

Fabrication of Ordered Mesoporous Nickel Oxide Based Thin Film Electrodes and Their Electrochemical Properties

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Mesoporous nickel oxide is a p-type semiconductor that finds its application in various fields like lithium-ion batteries, solar cells, energy storage, water splitting, and electronic device[1]. Those applications require high surface area and thin films. There are plenty of methods to synthesize mesoporous nickel oxide and nickel oxide nanoparticles, like sol-gel, electrodeposition, microwave synthesis, etc.[1].

In this work, the molten-salt-assisted self-assembly (MASA) method was adopted to synthesize mesoporous nickel oxide (m-NiO) and nickel manganese oxide (m-Ni_xMn_{1-x}O)[2].

Both m-NiO and m-Ni_xMn_{1-x}O thin film electrodes were fabricated by spin-coating clear ethanol solutions of nickel and manganese salts with two surfactants (cetyltrimethylammonium bromide, CTAB, and 10 lauryl ether, C₁₂E₁₀) on top of FTO substrates, followed by calcination at high temperatures to ensure formation of the mesoporous oxide.

The thin films were analyzed in a wide range of salt-to-surfactant mole ratio, manganese salt-to-nickel salt mole ratio, and characterized by using powder x-ray diffraction (PXRD), N₂ - adsorption desorption measurement, x-ray photoelectron spectroscopy (XPS), imaging techniques (SEM and TEM) and electrochemical analysis.

The N₂ - adsorption desorption measurement gives a typical type IV isotherm that is characteristic for mesoporous materials. The surface area of m-NiO and m-Ni_{0.5}Mn_{0.5}O, calcined at 350 °C can reach up to 164 m²/g and 191 m²/g, respectively. Analysis of XRD pattern gives 3-4 nm crystalline pore walls for both oxides and in good agreement with surface area analysis.

Both mesoporous nickel oxide and manganese nickel oxide electrodes display promising electrocatalytic activity towards oxygen evolution reaction (OER), and have an overpotential of 298 and 223 mV, respectively, at 1 mA/cm².

During chronopotentiometry (CP) and cyclic voltammetry (CV) experiments, the very top surface of NiO pore wall transforms to Ni(OH)₂ that in the reverse cycle, transforms to NiOOH, and these two species are active in the water oxidation process[3]. The electrochemical cell is represented in Figure 1. Addition of manganese stabilizes the Ni(OH)₂ transformation on top of NiO core and improves the overpotential values.

The galvanostatic charge discharge (GCD) experiment show that NiO has high specific capacitance of 140 mF/cm² at 0.1 mA/cm² current density.

Moreover, due to unique optical properties, NiO shows electrochromic behavior with cycling, and salt-surfactant liquid crystalline gel electrolyte can be used to create an electrochromic device (see Figure 2). The contrast between transparent and dark states can be monitored by changing humidity, calcination temperature, and thickness of the film.

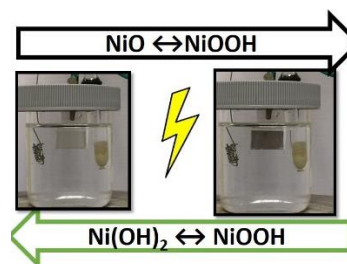


Figure 1. Three electrode electrochemical cell for m-NiO analysis.

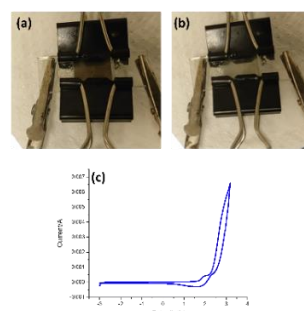


Figure 2. (a) The dark (b) and bleached states of m-NiO electrode, (c) CV of m-NiO-350 electrode from two electrode cell.

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