity_{(discharge)}}{Total\ Capacity_{(charge)}} \times 100 \quad (S4)$$

$$Energy\ Efficiency = \frac{Total\ Energy_{(discharge)}}{Total\ Energy_{(charge)}} \times 100 \quad (S5)$$

Cyclic Voltammetry

With the aim to investigate the reversibility of the Bi_2O_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_2O_3/Bi redox process. Besides, increase of intensity peaks indicates the increment of the Bi_2O_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_2O_3 material.

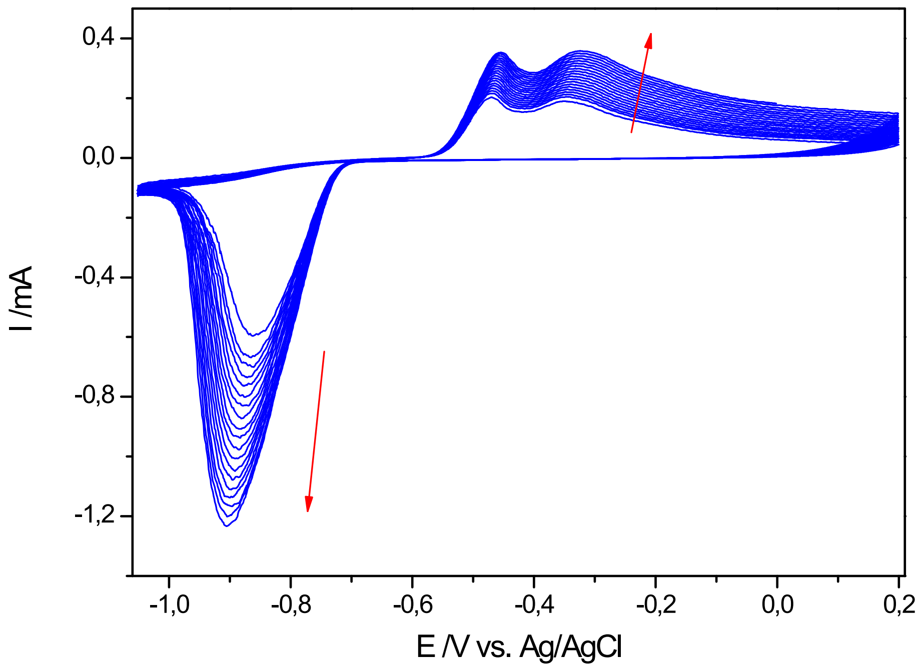

Figure S1. Consecutive Cyclic Voltammograms of Bi_2O_3 in 0.1M KOH. Arrows indicate the increase of intensity peaks with the cycling. V= 20 mV/s

Coulombic Efficiency with the cycles

Figure S2 shows the coulombic efficiency for the 190 cycles carried out to a two Zn/PVA-KOH/Bi_2O_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.

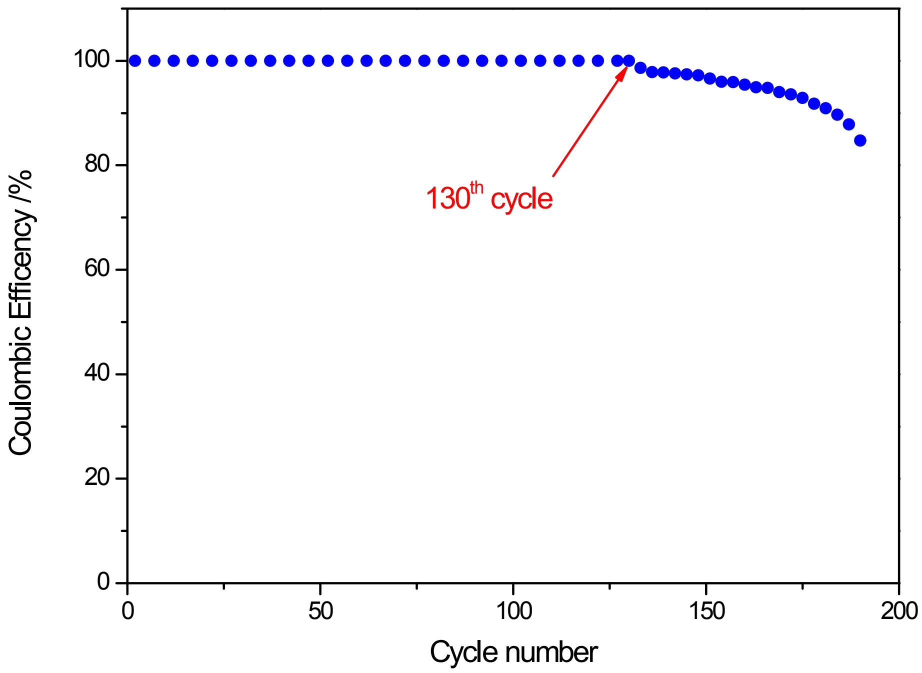

Figure S2. Coulombic Efficiency vs. cycle number for a connected in series two-batteries pack.

