A structural study of Ni/NiO interface materials by Rietveld Refinement and DFT calculations

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Abstract: Electrochemical capacitors (ECs) are devices that combine both the specific energy of the batteries and the specific power of the conventional capacitors characteristics [1]. This feature allows electrochemical capacitors to be present in the industries of renewable energy, digital cameras, mobile phones and electric vehicles [2]. The mixed transition-metal oxides are emerging as promising electrode materials for ECs, due to their high electrochemical activities owing to the complex chemical compositions and their synergetic effects contribute to the exceptionally high specific capacity/capacitance [3].

The interface materials were obtained by calcination of a polymeric resin prepared by Pechini method. The X-ray diffraction (XRD) patterns were obtained using a SHIMATZU XRD-6000 model which provides Cu $K_\alpha$ radiation ($\lambda=1.544\text{Å}$). To obtain the microstructural data of the Ni, NiO and Ni/NiO materials, a Rietveld refinement (see figure 1) [4] was performed using the General Structure Analysis System (GSAS) program [5] suite with the EXPGUI interface [6].

All theoretical calculations were performed using the Ni and NiO crystallographic information file (CIF – ICSD 260169 and 9866, respectively). Calculations were performed using density function theory (DFT) [7,8] with the plane wave-pseudopotential framework, as implemented in the Quantum-ESPRESSO (QE) [9] package, with in the generalized gradient approximation (GGA). Electronic interactions were described by Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [10] with ultrasoft pseudopotential. We performed the electronic energy minimization with a tolerance of $10^{-6}\text{Ry}$ estimated scf accuracy, using a plane wave kinetic energy cutoff of 175 Ry and 700 for the charge densities. The Brillouin zone (BZ) sampling is carried out with a 8 x 8 x 8 Monkhorst-Pack k-points grid. The strain effects were calculated applying a strain compressive and tensile, consequently varying the volume of unit cell. The equilibrium volume parameters and bulk modulus were obtained by fitting energy vs volume curve to the Murnaghan, Birch-Murnaghan, Poirier-Tarantola and Vinet equation of state – EOS (see figure 2). The stress tensor
were obtained after full relaxations of all internal atomic coordinates by means of the conjugate gradient (CG) technique.

![Figure 1](image1.png)

**Figure 1** – Adjust by Rietveld method between the experimental and calculated X-ray diffraction patterns for the (A) NiO and (B) NiO/Ni.

The Fig. 1 show that the results obtained by the Rietveld refinement method were in good agreement with the observed XRD patterns. The Fig. 2 show relation between energy versus volume curve with fitting of EOS. The value of the bulk modulus obtained from EOS were in good agreement with the eq. Murnaghan for Ni of 253.52 GPa with experimental value of 229 GPa and for NiO of 278.77 GPa with experimental value of 205 GPa.

![Figure 2](image2.png)

**Figure 2** - The energy as a function of the volume with fitting of EOS for the (A) Ni and (B) NiO

**Key-words**: Ni/NiO interface, Rietveld refinement, DFT.

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**References**: