Kinetics of hydrogen evolution reaction on Zr$_{0.5}$Ti$_{0.5}$V$_{0.6}$Cr$_{0.2}$Ni$_{1.2}$ alloy in KOH electrolyte

SHALINI RODRIGUES, N MUNICHANDRAIAH* and A K SHUKLA*

Solid State and Structural Chemistry Unit, 1Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

MS received 10 August 2000

Abstract. A hydrogen-storage alloy of the composition Zr$_{0.5}$Ti$_{0.5}$V$_{0.6}$Cr$_{0.2}$Ni$_{1.2}$ has been investigated for corrosion resistance and hydrogen-evolution reaction (HER) in KOH electrolyte of varying concentrations. Activation of the electrode by absorption of hydrogen takes place after prolonged cathodic polarization in the potential range of HER. Prior to activation, the open-circuit potential is about –0.4 V vs Hg/HgO, OH$^-$, at which the alloy electrode tends to undergo corrosion with oxygen-reduction reaction (ORR) as the conjugate reaction. The corrosion–current density measured from Tafel polarization of ORR is found to be independent of KOH concentration and has an average value of about 30 µA cm$^{-2}$. Subsequent to activation, the open circuit potential of the electrode is shifted to about –0.93 V vs Hg/HgO, OH$^-$, which is equal to the reversible potential of HER. The exchange current density values measured from Tafel polarization of HER are marginally higher in relation to the values obtained before the electrode is activated. Alternating-current impedance spectra in the Nyquist form contain two overlapped semicircles. The high-frequency semicircle is attributed to the electrode geometry, while the low-frequency semicircle is due to the charge-transfer reaction and double-layer capacitance. The impedance data are analyzed by a non-linear least square curve fitting technique and impedance parameters are evaluated.

Keywords. Hydrogen-storage alloy; hydrogen-evolution reaction; Tafel polarization; a.c. impedance; exchange-current density.

1. Introduction

In recent years, replacement of the toxic cadmium electrodes of nickel/cadmium batteries with metal hydride (MH) electrodes has resulted in environment friendly nickel/metal hydride (Ni/MH) batteries. However, the development of metal hydride (MH) electrode materials, which yield high energy per unit weight with a long charge/discharge cycle life, has been challenging. To this end, several AB$_2$ and AB$_5$-type alloys have been investigated (Appleby et al 1973). Although AB$_2$-type alloys were preferred in the past, presently the preference is for AB$_5$-type alloys (Ganesh Kumar 1999). When a metal hydride electrode in an alkaline electrolyte (usually 6 M KOH) is subjected to charging, reduction of H$_2$O molecule takes place producing atomic hydrogen on its surface in adsorbed state. Penetration of adsorbed hydrogen into the bulk of the electrode material results in the formation of metal hydride, which behaves as a reservoir of hydrogen in the rechargeable battery. Accordingly, the formation of metal hydride is an intermediate step of hydrogen-evolution reaction (HER) on hydrogen adsorbing alloys, which has been a subject of extensive investigation at various electrode materials both in acidic and alkaline electrolytes (Frumkin 1963; Enyo 1983; Trasatti 1992).

An AB$_2$-type hydrogen adsorbing alloy of the composition Zr$_{0.5}$Ti$_{0.5}$V$_{0.6}$Cr$_{0.2}$Ni$_{1.2}$ was recently investigated for rechargeable Ni/MH and Ag/MH batteries (Ganesh Kumar et al 1998, 1999, 2000; Rodrigues et al 1999a). The MH electrodes were made by pasting fine particles of this alloy mixed with PTFE binder on Ni-current collectors. An electrode required several (~10) charge/discharge cycles of activation in 6 M KOH to achieve a maximum discharge capacity of ~320 mAh g$^{-1}$. During the process of activation, the alloy surface apparently became conductive for penetration of absorbed hydrogen atoms inside the particles. Subsequent to activation, the open-circuit potential (OCP) of the MH electrode reached a value close to the reversible potential of HER, viz. –0.93 V vs Hg/HgO, OH$^-$, from a state of mixed potential. Thus, the HER appears to be sensitive to the catalytic and adsorptive nature of the electrode surface. The surface nature of the alloy before activation could be different from the surface nature after hydride formation. Accordingly, the kinetics of HER are expected to differ before and after hydride formation. In this communication, we therefore report the kinetics of HER studies by d.c. polarization and
a.c. impedance spectroscopy on a Zr_{0.5}Ti_{0.5}V_{0.6}Cr_{0.2}Ni_{1.2} alloy ingot electrode before and after its activation. The study suggests that the alloy ingot has a tendency to corrode prior to its activation but corrosion reaction is seemingly ceased subsequent to the hydride formation.