SEM images of Bi_2O_3 electrodes

Figure S3 and S4 show the SEM images of the pristine and soaked in KOH Bi_2O_3 electrodes, respectively. A clear surface change is observed when the Bi_2O_3 electrode is immersed in a KOH solution.

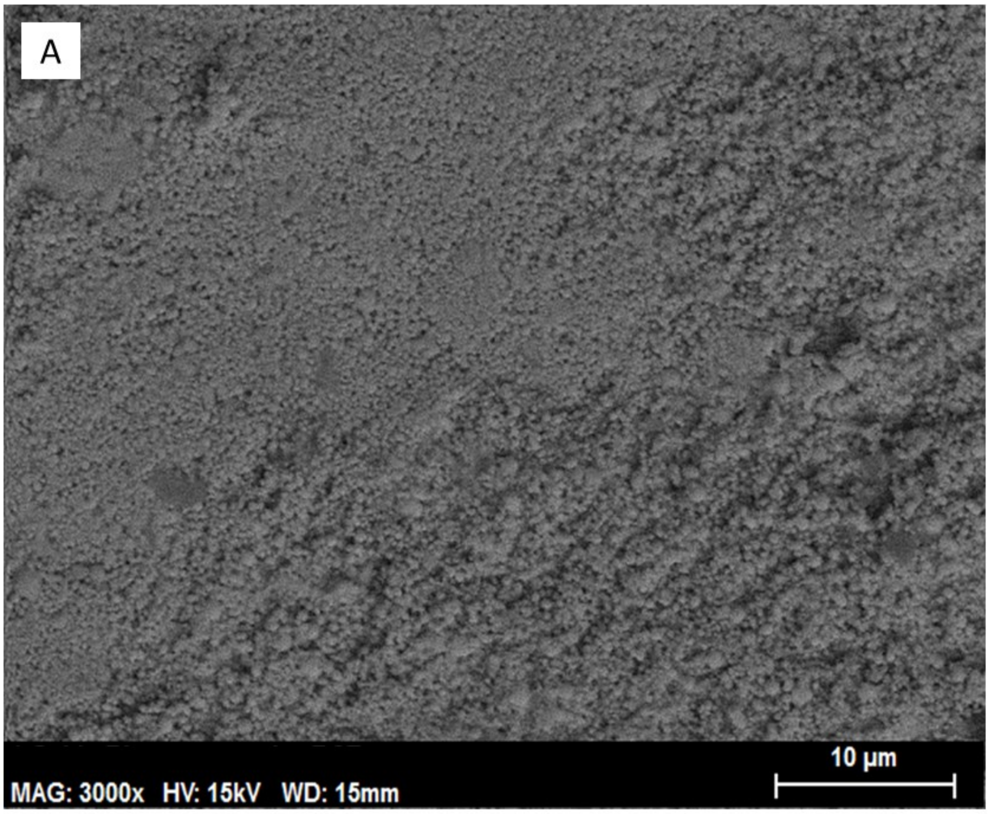

Figure S3. SEM image of the pristine Bi_2O_3 supported in Ni foam.

