Pulsed Electrodeposited Nickel – Cerium for Hydrogen Production Studies

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**ABSTRACT.** The approach of alloying different elements results in new alloy phase with exclusive properties that could be a potential candidate in various applications. In the present work an attempt has been made to electrodeposit Nickel-Cerium (Ni-Ce) alloy. Nickel is an intriguing metal with much availability in earth’s crust. The catalytic power of Nickel based alloys towards hydrogen evolution reaction has been already reported for Nickel-Metal alloys, NiO/Ni and Nickel-Rare Earth metals \cite{1, 2}. Furthermore, alloying of Nickel with rare earth materials induces significant properties. Amongst rare earth elements, Cerium is a unique lanthanide element which has attracted more attention owing to its different electronic structures such as Ce\textsuperscript{3+} and Ce\textsuperscript{4+} which could result in different optical and catalytic properties. Ni-Ce coatings were electrodeposited on stainless steel substrate by pulsed electrodeposition technique \cite{3} form acidic aqueous bath of Nickel acetate and Cerium acetate. Boric acid is used as an additive for smoother deposition of the sample. The deposition was found to be favoured at applied current density of 10 mA/cm\textsuperscript{2}. X-Ray diffraction, High Resolution scanning Electron Microscopy and Energy dispersive spectroscopy were used to characterize the prepared sample.

**Introduction.** Hydrogen Evolution Reaction (HER) is of great importance since hydrogen is one amongst eco-friendly sources of energy with large energy density which makes it a potential candidate in energy storage and as an energy carrier. The splitting of water, hydrogen production from acidic/alkaline solutions are the popular methods of HER. The most efficient way of producing hydrogen with least amount of energy is to scale down the cathodic over potential in the electrolysis process. Accordingly a suitable choice of electrode material is necessary. Noble metals such as platinum and its alloys are developed and exhibit good activities indeed. However, high costs of these materials are often very prohibitive. Ni-based catalysts show improved properties \cite{1, 2} as electrodes and catalysts for HER. Rare earth elements are major alloying elements and the inclusion of rare earth elements gives higher functional properties to the material. An attempt has been made to alloy cerium with nickel through pulsed electrodeposition and characterized. The electrochemical activity of the Nickel-Cerium (Ni-Ce) are investigated through cyclic voltammetry.

**Experimental Procedure**

The Nickel-Cerium film is electrodeposited by employing galvanostatic pulsed electrodeposition technique on Stainless steel (cathode) substrate of grade 316L while graphite sheet serves as the anode. The electrodes were kept stationary with a distance of 2 cm between them. 0.1 M of Boric acid added as an additive which helps for smooth deposition of sample on the substrate. The electrolytic bath consists of Nickel acetate tetrahydrate and Cerium (III) acetate hydrate in the ratio of 4:1. The cathodic deposition is made on an area of 10 cm\textsuperscript{2} in the stainless steel with a applied current density of 10 mA/cm\textsuperscript{2}. The pH of the bath is maintained ~2. The duration of deposition is 40
minutes with 40% Duty cycle at room temperature. After deposition, the deposits were rinsed 4 to 5 times with de-ionized water and dried.

Results and discussion

Structural studies

The structural analysis of the as-deposited Ni-Ce is characterized using XRD. From the XRD pattern (Fig.1), there is no distinct peaks for Ni-Ce appears in the pattern but there is a shift in the peaks towards higher angle on comparison with pure Ni peaks (JCPDS no. 01-089-7128). There is no intermetallic phase formed between Ni and Ce. However there is a possibility of formation of Ni-Ce solid solution.

Morphological Studies

The surface morphology of the Ni-Ce film is characterized through HR-SEM. The SEM image reveals smooth deposition of irregular shaped grains. The size of the grains are calculated using ImageJ
software which ranges from 90 nm to 400 nm. The thickness of the film is calculated from the cross section view and estimated to be approximately one micrometre.

**Compositional analysis and Elemental mapping**

![EDX Image of Ni-Ce](image1)

Fig. 3. EDX Image of Ni-Ce.

Fig. 3 denotes the EDX spectrum of the Ni-Ce which evidences the presence of Ni and Ce in the film. The standard electrode potentials of Ni (-2.5 V) and Ce (-2.3 V) are nearly close and this favours the deposition of Nickel and Cerium simultaneously. Elemental mapping of Ni-Ce film (Fig.4) further confirms the presence of cerium in the sample. The red spots represent the presence of nickel and the green dots represents the occurrence of cerium in the sample. Absence of any other peaks in the spectrum shows the purity of the sample.

![Elemental mapping of Ni-Ce](image2)

Fig. 4. Elemental mapping of Ni-Ce.

**Electrochemical studies**

The cyclic voltammetry (Fig. 5 (a)) and linear sweep voltammetry (Fig.5 (b)) curves are recorded using three electrode electrochemical cell setup at room temperature. Ni-Ce deposited on the stainless steel substrate was taken as the working electrode and platinum is taken as the counter electrode while saturated calomel electrode serves as the reference electrode. The performance of Ni-Ce towards HER was tested in 0.5 M KOH alkaline solution at a scan rate of 50 mV/s.
From the LSV the tafel plot of Potential Vs log i is drawn (Fig.6) over the kinetically controlled region. The tafel slope is evaluated to be 304 mV/decade. The tafel slope values for the rate determining step of HER are 120 mV/dec, 40 mV/dec and 30 mV/dec for Volmer, Heyrovsky and Tafel steps respectively. The obtained tafel slope of 304 mV/dec suggests that hydrogen evolution on Ni-Ce electrode probably occurs by tafel mechanism[5].

Summary. Nickel-Cerium coating on stainless steel substrate is successfully deposited using pulsed electrodeposition method. The prepared film is characterized through XRD, HRSEM, EDX and Cyclic Voltammetry. The XRD peaks show the formation of Ni peaks. The HRSEM depicts the formation of irregularly shaped grains. The EDX and elemental mapping analyses confirmed the presence of nickel and cerium in the sample. From the electrochemical studies, the tafel slope is calculated and suitable mechanism for hydrogen evolution with Ni-Ce as working electrode is proposed.
References


Cite the paper