Electrochemical Behaviour of Ni and Ni-PVC Electrodes for the Electrooxidation of Ethanol

(Tingkah Laku Elektrokimia Pengoksidaan Etanol Menggunakan Elektrod Ni dan Ni-PVC)

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ABSTRACT

In this study, two nickel based electrodes were prepared; nickel foil and nickel-polyvinylchloride (Ni-PVC), in order to study their electrochemical behavior using cyclic voltammetry, CV and chronocoulometry, CC. Ni electrode was prepared from Ni metal foil while Ni-PVC electrode was prepared by mixing a weighed portion of Ni powder and PVC in THF solvent, swirled until the suspension was homogeneous and drying the suspension in an oven at 50°C for 3 h. The dry sample was then placed in a 1 cm diameter stainless steel mould and pressed at 10 ton/cm². From CV data, Ni-PVC electrode showed a better electrochemical behavior compared to Ni metal foil electrode. The use of Ni-PVC electrode at higher concentration of supporting electrolyte (1.0 M KOH) was better than at lower concentration of the same supporting electrolyte in electroxidation of ethanol. In addition to acetic acid, the oxidation of ethanol also produced ethyl acetate and acetaldehyde.

Keywords: Acetic acid yield; chronocoulometry; cyclic voltammetry

INTRODUCTION

Electroxidation is one of the electrosynthesis processes that are widely used. The selections of electrode materials for electroxidation reaction are always limited by the oxidation of many metals at relatively low anodic potentials, e.g., mercury, nickel and copper. There are fewer suitable anode materials compared to cathode materials, because anodes must be stable to corrosion processes. In some cases, the anodes must be chemically resistant to the intermediates and end products of the electrochemical reaction. Fe and Ni are especially good in aqueous alkaline solution, where they are reasonably stable to corrosion. Besides chemical and electrochemical stability, electrodes chosen for industrial use should be relatively inexpensive, highly conducting and have electrocatalytic properties (Riyanto et al. 2008).

Since 1970, oxidation of organic compound on the nickel electrode in alkaline solutions has been extensively investigated (Yi et al. 2007). Jafarian et al. (2003) reported the electrochemical oxidation behaviour of methanol on a Ni electrode. In addition, Ni(III) was used to oxidize methanol and it was found that the final oxidation product of methanol is acetic acid. According to Lund & Hammerich (2001), other products like aldehydes, acetals, esters, ethers and even hydrocarbons may also be produced in the electroxidation of primary alcohols with potassium hydroxide (KOH) as supporting electrolyte. The mechanism of electroxidation process using nickel as an anode material and KOH as supporting electrolyte was proposed as follows:

\[
\begin{align*}
\text{Ni} & \rightarrow \text{Ni(OH)}_2 \quad \text{(surface)} \\
\text{Ni(OH)}_2 & \rightarrow \text{NiO(OH) + H}^+ \quad \text{(surface)}
\end{align*}
\]  

(1)

\[
\begin{align*}
\text{NiO(OH) + RCH}_2\text{OH} & \rightarrow \text{Ni(OH)}_2 + \text{RCHOH}
\end{align*}
\]  

(2)
According to Shen and Xu (2006), the use of pore electrode will increase the Tafel slope which electrodes with a higher internal surface area will have a higher electrocatalytic activity. Nickel powder dispersed on polymeric matrices (epoxy, polyester and polyvinylchloride) can be used as electrodes or current collectors for oxygen evolution reaction (OER) in alkaline solution at room temperature (Davila et al. 2001; Jimenez et al. 2000; Pereira et al. 2004).

In the present paper, we report the results of investigations of replacing the Ni metal foil with Ni powder incorporated with inert material, PVC in order to increase the selectivity and electrochemical nature of the electrode. The new electrode was designated as Ni-PVC electrode. The evaluations of the electrode were carried out by two electrochemical methods, cyclic voltammetry (CV) and chronocoulometry (CC).

MATERIALS AND METHODS

SOLUTION

KOH (Merck) was used as the supporting electrolyte. KOH solution was prepared by dissolving its analytical-reagent grade in deionised water. Nitrogen was used to deaerate the solutions and to keep an inert atmosphere over the solution during the oxidation process. Ethanol solution (BDH) with original concentration of 17.13 M was used without further purification.

