Characterization of electrochemically deposited films from aqueous and ionic liquid cobalt precursors toward hydrogen evolution reactions

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ABSTRACT

Electrodepositions of cobalt films were achieved using an aqueous or an ethylene glycol based non-aqueous solution containing choline chloride (vitamin B4) with cobalt chloride hexahydrate precursor toward hydrogen evolution reactions from sodium borohydride ($NaBH_4$) as solid hydrogen feedstock (SHF). The resulting cobalt films had reflectivity at 550 nm of 2.2% for aqueously deposited films (ACoF) and 1.3% for non-aqueously deposited films (NCoF). Surface morphology studied by scanning electron microscopy showed a positive correlation between particle size and thickness. The film thicknesses were tunable between >100 μm and <300 μm for each film. The roughness (Ra) value measurements by Dektak surface profiling showed that the NCoF (Ra = 165 nm) was smoother than the ACoF (Ra = 418 nm). The NCoFs and ACoFs contained only α phase (FCC) crystallites. The NCoFs were crystalline while the ACoFs were largely amorphous from X-ray diffraction analysis. The NCoF had an average Vickers hardness value of 84 MPa as compared to 176 MPa for ACoF. The aqueous precursor has a single absorption maximum at 510 nm and the non-aqueous precursor had three absorption maxima at 630, 670, and 695 nm. The hydrogen evolution reactions over a 1 cm^2 catalytic surface with aqueous $NaBH_4$ solutions generated rate constants (K) = equal to 4.9×10^{-3} min^{-1}, 4.6×10^{-3} min^{-1}, and 3.3×10^{-3} min^{-1} for ACoF, NCoF, and copper substrate respectively.

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1. Introduction

The unique properties of the cobalt materials including corrosion resistance, thermal stability, magnetic properties make them valuable to be applied in many different fields such as: medical applications, aerospace applications, energy applications, radar absorbing materials, magnetic materials, and as catalysts [1–15]. The properties of cobalt films are influenced by crystallinity and film thicknesses [1–6]. Decreasing cobalt particle size to the nanoscale enhances the catalytic and magnetic properties [1,7]. The core phase of the metal particles has generally been face-centered cubic and non-magnetic. Whereas the shell of the particles are hexagonal close packed and exhibit magnetic properties [1–5].

Cobalt based materials show great promise in many energy applications [8–10]. Specifically, cobalt-based films have been applied as electrodes in hydrolysis reactions. They are currently being researched as a cheaper replacement for platinum mesh electrodes and have demonstrated higher cycling stability and efficiency as a result of their catalytic properties [11,12]. Improvements to hydrolysis catalyst electrodes are an important area of research inquiry because of the long-term applicability of hydrogen gas as a replacement for carbon-based fuels. Furthermore, 5% efficiencies have been achieved using solvated cobalt oxide nanoparticles to perform hydrolysis in a solar active application as photocatalysts [7]. Reactions using cobalt oxide as a photocatalyst could provide a breakthrough in oxygen and hydrogen fuel production.

Typical cobalt electro-depositions are described as a silvery-gray coating, prized for their oxidative stability, and are fabricated from aqueous cobalt salt solutions [13]. Ionic liquids are emerging as a possible solvent replacement for water in electrodepositions because of their larger potential window [16]. Further, ionic liquids do exhibit a pH making their treatment less intensive than that of aqueous waste [17]. Many electrodeposition studies of ionic liquid liquids have found a higher deposition rate, and the capability to deposit visually varying films [16,18–21].

Hydrogen gas is an excellent alternative energy source because of its higher specific energy (142 MJ/kg) and green emissions as compared to fossil fuels. Solid hydrogen feedstocks (SHF) are desired because of the dangers involved in the transportation of pressurized gases and is a large area of study. Further, the search for feedstocks that can evolve hydrogen gas in green conditions would be optimal. $NaBH_4$ is one of such storage materials because it reacts readily with water to produce hydrogen gas. The oxidation reaction that $NaBH_4$ undergoes in water is slow and many materials are being studied for catalytic activity within this reaction [22].

The purpose of this study was to characterize the non-aqueous electrochemical depositions of cobalt chloride and compare to aqueous depositions of cobalt under the same conditions from a macro to nano-scale and to further investigate novel non-aqueous bulk depositions of cobalt and test the reactivity of the films for hydrogen evolution from sodium borohydride as SHF.

2. Experimental

The two cobalt chloride hexahydrate ($CoCl_2·6H_2O$) (Fisher Scientific, 99%) electrolytic solutions were prepared with the same molarity (0.33 M). Prior to addition of the $CoCl_2·6H_2O$, a non-aqueous solvent was prepared at $70°$C in a 7:6 wt ratio of choline chloride (ChCl) (Alfa Aesar, 98%) to ethylene glycol (EG) (Fisher Scientific, Certified) [16,18,23–27]. The non-aqueous solution was kept at $70°$C to maintain solvation of the ChCl and $CoCl_2·6H_2O$ during all steps of the preparation and deposition [18]. For aqueous precursor preparation, $CoCl_2·6H_2O$ was solvated in deionized water, then acidified drop wise with 6 M HCl to a pH of 2.03 and maintained at $25°$C throughout deposition.