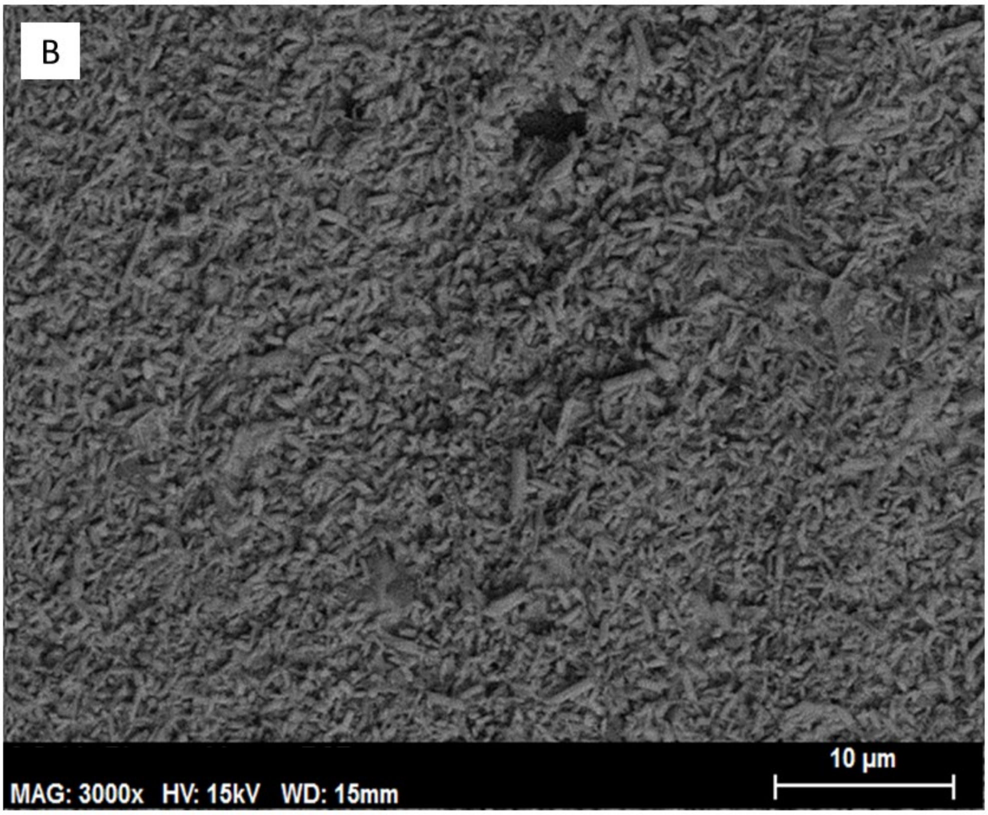

Figure S4. SEM image of the Bi_2O_3 supported in Ni foam and soaked in KOH solution.

XPS measurements

Sample	Binding energy 4f7/2 (eV)	FWHM 4f7/2 (eV)	Area 4f7/2 (%)	Error (%)
recharged				
Bi^0	156.0	1.5	2	3
Bi^{n+}	157.8	1.7	15.4	0.6
Bi^{3+}	159.1	2.3	82.3	0.6
discharged				
Bi^0	155.9	1.5	4	3
Bi^{n+}	157.7	1.7	45.9	0.4
Bi^{3+}	159.3	2.5	50.4	0.4

Table S1. Binding energies, areas and FWHM for Gaussian fits of XP Bi $4_{f7/2}$ spectra

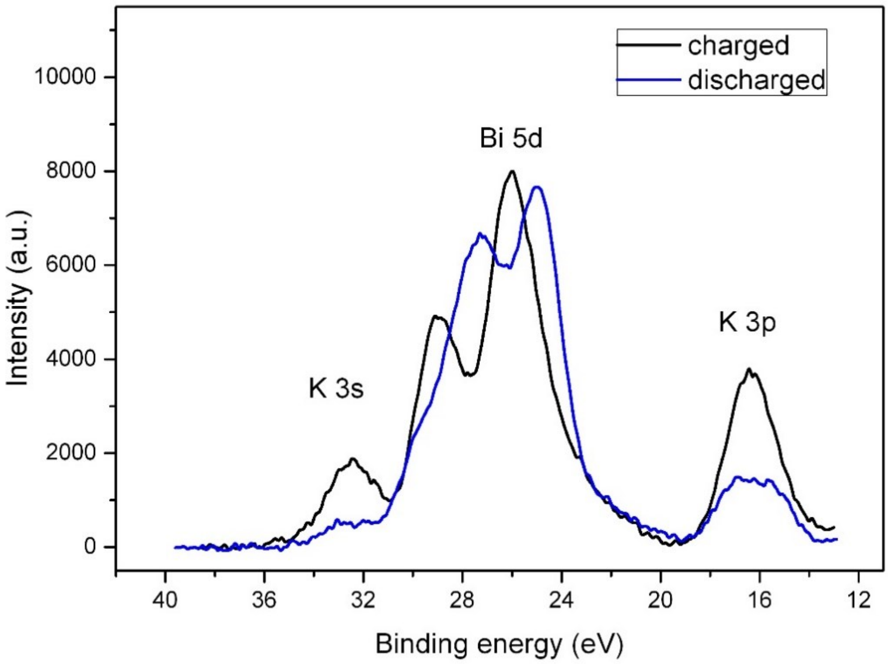

Figure S5. K 3p, Bi 5d and K3s XP spectra for the discharged electrode (blue line) and recharged electrode (black line).