PREPARATION OF ELECTRODES

The Ni metal foil electrode was prepared using its metal foil (99.98% purity, Aldrich Chemical Company). A 0.5 mm thickness Ni foil was cut into approximately 1 cm × 1 cm piece, connected to a silver wire with silver conducting paint and sealed in a glass rod. Subsequently, epoxy gum was applied to cover the silver wire connecting surface. The Ni-PVC electrode was prepared by mixing a weighed portion of Ni powder (100 mesh in size and 99.9% purity, Aldrich Chemical Company) and PVC in 4 mL tetrahydrofuran (THF) solvent and swirled flatly to homogeneous followed by drying in an oven at 50°C for 3 h. The mixture was placed in 1 cm diameter stainless steel mould and pressed at 10 ton/cm². A typical pellet contained approximately 95% of Ni powder and 5% of PVC polymer (W/W). The total weight of pellet obtained is approximately 1.5 g. The same treatments as Ni metal foil were later carried out for Ni-PVC electrode preparation.

THE ANALYSIS OF ELECTROCHEMICAL OXIDATIONS PRODUCTS

Analysis of the electrochemical oxidations products were carried out by High Performance Liquid Chromatography (HPLC) using equipment that comprised of a pump (Waters 1515 Isocratic HPLC Pump), a column (C18) completed with two detectors, UV-visible detector (Waters 2487, Dual λ Absorbance Detector) and a differential refractometer set on line. Chromatograms were recorded and integrated by an integrator-calculator (Merck-Hitachi D-2500). All experiments were carried out at room temperature. The acetanilide in 0.1% H₃PO₄ (88%;12%) were used as mobile phase throughout.

ELECTROCHEMICAL MEASUREMENTS USING CV AND CC

Universal Pulsa Dynamic EIS, Voltammetry, Voltalab potentiostat (Model PGZ 402) was used for the electrochemical measurements while data acquisition was accomplished using the Voltamaster 4 software. Voltammetric experiments were carried out in a three electrodes system using Ni or Ni-PVC as a working electrode (anode), Saturated Calomel Electrode (SCE) as reference electrode and platinum wire as the counter electrode. All potentials given are with respect to the SCE reference electrode.

In voltammetry, information about an analyte is obtained by measuring the current as the potential is varied (Kissinger & Heineman 1996; Zoski 2007). In particular, it offers a rapid location of redox potentials of the electroactive species and convenient evaluation of effect of media upon the redox process (Wang 2000). Measurement of the time dependence of the flow of charge constitutes the procedure is known as chronocoulometry, where the charge Q of the current is monitored as a function of time. Applications of this technique include measurement of electrode surface area, diffusion coefficients, concentration, kinetics of both heterogeneous electron transfer reactions and chemical reactions coupled to electron transfer, absorption and the effective time window of an electrochemical cell (Bott & Heineman 2004). The method offers certain advantages when, for instance, an electroactive reactant is adsorbed at the electrode surface.

EXPERIMENTAL PROCEDURE

The electrolysis process of ethanol was performed in a solution of 1.0 M and 0.1 M KOH respectively, at room temperature. The electrochemical studies by cyclic voltammetry and oxidation of ethanol by potentiostatic (chronocoulometry) method were performed in 25 mL capacity glass electrochemical cell. Electrolysis products were analyzed using high performance liquid chromatography (HPLC).

RESULTS AND DISCUSSION

CYCLIC VOLTAMMETRY USING NI AND NI-PVC ELECTRODES

Figure 1(a) and (b) shows the CV of Ni metal foil and Ni-PVC electrodes in 1.0 M KOH. The voltammetric response of both electrodes in alkaline solution shows sharp anodic and cathodic peaks, appearing at the same potential
for both the Ni metal foil and the Ni-PVC electrodes, respectively. For both peaks, higher current densities were recorded with the Ni-PVC electrodes compared to the Ni metal foil electrode. Variation in the efficiency of the electrode towards the oxygen evolution reaction (OER) was probably due to morphological differences between Ni-PVC composite and the Ni foil electrodes. The existence of PVC as inert supporting material around the aggregates on nickel particles may have increased the active electrode surface area. A porous electrode was preferred to a compact one as the electrolyte can penetrate deep inside the bulk material and give electrochemical contact to a larger area (Mohandas & Fray 2004).

A1 (anodic) peak at Figure 1(a) and 1(b) represents the oxidation peak of Ni(II) to Ni(III) due to the transformation of Ni(OH)$_2$ to NiOOH (Casella et al. 1999; Grden & Klimek 2005; Medway et al. 2006; Parpot et al. 2004; Seghioeur et al. 1998; Yeo & Johnson 2001). Oxidation of Ni (0) to Ni (II) occurs at a more negative potential or hydroxide region (not shown in this CV). Based on CV, the reaction mechanisms of oxidation on the surface of Ni based electrode are as follows (Medway et al. 2006):

\[
\text{Ni} + 2\text{OH}^- \rightarrow \alpha\text{-Ni(OH)}_2 + 2e^- \\
\text{at } -0.8 \text{ up to } -1.5 \text{ V/SCE (3)}
\]

\[
\alpha\text{-Ni(OH)}_2 \rightarrow \beta\text{-Ni(OH)}_2 \\
\text{at } -0.8 \text{ V up to } 0 \text{ V/ SCE (4)}
\]

\[
\beta\text{-Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \\
\text{at } 0.1 \text{ V/ SCE (5)}
\]

