



The nickel supported platinum catalyst for anodic oxidation of ethanol in alkaline medium



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ARTICLE INFO

Article history:

Received 3 June 2015

Received in revised form 25 August 2015

Accepted 9 September 2015

Available online 14 September 2015

Keywords:

Electrooxidation
Ni–Pt catalyst
Exchange current
Intermediates
Reaction path

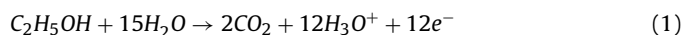
ABSTRACT

In search for cheaper anode catalyst for oxidation of ethanol, a few novel anodes were constructed by thin deposit of nano-crystalline Pt of varying load on planar Ni support by galvanostatic deposition to different extents from a millimolar solution of precursor salt in absence of any capping agent. The morphology and the excellent electrocatalytic activity of the electrodes were investigated by spectroscopic, microscopic, and electrochemical techniques. The studies reveal that the particles are agglomerated interconnected spherical shaped composite with a radius in the range of 12–50 nm. The change in electrocatalytic activity in reference to anodic oxidation of ethanol is found to depend on the composite effect of loading of Pt, composition of Ni–Pt binary catalyst and the diameter of the nano-crystallites constituting the electrodes. The anode containing ca. 50 atom% of Pt together with Ni at the surface shows the highest electrocatalytic activity with respect to current density, poison tolerance and exchange current density. For both Ni and Ni/Pt catalysts electrochemical oxidation of alkaline ethanol occurs through intermediates like acetaldehyde and sodium acetate. A possible path of reaction is also proposed.

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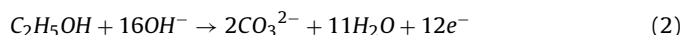
1. Introduction

In recent years, direct ethanol fuel cells (DEFCs) have gathered more attention and attraction as promising power source than methanol fuel cell. Methanol has higher volumetric energy density (4.82 kWhL^{-1}) than hydrogen (0.53 kWhL^{-1} at 20 MPa) and its storage, transportation and handling are easy but its toxicity, high crossover, slow kinetics etc. create problems for its development [1]. On the other hand ethanol is useful for its several intrinsic and additional advantages: low toxicity, low cost and high energy density (6.34 kWhL^{-1}) [2–4] etc. Ethanol can be produced in large quantities from biomass [5] and it is used as substantial energy source in ‘green technology’ [6,7]. Research for the development of ethanol fuel cells are mostly performed in acid medium for high proton conductivity, favourable oxygen dissolution thermodynamics and also easy removal of CO_2 after complete oxidation of ethanol [7–8], following Eq. (1):



However, in acid medium this oxidation process is slow and produces strongly adsorbed carbonaceous intermediates, so active

sites of catalyst are poisoned affecting fuel cell efficiency [9]. Less poisoning of electron source electrodes [10,11] and low over potential loss make alkaline medium beneficiary for ethanol oxidation reaction (EOR) [12]. So, high practical efficiency [13,14] is achieved due to high actual operating potentials for many fuel cells in alkaline medium. Complete ethanol oxidation in alkaline medium follows Eq. (2):

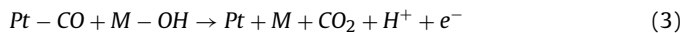


Scientific world has witnessed constant efforts to construct potential negative electrodes of cost effective fuel cells for transportation and stationary applications [15]. In many studies, Pt has been utilised as base metal of binary and ternary metal composite for electrocatalysis of oxidation of alcohols [1,16,17]. This is because that Pt is the standard and seemingly the unique and best single metal catalyst for anodic oxidation of hydrogen and the hydrogen-part of organic molecules, via, dehydrogenation. So, it is widely used as worth component of negative (anode) electrode material in both proton exchange membrane fuel cells (PEMFC) and direct alcohol fuel cells (DAFC) [18]. But, Pt is a quite costly metal. So many scientists have used suitable economic alternative to Pt e.g. Pd for electro oxidation of alcohol [19,20] without much loss of activity. Since electrode reactions occur essentially on the surface of the electrodes, it is believed that the formation of a stable thin layer of metal catalyst might reduce the cost of the anode sufficiently.

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Moreover, pure Pt exhibits fast poisoning [21] due to formation of a poisonous intermediate, Pt–CO and possibly other adsorbed carbonaceous intermediates during anodic oxidation of alcohols. Introduction of second and third oxophilic transition metal like Ru [22,23], Mo [24], Sn [25], Pd [3,26], Rh [18] etc. has been found to be very useful since the intermediate of the oxophilic metals, M–OH can destroy Pt–CO by the following electrodic reaction in acid medium [1,3,22]



and thus, continue activation by producing fresh metal sites for dehydrogenation and subsequent processes [27]. But, despite application of such metals the efficiency of DAFC is still not sufficient for practical applications. On the other hand, Ni forms NiOH [28] and Ni(OH)₂ at low potentials and NiOOH at higher potential [29] in alkaline media. These hydroxides may be useful to reduce deactivation of the positive electrodes by removal of the poisonous intermediate Pt–CO [30]. More over alloying of Ni with Pt may make Pt–CO bond weaker in strength by the decrease of the density of the states of Fermi level of Pt [30,31]. So, Wieckowski and his group [32] worked on methanol oxidation with Ni/Pt electrode and found better electrocatalytic activity than Pt in presence of Ni in acid medium. After combination with some metal or non-metals, Ni is also used for sensor of alcohols [33–35] due to its consistent electrochemical behaviour, particularly in alkaline medium. In our previous studies we observed the importance of optimum loading [3] and composition of some other electrocatalysts [29] (on planar electrode) to get the best performance of the anode used in electrooxidation of ethanol. Here, we report the influences of loading, composition and size of the crystallites of platinum deposited on the planar Ni support to get the best performance in context to the anodic oxidation of ethanol in alkaline medium. Techniques used in this study are cyclic voltammetry (CV), Chronoamperometry (CA), field emission scanning electron microscopy (FE-SEM) and energy dispersion X-ray spectroscopy (EDX).

