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Effect of nickel oxide synthesis conditions on its physical properties and electrocatalytic oxidation of methanol

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Nickel oxide (NiO) was synthesized using several methods and the various physical characteristics observed were correlated to differences in electrocatalytic activity, specifically relating to the oxidation of methanol in alkaline media. Room temperature NaOH-precipitated NiO showed the highest activity and stability towards methanol oxidation in hydroxide (0.005 M KOH) and carbonate (0.1 M Na_2CO_3) media of similar alkalinity. Rapid degradation of NiO electrodes was attributed to microcracking and disintegration associated with the formation of the γ-NiOOH/α-Ni$(OH)_2$ redox couple, in addition to repeated scans through the oxygen evolution reaction region. Carbonate electrolytes also exhibited average current ranges 3–4 times higher and charge transfer resistances around 85% lower than hydroxide electrolytes. This suggests carbonate may provide a better medium in terms of higher activity and more moderate alkalinity for electrochemical reactions than hydroxide solutions.

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1. Introduction

Nickel-based electrode materials have received considerable attention over the years as a result of their use in several applications, such as alkaline batteries, fuel cells, capacitors, sensors, and catalysts for various electrochemical reactions. Their stability in strongly alkaline environments, coupled with improved kinetics over acidic media and reduced cost compared to noble-metal catalysts, makes nickel a popular choice for a myriad of functions. Pure nickel oxide (NiO) and nickel hydroxide (Ni$(OH)_2$) have been synthesized for use in capacitors [1], batteries [2–4], and methanol oxidation for direct methanol fuel cells [5,6]. Various alloys incorporating nickel have also been investigated, such as Mn-substituted Ni$(OH)_2$ for Ni-metal hydride batteries [7], activated carbon fibers mixed with NiO for methane adsorption [8], polyaniline-supported Ni films for methanol oxidation [9], Ni-modified salophen catalysts for use in electrochemical sensors and methanol fuel cells [10], perovskite-type La–Sr–Ni electrodes for methanol fuel cells [11], and composite Ni–Mo–Si coatings for oxygen evolution/detection [12]. In many cases, the addition of nickel improved activity and stability over corresponding single-metal electrocatalysts.

Several different synthesis methods are reported for these pure Ni-based and Ni-alloyed catalysts. Electrodeposition and co-deposition are used frequently to produce thin films on various substrates, including polymers, glassy carbon, and graphite [5,6,9,12–16]. Other non-solution synthesis techniques include high-temperature decomposition of commercial precursors [17] and spray pyrolysis [18]. However, the most common and facile synthesis methods employed are aqueous-phase precipitations using soluble nickel salts. NH_4OH- and NaOH-induced precipitations of Ni catalysts under various synthesis conditions resulted in an array of physical characteristics [3,17,19–21]. The implications of these physical characteristics on electrochemical performance, however, are often not well understood.

In this study, we have attempted to make these connections and shed light on the electrochemical activity of nickel oxide in alkaline media. NiO is a catalyst for the oxidation of organic compounds and, thus, a potential candidate for sensor applications [5,6,9–11,15,16,22], but its activity is affected by competing reactions and physical attributes caused by differences in synthesis techniques. We examined the physical properties of nickel oxides made from several aqueous-phase synthesis methods and discuss their effect on the methanol oxidation reaction; in addition to the effect of other factors, such as electrolyte selection and competing reactions. Their activity and stability in both hydroxide and carbonate media were investigated using cyclic voltammetry and electrochemical impedance spectroscopy.

2. Experimental

2.1. Materials synthesis

All reagents were used as received, and all water used was ultra-pure 18.2 MΩ deionized water from a Millipore Direct-Q

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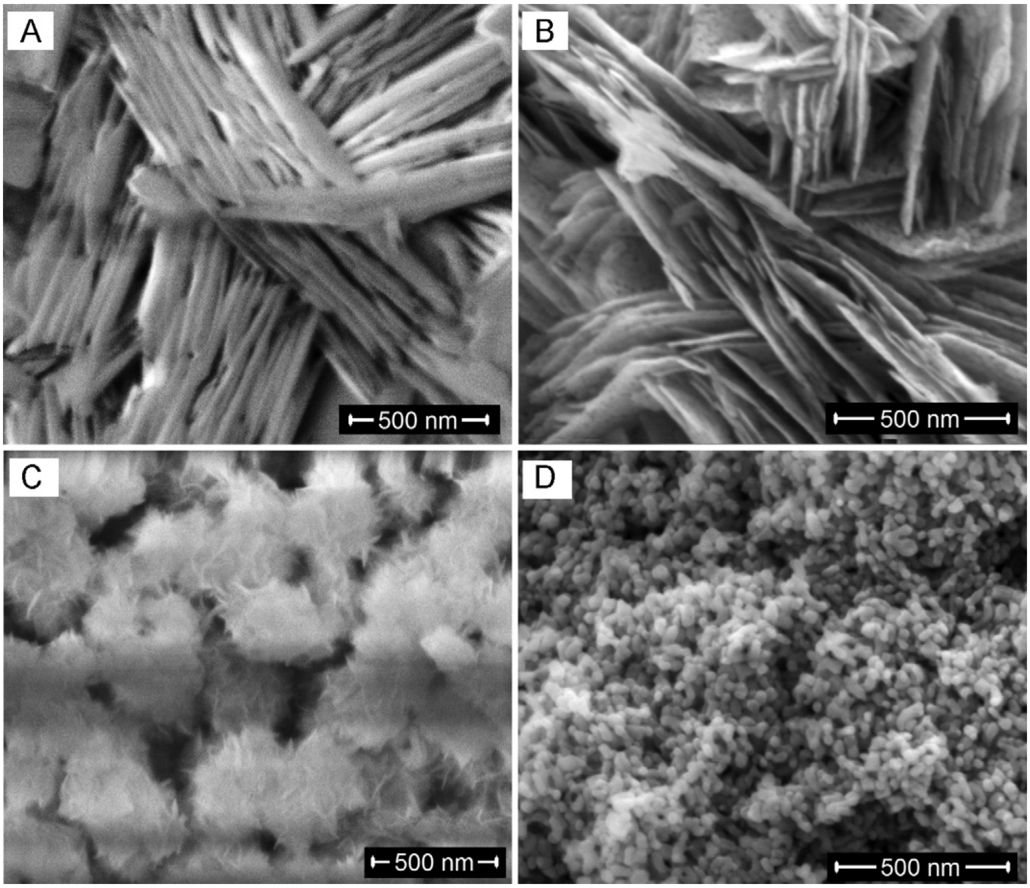