2. Experimental

An ingot of about 500 g of Zr_{0.5}Ti_{0.5}V_{0.6}Cr_{0.2}Ni_{1.2} alloy was prepared from the spongy elements by repeated arc melting in an argon atmosphere. A powdered sample of the ingot was subjected to XRD and SEM studies. The data suggested that the alloy was homogeneous in composition and its structure conformed to AB_{2}-Laves phase. Small pieces of the alloy were separated from the ingot and surfaces of these pieces were polished to a smooth finish. An electrode was made by mounting an ingot in a PTFE holder, which was provided with a stainless steel current collecting rod. The crevices between the ingot electrode and PTFE were sealed with an epoxy resin. Area of the electrodes exposed to the electrolyte was in the range of 0.16–0.2 cm². The electrodes were etched in concentrated HCl for a few seconds, washed copiously in distilled water and dried at 80°C before use. The electrode was inserted into a glass cell, which was fitted with two symmetrical large area nickel counter electrodes and a Hg/HgO, OH⁻ (6 M KOH) reference electrode (MMO). Experiments were carried out in KOH electrolyte of varying concentrations in the range between 0.2 M and 6 M which were prepared using analar grade KOH in doubly-distilled water and were subjected to pre-electrolysis before use.

Polarization experiments were carried out in stirred electrolytes by sweeping the electrode potential at a scan rate of 0.1 mV s⁻¹ employing a potentiostat (EG&G PARC Versatstat). Cyclic voltammetric experiments were carried out in unstirred electrolytes at a scan rate of 10 mV s⁻¹. A.c. impedance spectroscopy was carried out in the frequency range 100 kHz–10 mHz at an excitation signal of 5 mV using electrochemical impedance analyzer (EG&G PARC model 6310). The impedance data were analyzed by non-linear least square fitting procedure (Boukamp 1989). All experiments were carried out at 20 ± 1°C.

3. Results and discussion

A Zr_{0.5}Ti_{0.5}V_{0.6}Cr_{0.2}Ni_{1.2} alloy electrode was subjected to potential cycling in 6 M KOH covering both the HER and oxygen-evolution reaction (OER) (figure 1). The increase in current at about −1.2 V vs MMO is due to HER. It is noteworthy that the HER is shifted cathodically by about 0.3 V from its reversible value of −0.93 V vs MMO. In a similar fashion, the OER occurs at potentials positive to 0.6 V vs MMO, which is also shifted anodically from its reversible value of 0.3 V vs MMO. In the potential region close to the commencement of OER, a pair of current peaks appears which could be attributed to oxidation of one of the metallic constituents of the Zr_{0.5}Ti_{0.5}V_{0.6}Cr_{0.2}Ni_{1.2} alloy electrode. Considering the composition of the alloy, the metallic element undergoing oxidation appears to be Ni.

The OCP of the alloy electrode in KOH electrolyte was in the range between −0.2 and −0.4 V vs MMO. Subsequent to its activation, however, it equilibrated to about −0.93 V vs MMO, which is the reversible potential for HER. This suggests that the electrode behaves as a reversible hydrogen electrode only after its activation. Prior to this, it is under a state of corrosion and the open-circuit potential (E_{oc} = −0.4 V vs MMO) is a mixed potential. The partial reactions, which impart a mixed potential to the electrode, could schematically be written as follows:

\[ \text{M} \rightarrow \text{M}^{n+} + n\text{e}^{-}. \]  

Figure 1. Cyclic voltammogram of a Zr_{0.5}Ti_{0.5}V_{0.6}Cr_{0.2}Ni_{1.2} alloy electrode in 6 M KOH in the potential range between −1.4 V and +0.8 V vs MMO at a scan rate of 10 mV s⁻¹. Area of the electrode: 0.16 cm².