C1 (cathodic) peak in Figure 1(a) and 1(b) represents two crystallographic forms of $\alpha$ and $\beta$ nickel oxyhydroxide (Casella et al. 1999). Nickel oxyhydroxide is capable of oxidizing a number of functional groups, for example primary alcohols which may be oxidized to carboxylic acids. Nickel has been reported to be a good electrode for the oxidation of various organic compounds (Lund & Hammerich 2001). A redox couple of nickel, i.e., nickel hydroxide (Ni(OH)$_2$) and nickel oxyhydroxide (NiOOH), was shown to be involved in the oxidation of alcohol at nickel electrodes in alkaline media (Kim & Park 1999). NiOOH involved in the reaction oxidizes ethanol to acetaldehyde and further oxidizes the latter to acetic acid. Most of the acetaldehyde was oxidized to acetic acid because its oxidation rate is faster than ethanol. The reaction of organic compounds with the nickel oxides of higher valences is usually the rate determination step (Riyanto 2007).

One of the ways to clarify the oxidation area is to change the scan rate. With increasing scan rates, the anodic peak was shifted slightly to the more positive potential direction and the cathodic peak moved a little towards the negative potential (Figure 2a). The peak current densities increased remarkably with increasing scan rates, but the ratio of the anodic to cathodic peak current ($I_a/I_c$) was above unity. It indicates that the Ni(II) to Ni(III) oxide transformation process is quasi reversible (Kibria & Taradfar 2002).

Supporting electrolyte (KOH) concentration affected both anodic and cathodic peaks. With increasing KOH concentration, both the anodic and the cathodic peaks shifted slightly to the more negative potential direction (Figure 2(b)). The peak current densities increased slightly with increasing KOH concentration, and the ratio of the anodic to cathodic peak current ($I_a/I_c$) also increased. In the presence of higher concentration of OH$^-$, Ni is easily oxidized to Ni(OH)$_2$ and reacts further with OH$^-$ to form NiOOH. NiOOH is required in the oxidation of ethanol with Ni based electrode.

Nickel is known to has oxidation states of Ni (0), Ni(II), Ni (III) and Ni (IV) (Kim & Park 1999). Figure 3 shows the cyclic voltammograms of 0.25 M ethanol and without ethanol in 1.0 M KOH using Ni-PVC as working electrode. With ethanol in the reaction mixture (curve a), at
300 mV and below, the oxidation of ethanol is sustained by the involvement of adsorbed hydroxyl group (from KOH) on the electrode surface, while at higher potentials region (300 mV to 500 mV) the electrooxidation process is attributed to formation of NiOOH species. However, without ethanol (curve b), the adsorption of hydroxyl group (from KOH) and the formation of NiOOH on the electrode surface occurred at lower potential (Figure 3). Adsorption of ethanol on the electrode surface occurs immediately after the formation of NiOOH is completed. Both C1 and C2 peaks are the cathodic peaks which represent βNiOOH and γNiOOH, respectively (Grden & Klimek 2005).

The reaction mechanisms of electrocatalyst on the surface of Ni based electrode are as follows (Kim & Park 1999):

\[
\text{OH}^- + \text{Ni(OH)}_2 \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (6)
\]

\[
\text{NiOOH} + \text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{Intermediate 1} + \text{Ni(OH)}_2 \quad (7)
\]

\[
\text{NiOOH} + \text{Intermediate 1} \longrightarrow \text{CH}_3\text{CHO} + \text{Ni(OH)}_2 \quad (8)
\]

\[
\text{NiOOH} + \text{CH}_3\text{CHO} \longrightarrow \text{Intermediate 2} + \text{Ni(OH)}_2 \quad (9)
\]

\[
\text{NiOOH} + \text{Intermediate 2} \longrightarrow \text{CH}_3\text{COOH} + \text{Ni(OH)}_2 \quad (10)
\]

According to the above mechanism, nickel oxyhydroxide (NiOOH) participates in ethanol electrooxidation process. On the Ni electrode, ethanol is oxidized to acetaldehyde and is further oxidized to acetic acid. Most of the acetaldehyde is oxidized to acetic acid because the rate of oxidation of acetaldehyde is faster than that of ethanol. The other mechanisms that have been suggested for the oxidation of primary alcohol are as follows (Motheo et al. 2006):

\[
\text{Ni(OH)}_2 + \text{OH}^- \longrightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (11)
\]

\[
\text{NiOOH} + \text{RCH}_2\text{OH} \longrightarrow \text{Ni(OH)}_2 + \text{RC HOH} \quad (12)
\]

\[
\text{RC HOH} + 3\text{OH}^- \longrightarrow \text{RCOOH} + 2\text{H}_2\text{O} + 3e^- \quad (13)
\]
From the above mechanism, Ni(OH)$_2$ reacts with OH$^-$ to form NiOOH on the electrode surface and furthermore, ethanol is adsorbed to the surface of the electrode. NiOOH reacts as a catalyst to form the intermediate products. OH species from KOH or water have an important role in the reaction (6), (11) and (13). As a consequence supporting electrolyte concentration (KOH) has a large effect on the electrooxidation of ethanol. The proposed mechanism that is involved in the electrooxidation of ethanol to acetic acid using nickel electrode is summarized in Figure 4.