Fig. 1. SEM micrographs of reflux-precipitated (A) $Ni(OH)_2$ and (B) NiO, and RT NaOH-precipitated (C) $Ni(OH)_2$ and (D) NiO.

3UV purification system. Reflux-precipitated nickel oxide (reflux-NiO) was synthesized by preparing 50 mL of 0.5 M $Ni(NO_3)_2·6H_2O$ (Acros, 99%) in 10 M NH_4OH (Fisher, certified ACS Plus) and boiling the solution under reflux for 24 h, then allowing it to rest at room temperature for 24 h. The resulting green, precipitated precursor (reflux-$Ni(OH)_2$) was rinsed several times with deionized water, then dried on a hot plate at 90 °C overnight. The resulting powder was calcined in air at 500 °C for 2 h yielding NiO.

Sodium hydroxide-precipitated nickel oxide (NaOH-NiO) was synthesized by preparing 50 mL of aqueous 0.5 M $Ni(NO_3)_2·6H_2O$ under constant stirring. Two $Ni(OH)_2$ precipitation temperatures were investigated, room temperature (~20 °C) and the solution boiling point (~102 °C). Solution temperature was measured using a Hannah instruments HI9063 K-type thermocouple. NaOH pellets (Fisher, NF/EP/BP/FCC) were ground into a fine powder and then gradually added until the pH rose to between 8 and 10 to ensure complete precipitation of $Ni(OH)_2$. Solution pH was actively measured using an Accumet Excel XL60 Dual Channel pH/Ion/Conductivity/DO Meter. The solution was then capped and set aside for 24 h. The resulting green, precipitated precursors from each solution were rinsed several times with deionized water, dried overnight on a hot plate at 90 °C and then calcined in air at 500 °C for 6 h. Nickel hydroxide precursors and nickel oxide powders prepared by this method at room temperature are denoted RT NaOH-$Ni(OH)_2$ and RT NaOH-NiO, respectively, and those synthesized at the boiling temperature are denoted BT NaOH-$Ni(OH)_2$ and BT NaOH-NiO, respectively.

2.2. Instrumentation and techniques

Catalyst microstructure was determined using an FEI Quanta FEG250 scanning electron microscope (SEM). Specific surface areas were obtained through Brunauer–Emmett–Teller analysis (BET) using a Micromeritics ASAP 2020 system. A Bruker D8 Advance X-ray diffractometer (XRD) with a Cu $K\alpha_1$ ceramic X-ray tube ($\lambda = 0.1540562$ nm) was used to evaluate crystal structure and average grain boundary size. X-ray photoelectron spectroscopy (XPS) was performed using a Physical Electronics multiprobe with a Perkin–Elmer dual anode X-ray source. Thermogravimetric analysis (TGA) was performed concurrently with differential scanning calorimetry (DSC) using a Netzsch STA 449 F3 Jupiter Simultaneous TG-DTA/DSC Apparatus. For each of these simultaneous thermal analysis (STA) tests, approximately 20 mg of catalyst precursor was placed into a sample alumina crucible with a punctured lid to allow vapors that formed during calcination to escape. An empty alumina crucible with a punctured lid was used as a reference.

2.3. Electrochemical tests

Electrochemical tests were performed in a custom three electrode cell (Adams & Chittenden) using an Autolab PGSTAT302N Potentiostat (Eco Chemie) with a platinum flag as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All working electrodes were fabricated by preparing between 10 and 20 mL of a 0.3 mg/mL dispersion of the selected catalyst in deionized water and placing it in an ultrasonic bath until the catalyst particles were uniformly distributed throughout. Next, 20 μL of the dispersion was deposited onto a glassy carbon (GC) disk electrode (Pine Instrument Company, $A = 0.196\ cm^2$) and spin dried at 450 rpm for 1 h using a Pine AFMSRCE modulated speed rotator. Once dry, 20 μL of a 0.05 wt.% Nafion solution (DuPont) was deposited on the GC electrode and spin dried. Nitrogen gas (Airgas) was bubbled in each solution for 1 h prior to each electrochemical

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