Figure 2. Tafel plot of a Zr_{0.5}Ti_{0.5}V_{0.6}Cr_{0.2}Ni_{1.2} alloy electrode in 6 M KOH in the potential range between −0.35 V and −1.4 V vs MMO. Area of the electrode: 0.16 cm².
Table 1. Electrode kinetic data for the corrosion ($i_{\text{cor}}$) and HER (Tafel slope, $\alpha$ and $i_0$) occurring on the Zr$_{0.5}$Ti$_{0.5}$V$_{0.6}$Cr$_{0.2}$Ni$_{1.2}$ alloy electrode prior to its activation in KOH electrolyte.

<table>
<thead>
<tr>
<th>$C_{\text{KOH}}$ (M)</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel slope (V)</td>
<td>0.168</td>
<td>0.159</td>
<td>0.156</td>
<td>0.146</td>
<td>0.167</td>
<td>0.167</td>
<td>0.130</td>
<td>0.146</td>
<td>0.146</td>
<td>0.146</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.357</td>
<td>0.377</td>
<td>0.384</td>
<td>0.410</td>
<td>0.370</td>
<td>0.359</td>
<td>0.461</td>
<td>0.410</td>
<td>0.410</td>
<td>0.400</td>
</tr>
<tr>
<td>$i_0 \times 10^6$ (A cm$^{-2}$)</td>
<td>5.63</td>
<td>3.13</td>
<td>2.50</td>
<td>1.88</td>
<td>3.75</td>
<td>1.25</td>
<td>1.25</td>
<td>4.38</td>
<td>2.50</td>
<td>6.25</td>
</tr>
<tr>
<td>$i_{\text{cor}} \times 10^6$ (A cm$^{-2}$)</td>
<td>1.06</td>
<td>1.25</td>
<td>2.5</td>
<td>1.88</td>
<td>1.25</td>
<td>1.25</td>
<td>1.25</td>
<td>1.25</td>
<td>3.75</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Reaction (1) represents the oxidation of metal (M) or a metallic element of the alloy, which undergoes corrosion and reaction (2) represents the conjugate reaction in which the electrons liberated during reaction (1) are consumed. The corrosion potential ($E_{\text{cor}}$) is determined by the kinetics of both these reactions. In the present case, since the corrosion potential of the alloy ingot is positive to the reversible potential for HER by about 0.5 V, HER cannot take place as the cathodic conjugate reaction. Consequently, the reduction of dissolved oxygen in the electrolyte (ORR),

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-,$$

is the most probable reaction.

The cathodic polarization behaviour of the electrode is shown in figure 2. Two linear segments of the cathodic polarization curve are clearly present in KOH electrolyte with varying concentrations employed during this study. The segment between $E_{\text{cor}}$ and −0.93 V vs MMO is the Tafel component of ORR (reaction 3) and the other segment at potentials cathodic to −0.93 V vs MMO is due to HER. The value of corrosion current density ($i_{\text{cor}}$) obtained by extrapolation of the ORR Tafel line to $E_{\text{cor}}$ is 30 µA cm$^{-2}$.

In order to substantiate reaction (3) as the cathodic conjugate reaction during corrosion of the alloy ingot, polarization experiments were also conducted in O$_2$ saturated and de-aerated (by argon gas) 6 M KOH electrolyte. The values of $i_{\text{cor}}$ obtained are 130 µA cm$^{-2}$ and 6 µA cm$^{-2}$ in O$_2$ saturated and de-aerated 6 M KOH electrolyte, respectively. An increase in the value of $i_{\text{cor}}$ in O$_2$ saturated electrolyte and a decrease in the de-aerated electrolyte clearly suggests reaction (3) to be the cathodic reaction for corrosion of the alloy ingot. Polarization measurements were carried out in aerated KOH electrolytes of varying concentrations and $i_{\text{cor}}$ values were obtained as given in table 1. Interestingly little dependence of $i_{\text{cor}}$ of the alloy was observed on KOH concentration.

