

Enhancing the Electrochemical Performance of ZnO-Co₃O₄ and Zn-Co-O Supercapacitor Electrodes Due to the In Situ Electrochemical Etching Process and the Formation of Co₃O₄ Nanoparticles

Abstract: Zinc oxide (ZnO) and materials based on it are often used to create battery-type supercapacitor electrodes and are considered as promising materials for hybrid asymmetric supercapacitors. However, when creating such electrodes, it is necessary to take into account the instability and degradation of zinc oxide in aggressive environments with a non-neutral pH. To the best of our knowledge, studies of the changes in the properties of ZnO-containing electrodes in alkaline electrolytes have not been carried out. In this work, changes in the structure and properties of these electrodes under alkaline treatment were investigated using the example of ZnO-containing composites, which are often used for the manufacturing of supercapacitor electrodes. Supercapacitor electrodes made of two materials containing ZnO were studied: (i) a heterogeneous ZnO-Co₃O₄ system, and (ii) a hexagonal h-Zn-Co-O solid solution. A comparison was made between the structure and properties of these materials before and after in situ electrochemical oxidation in the process of measuring cyclic voltammetry and galvanostatic charge/discharge. It has been shown that the structure of both nanoparticles of the heterogeneous ZnO-Co₃O₄ system and the h-Zn-Co-O solid solution changes due to the dissolution of ZnO in the alkaline electrolyte 3.5 M KOH, with the short-term alkaline treatment producing cobalt and zinc hydroxides, and long-term exposure leading to electrochemical cyclic oxidation-reduction, forming cobalt oxide Co₃O₄. Since the resulting cobalt oxide nanoparticles are immobilized in the electrode structure, a considerable specific capacity of 446 F g⁻¹ or 74.4 mA h g⁻¹ is achieved at a mass loading of 0.0105 g. The fabricated hybrid capacitor showed a good electrochemical performance, with a series resistance of 0.2 Ohm and a capacitance retention of 87% after 10,000 cycles.

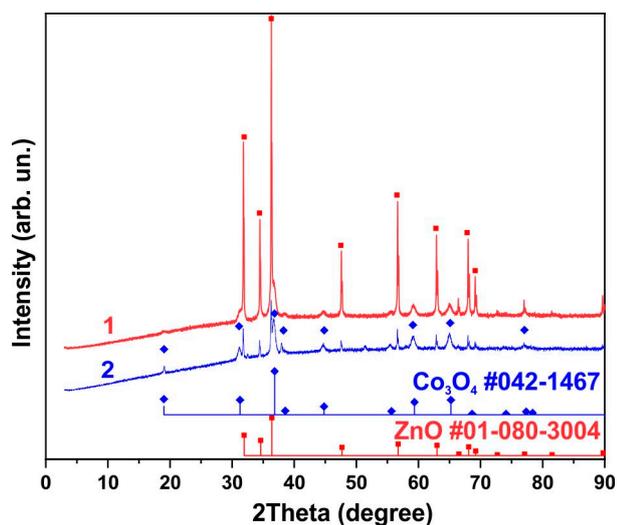


Figure S1. XRD data of the ZnO+Co₃O₄ sample after AcZn+AcCo synthesis and annealing at 450°C in air (1); the same sample after subsequent etching in 3.5 M KOH for 40 min (2).

Figures S2-S7 show the electrochemical characteristics of the hybrid capacitor.

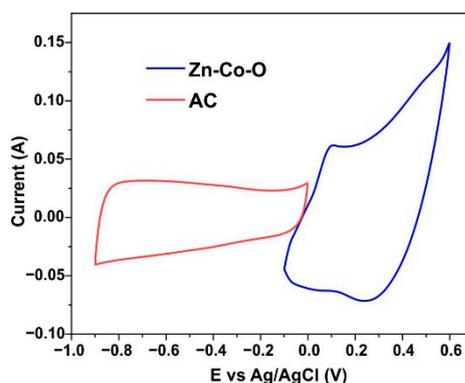


Figure S2. CV curves of h-Zn-Co-O/NF sample with an active mass of 0.025 g as the positive electrode and an AC/NF sample as negative electrode. CV curves were recorded in a three-electrode system at a scan rate of 0.01 V s⁻¹.

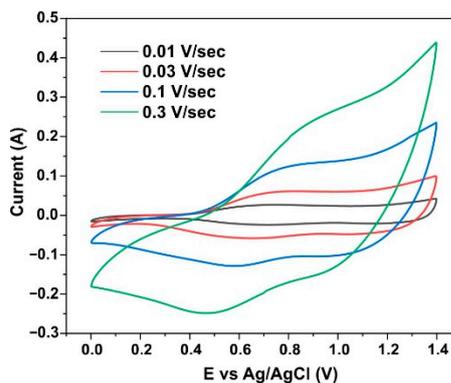


Figure S3. CV curves of h-Zn-Co-O/AC/NF capacitor at different scan rates of 0.01–0.3 V s⁻¹.