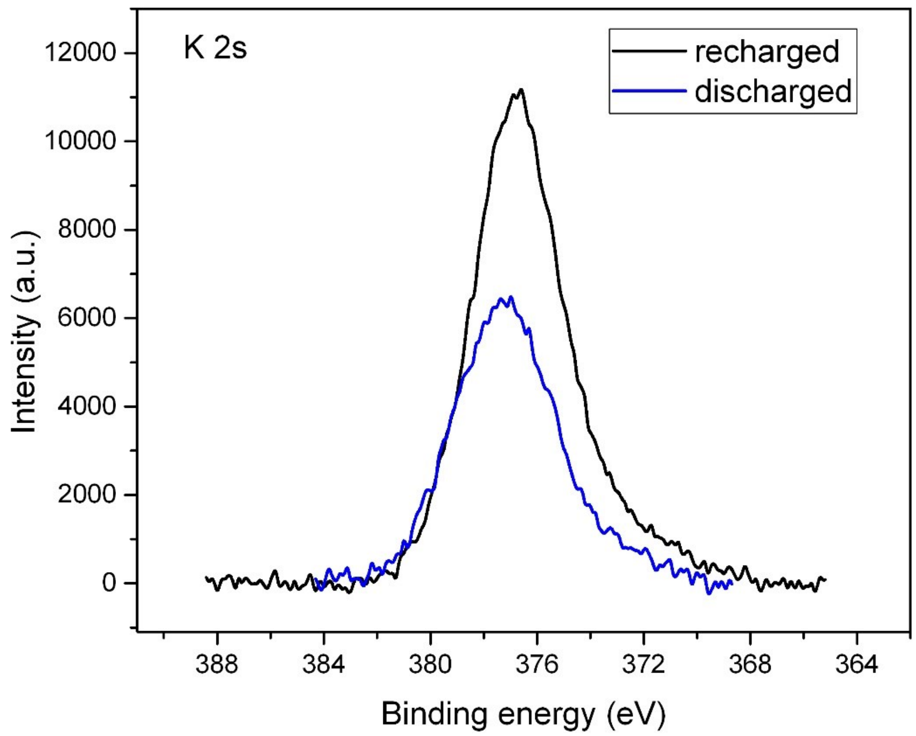

Figure S6. K 2s XP spectra for the discharged electrode (blue line) and recharged electrode (black line).

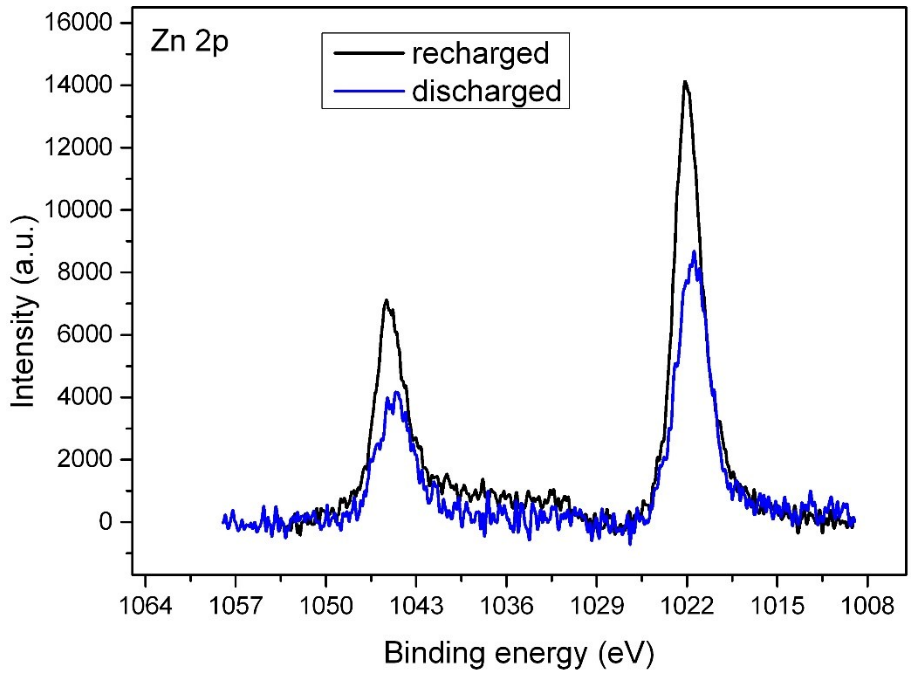

Figure S7. Zn 2p XP spectra for the discharged electrode (blue line) and recharged electrode (black line).