2. Experimental

2.1. Reagents and preparation of electro-catalyst

Ni-foil (>99.9% gold levels, Aldrich Chemical Company Inc.) having thickness of 0.0125 cm was used as substrate for the Pt-deposition. The mid portion of the foil was wrapped with the Teflon tape (Champion), and the two bare portions were cleaned, polished and degreased and finally washed with distilled water and dried. One bare portion was used for electrical connection. The other portion was used for Pt deposition. Construction of Ni/Pt electrodes was done by cathodic deposition of Pt on Ni support at room temperature by applying a galvanostatic current density of 30 mA cm⁻² for 1, 5, 10, 30, 60 and 120 min. The corresponding electrodes are represented as Ni/Pt1, Ni/Pt5, Ni/Pt10, Ni/Pt30, Ni/Pt60 and Ni/Pt120, respectively, of apparent (geometrical) surface area 0.045 cm², throughout the whole study. The (0.04% m/v) solution for deposition of Pt was made from 2 mass% chloroplatinic acid (H₂PtCl₆, 4H₂O) in 2 M HCl and the deposition on Ni is executed in 2 M HCl. The salt for preparation of chloroplatinic acid solution was taken from Arora Matthey Ltd. and used as received. Large Pt foil (3 cm²) was used as a counter electrode for deposition. All the reagents used were of AR grade and water throughout the experiment was triply distilled. For metal deposition, constant current charger (DB-300, DB Electronics) were used as current source. In the experiment of product analysis, a current density of 30 μA cm⁻² was drawn for 72 h from a two-compartment cell containing 1 M EtOH in 1 M NaOH solution in N₂ atmosphere using Ni and Ni/Pt30 electrocatalysts as anodes in separate experiments

and large Pt electrode as cathode in both cases. The resulting solution present in anode compartment was dried in vacuum and the obtained semi solid product for each electro catalyst was used for FTIR study (Perkin Elmer, Spectrum RX1, Resolution 4 cm⁻¹).

2.2. Electrochemical measurements

Two compartment glass cell fitted with a three electrode assembly was used where Hg/HgO/OH⁻ (1 M) (MMO) electrode [equilibrium electrode potential ~0.1 V with respect to Standard Hydrogen Electrode (SHE)] and a large Pt foil were used as reference and counter electrode respectively in all electrochemical measurements. CV and CA studies [36] were carried out for each electrode in 1 (M) EtOH in 1 M NaOH and in 1 M NaOH in absence of ethanol (blank) using computer aided Potentiostat/Galvanostat Instrument (AUTOLAB Company). The Cyclic Voltammograms were recorded during multiple scanning until a steady CV is achieved. Before each study, electrodes were allowed to equilibrate until a high negative value of steady open circuit potential is obtained. Any further activation by sweep of potential or any other means was avoided during all electrochemical measurements. Surface characterization were done by SEM (JEOL-JSM-6360) study at an accelerating potential of 5KV and by energy dispersive X-ray (EDX) using an INCAX-Stream Oxford instruments (UK) coupled with the scanning electron microscope.

3. Result and discussion

3.1. Surface study of the electrodes

In order to have knowledge of morphology of the electrochemically deposited electrodes, analysis of FE-SEM images was performed. Higher resolution FE-SEM images of the selected Ni/Pt electrodes (Ni/Pt1, Ni/Pt10, Ni/Pt30 and Ni/Pt60) are presented in Fig. 1(a–d). Fig. 1(a) reveals the deposition of white granules of Pt having average diameter of ca. 12 nm on the relatively black and flat nickel surface. Most of the granules are distinguishable, although the formation of layer structure has already started. Fig. 1(b) shows relative increment of the layer in comparison to granular structure. The development of layer structure is associated with the development of large black holes and the granules having diameter of ~25 nm are deposited on the layers. Thus, it indicates that small granules are the building blocks of layers.

In Fig. 1(c,d), it reveals that several layers with some holes are formed by the granules of greater size (~35–50 nm) and these are the building units of layer structure. So, on successive addition of Pt onto Ni supported Pt matrix, particle size increases followed by agglomeration of particles and formation of multilayer. It indicates apparently that surface sites for reaction or catalytic surface is gradually increased on gradual introduction Pt up to a certain limit and then decreased. So, overall morphology of the surface changes gradually on successive addition of Pt on Ni surface. Fig. 1(e) depicts a representative EDX spectrum of Ni/Pt5 electrode. EDX spectra at different position of micrograph and at different individual structure reveal almost same mutual composition.

3.2. Electrochemical characterisation of the constructed electrode

Fig. 2(a) shows the cyclic voltammograms (CVs) of the constructed electrodes in alkali (1 M) in the potential region of –0.9 to +0.6 V, at room temperature (298 K) with a scan rate of 0.05 Vs⁻¹. The electrodes were subjected to triangular potential sweep for several times until a reproducible voltammogram for each was obtained. The inset of Fig. 2(a) represents the voltammograms for pure Pt wire in absence of Ni. For Ni catalyst, hydroxyl ion

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