**CHRONOCOULOMETRY**

Figure 5 shows the results of chronocoulometry for the electrooxidation of ethanol in 1.0 M KOH using Ni and Ni-PVC electrode. According to chronocoulometry plot, Ni-PVC electrode has a higher Q (charge) value compared to Ni metal foil electrode, showing that more ethanol was adsorbed at the electrode surface (Figure 5). Hence higher percentage of ethanol was oxidized if Ni-PVC electrode was used.

**FIGURE 4.** The proposed reaction mechanism for the electrooxidation of ethanol to acetic acid at nickel electrode

**FIGURE 5.** Chronocoulometry of 0.25 M ethanol in 1.0 M KOH at a potential 1.05 V. Electrode area approximately 1.0 cm$^2$
TABLE 1. Yield of acetic acid obtained by the HPLC analysis for the electrolysis of 0.25 M C₆H₅OH at E = 1.05 V and at room temperature. Electrode surface area is approximately 1.0 cm² and electrolysis time in 6 h

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>KOH Electrolyte (M)</th>
<th>Acetic Acid Yield (%)</th>
<th>Current Density (mA/cm²)</th>
<th>Current Efficiency (%)</th>
<th>Energy Consumption (kWh/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.1</td>
<td>8.10</td>
<td>23.95</td>
<td>39.30</td>
<td>4778</td>
</tr>
<tr>
<td>Ni-PVC</td>
<td>0.1</td>
<td>18.68</td>
<td>178.86</td>
<td>12.13</td>
<td>15482</td>
</tr>
<tr>
<td>Ni</td>
<td>1.0</td>
<td>69.94</td>
<td>182.30</td>
<td>44.56</td>
<td>4213</td>
</tr>
<tr>
<td>Ni-PVC</td>
<td>1.0</td>
<td>84.93</td>
<td>254.34</td>
<td>38.79</td>
<td>4841</td>
</tr>
</tbody>
</table>

ANALYSIS OF ELECTROOXIDATION PRODUCTS

The results obtained for the electrolysis of 0.25 M ethanol at 1.05 V for 6 h are presented in Table 1. According to the HPLC results, the electrooxidation of ethanol using Ni metal foil and Ni-PVC electrode showed that higher percentage of acetic acid was formed if the latter electrode was used. The surface activity for the electrooxidation of ethanol on Ni metal foil or Ni-PVC electrodes in alkaline solution can be correlated to the coverage of the OH species, which is a reactive intermediate. The higher value of supporting electrolyte concentration may be a consequence of the preadsorption of the reactant on the electrode surface due to the increasing amount of hydroxide ion. This suggests that the oxidation of ethanol occurred by a mechanism which includes the participation of the higher valence surface of nickel oxyhydroxide (NiOOH). Table 1 shows that lower concentration of supporting electrolyte may decrease the production of acetic acid, due to the lower amount of NiOOH formed and ethanol adsorbed on the electrode surface. The morphology of the electrode surface also may play an important role in determining the percentage of acetic acid produced and this can be support by Contreras et al. (2007) that realized the Ni-PVC electrode has good mechanical and electrical properties. The electrocatalytic activity or anode efficiency can be increase using porous. The electrical, mechanical and morphology characteristics of these composite materials (Ni-PVC) show attractive electrochemical features compared with the massive nickel (Jimenez et al. 2000).

CONCLUSION

The electrochemical oxidation of 0.25 M ethanol in KOH on Ni metal foil and Ni-PVC electrodes was evaluated. The voltammetric response of both electrodes in alkaline solution shows sharps anodic and cathodic peaks appearing at the same potential but higher current densities were recorded with the Ni-PVC electrode. According to the HPLC analysis, Ni-PVC electrode produced higher percentage of acetic acid compared to Ni metal foil electrode. This indicates that powder electrode (Ni-PVC) with a porous and rough surface have a better electrochemical (CV and CC) characteristics compared to Ni metal foil electrode. Hence, Ni-PVC electrode has a better ability to electrochemically oxidize ethanol to acetic acid compared to Ni metal foil electrode.

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