Copper substrates of $2 cm^2$ (Goodfellow 99.95%) were used as deposition cathodes. The cathodes were briefly submerged in glacial HCl (Fisher Scientific) to remove the oxide layer, rinsed in DI water, dried, then attached as working electrodes in the electrochemical cell filled with precursor solution. The working deposition area was isolated using polyimide tape. The two variations of cobalt depositions were synthesized using a double-jacketed standard three-probe electrochemical cell (Princeton Applied Research) with Gamry electrochemical software and hardware (PCI-4G750). Temperature of the electrochemical cell was maintained by Julabo F25 water bath/circulator. High-density carbon rods were used as the counter and reference electrodes to prevent contamination of other metal ions. Optimal redox voltage for aqueous precursor was determined to be ~2 V, and ~1.5 V for non-aqueous based on cyclic voltammetry. In order to achieve a black film, a 3 V potential was run between the working and counter electrodes for varied times (10, 15, 30 min) for both precursor solutions [18,20,21]. At the 3 V potential, the current density was 65 mA per cm^2 and 120 mA per cm^2 for aqueous and non-aqueous precursor solutions respectively [18]. Samples were rinsed then bath sonicated in deionized water to remove residual electrolyte after their electro-deposition cycle. After rinsing, films were stored in isopropanol to prevent oxidation until characterization.

UV–vis spectroscopy (Hitachi U-3900) was used to characterize the precursors. The non-aqueous solution was characterized after dilution by adding one drop of precursor to 3.95 mL of the original eutectic solution and the aqueous solution was characterized as prepared. The spectra were normalized for comparison. UV–vis reflectivity measurements of cobalt depositions were obtained using Ocean Optics hardware and software with reflectivity attachment. Sputter coated aluminum was used as a standard for these measurements representing maximum reflectivity.

Morphology, particle size, lateral homogeneity, and atomic composition of cobalt depositions were characterized using FE-SEM (Hitachi S-4700) with EDS attachment (Ametek EDAX). Thicknesses of the cobalt films were measured using backscatter SEM (Phenom G2 Pro) of cross-sectional micrographs. The roughness and hardness of the films were determined using a Dektak 2D surface profiler and Vickers micro-hardness tester (Shimadzu) respectively. The sticky tape test was utilized to qualitatively analyze the adhesion of deposited films to the substrates.

Structure and grain size of crystallites within the two cobalt films were analyzed using Rigaku X-ray diffraction and were compared to ICDD-JSPDC cards as follows; Co hexagonal close packed (HCP) from 05 to 0727, Co face centered cubic (FCC) from 01 to 1259 and Cu FCC from 04 to 0836. The spectra were normalized for comparison. Electrodeposition parameters were duplicated to minimize differences in crystal structure caused by variation in voltage. Tighter crystal packing has been achieved by increasing voltage and is characterized by peak-shifts in XRD [21].

Catalytic activity of the two depositions in hydrogen evolution reactions was characterized using a gravimetric water displacement system [28]. The reaction of 100 mL of $8.35 × 10^{-4}$ molar $NaBH_4$ (J.T. Baker 98%) was catalyzed using 1 cm^2 of the depositions and using the copper substrate as a baseline. The water displaced by the reaction was measured by an Ohaus Pioneer Balance (Pa124) with proprietary mass logging software.

3. Results and discussion

The visually differing precursor solutions are shown in Fig. 1 inset and the UV–vis absorption spectra of the dilute non-aqueous and as prepared aqueous solutions are shown in Fig. 1. The aqueous $Co(II)Cl_2$ precursor solution had a single maximum at 510 nm (2.43 eV). The non-aqueous precursor had three maxima at 630 (1.96 eV), 670 (1.85 eV), and 695 nm (1.78 eV).

The non-aqueous $Co(II)Cl_2$ solution showed three spin-allowed bands indicating tetrahedral cobalt(II) complexes, that is, $^4A_2(F)$ to $^4T_2(F)$, $^4A_2(F)$ to $^4T_1(F)$, and $^4A_2(F)$ to $^4T_1(P)$. Usually such complexes show two bands between 690 and 625 nm, which can be assigned to $^4A_2(F)$ to $^4T_2(F)$ and $^4A^2(F)$ to $^4T_1(F)$, respectively; $^4A_2(F)$ to $^4T_1(P)$ are usually observed as a well-defined shoulder at ~550 nm [29].

The SEM micrographs (Fig. 2) reveal the lateral coverage of the cobalt micro-particles over the copper substrates. The comparisons of Fig. 2(B–D) show the differences in packing and homogeneity of micro-particles by increasing deposition time. The non-aqueously deposited cobalt film (NCoF) is similar to a nickel film deposited using similar solvent [20,29]. Varying solvent can be compared in Fig. 2A and B. Fig. 2A shows the smaller micro-particles of the aqueously deposited cobalt film (ACoF) densely deposited with some inconsistency in coverage. Fig. 2B shows similar inconsistency, however much larger particle size and less dense particle packing.

The micrographs shown in Fig. 3 depict different surface morphologies. The NCoFs have a non-continuous film coverage as can be seen by the gaps between particles where the ACoF has a more continuous coverage. The particles deposited are more defined in the NCoFs and more conjoined in the ACoFs. The particles of the ACoF (Fig. 3B) were ~778 nm. The NCoF particle sizes increased as deposition time increased. At ten minutes of deposition time the NCoF particles were smaller than that of the ACoF particles, ~693 nm and increased to ~757 nm at 15 min. Expectedly at thirty minutes the particles were larger ~793 nm. Particle size for NCoF is directly proportionate to deposition time. There is no evidence of nanostructures from the SEM micrographs of both films. However, tunability of particle size could yield nano-scale cobalt particles for pulsed depositions.

The peaks of relevant film composition were of Co, Cu, O, and C (Fig. 4). Copper peaks which are also present in the XRD spec-