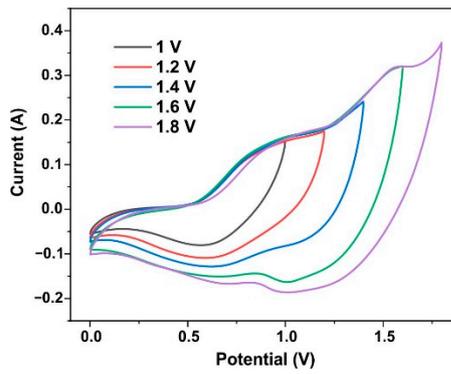


Figure S4. CV curves of the h-Zn-Co-O/AC/NF capacitor at different voltage windows, and at 0.1 V s^{-1} scan rate.

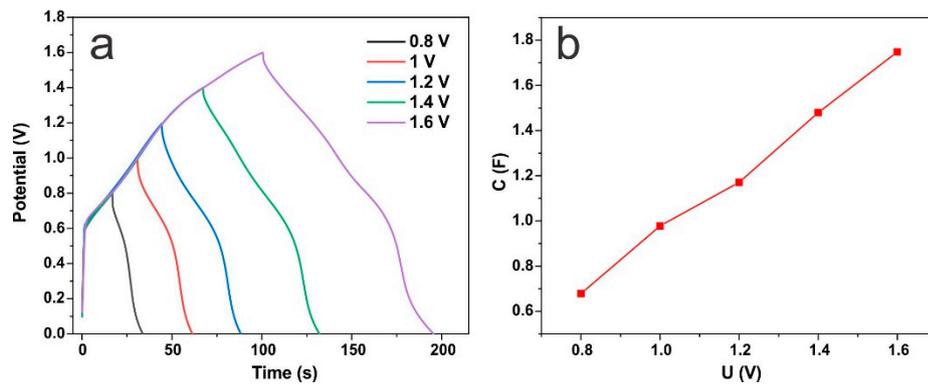


Figure S5. GCD curves of the h-Zn-Co-O/AC/NF capacitor at different operating potential windows, and at current of 32 mA (a); Plot of the capacity obtained from the GCD curves versus the operating potential window (b).

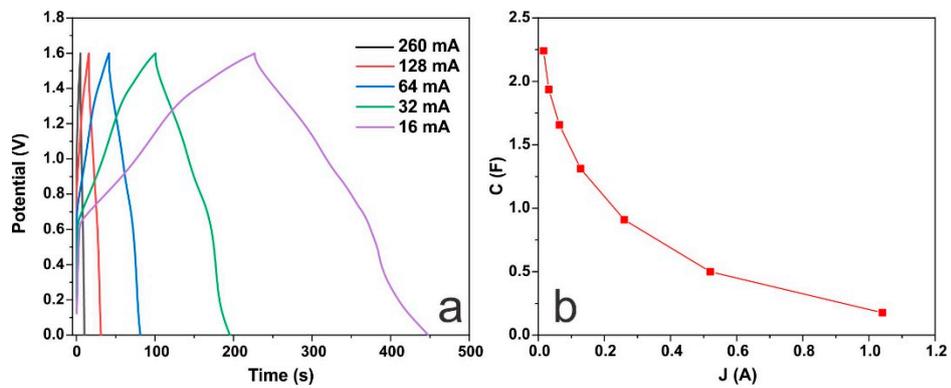


Figure S6. GCD curves of the h-Zn-Co-O/AC/NF capacitor at different current (a); Capacitance vs. current (b).

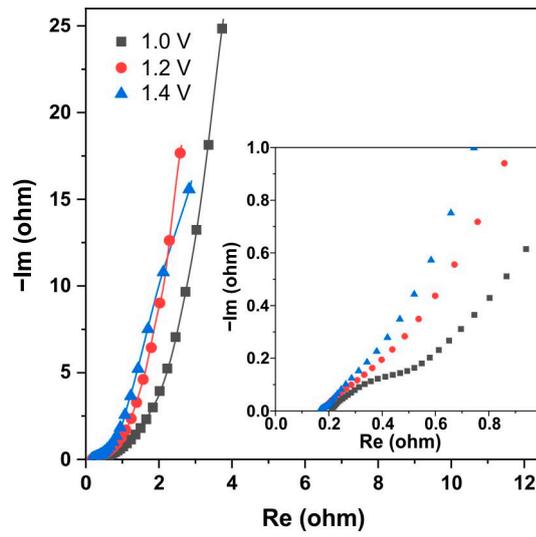


Figure S7. Nyquist plots of the h-Zn-Co-O/AC/NF capacitor in the frequency range of $0.003\text{--}5 \times 10^3$ Hz at various capacitor voltages; the inset indicates the Nyquist plots in the high-frequency region.