Conductivity measurements of Bi_2O_3 electrodes.

It is well known that Bi_2O_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_2O_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_2O_3 material, we have prepared the Bi_2O_3 electrodes depositing it in Nickel metallic foams or meshes. Figure S8 shows the I-V curves obtained for pure Bi_2O_3, Bi metal and the electrodes prepared depositing Bi_2O_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_2O_3 is deposited on Ni, the resistivity values obtained diminish with respect to pure Bi_2O_3. These conductivity increments are enough to permit using the Bi_2O_3 as active material of the positive electrode in the Zn/PVA-KOH/Bi_2O_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.

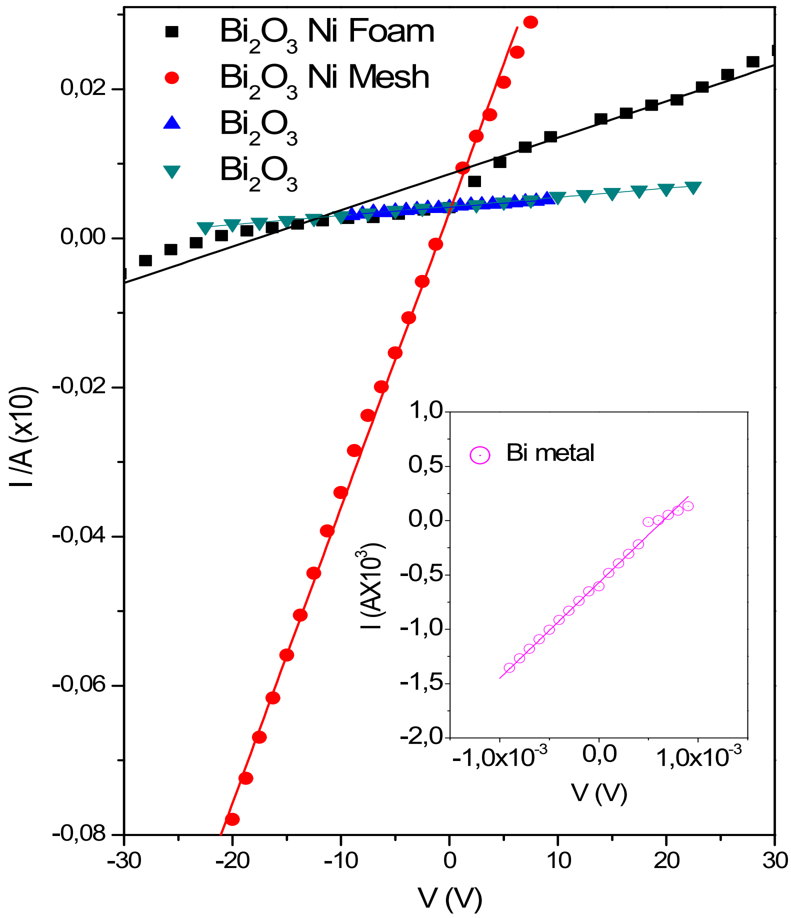

Figure S8. I-V curves obtained for pure Bi_2O_3, Bi metal and the electrodes prepared depositing Bi_2O_3 inside Ni foam and Ni mesh.

Table S2. Resistivity values (Ω·m) obtained for pure Bi_2O_3, Bi metal and the electrodes prepared depositing Bi_2O_3 inside Ni foam and Ni mesh.

Material	ρ (Ωm)
Bi_2O_3	$1{,}97\cdot10^{7}$
Bi_2O_3	$2{,}23\cdot10^{7}$
Bi_2O_3 + Ni foam	$4{,}94\cdot10^{6}$
Bi_2O_3 + Ni mesh	$6{,}06\cdot10^{5}$
Bi metal	$2{,}72\cdot10^{-3}$
Bi metal[6]	$1{,}17\cdot10^{-3}$

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