A.c. impedance data of the alloy ingot at OCP are shown in figure 3 as Nyquist and Bode plots. The appropriate equivalent circuit comprising corrosion resistance ($R_{\text{cor}}$) of the alloy, double-layer capacitance ($C_{dl}$) and
electrolyte resistance ($R_0$) is shown as the inset. The impedance data do not take the shape of a semicircle in the Nyquist plot (figure 3a), suggesting a high value of $R_\text{cor}$. The Bode plot (figure 3b) also suggests capacitive behaviour of the electrode as logarithmic modulus of impedance ($\log |Z|$) varies linearly with logarithmic frequency ($\log f$) with a slope of $-0.8$, which is close to the theoretical value of $-1$ for a pure capacitor. Also, the phase angle ($\phi$) is about $-70^\circ$ over a wide frequency range. Under these conditions, $|Z|$ is related to $C_{\text{dl}}$, as follows:

$$\log |Z| = -\log \omega - \log C_{\text{dl}}. \tag{4}$$

where $\omega = 2\pi f$. When $\omega = 1$, $\log |Z|$ becomes equal to $-\log C_{\text{dl}}$. The value of $C_{\text{dl}}$ obtained from figure 3b is $0.3 \text{ mF cm}^{-2}$. This value of $C_{\text{dl}}$ for Zr$_{0.5}$Ti$_{0.5}$V$_{0.6}$Cr$_{0.2}$Ni$_{1.2}$ electrode is much higher than the $C_{\text{dl}}$ (about $20 \mu\text{F cm}^{-2}$) for Hg/solution interface. Similar to the present study, high values of $C_{\text{dl}}$ are reported for solid electrodes such as Ni, Ni–Zn alloy, etc in alkaline electrolytes (Chen and Lasia 1991; Dumont et al 1993). The high values of $C_{\text{dl}}$ are perhaps due to pseudo capacitance, which arises due to adsorption of O$_2$, OH$^-$ or intermediates of reaction (1) at the alloy electrode/electrolyte interface. From impedance spectra recorded at different potentials, $C_{\text{dl}}$ values were evaluated. The variation of $C_{\text{dl}}$ with the electrode potential is shown in figure 4. The increase of $C_{\text{dl}}$ with increase of negative potential of the electrode could also be due to adsorption of intermediates of ORR (reaction 3), which occurs in the potential range between $-0.2$ and $-0.6$ V vs MMO.

The second region of the polarization curve (figure 2) is due to HER:

$$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-. \tag{5}$$

The mechanism of HER is generally considered to comprise the following three steps (Chen and Lasia 1991; Spataru et al 1996; Notoya 1997):

$$\begin{align*}
\text{H}_2\text{O} + \text{M} + e^- &\xrightleftharpoons[k_{-1}]{k_1} \text{MH}_\text{s} + \text{OH}^- , \tag{6} \\
\text{MH}_\text{s} + \text{H}_2\text{O} + e^- &\xrightarrow[k_{-2}]{k_2} \text{H}_2 + \text{M} + \text{OH}^- , \tag{7} \\
2\text{MH}_\text{s} &\xrightarrow[k_{-3}]{k_3} \text{H}_2 + 2\text{M} . \tag{8}
\end{align*}$$

The first step (reaction 6), known as Volmer reaction, is the primary electron transfer step resulting in the formation of hydrogen adsorbed on the electrode surface (MH$_\text{s}$) from H$_2$O molecule. It is followed by the second step (reaction 7) or/and the third step (reaction 8) for completion of HER (reaction 5). The reaction (7), known as Heyrovsky reaction, suggests the formation of H$_2$ molecule by desorption of surface hydrogen and a simultaneous reduction of H$_2$O molecule. Reaction (8), called as Tafel reaction, suggests the formation of H$_2$ molecule by a combination of two neighbouring surface hydrogen atoms.

A study of literature reveals that HER on Ni metal and Ni containing alloys proceeds via the Volmer–Heyrovsky mechanism with the Volmer reaction as the rate determining step (rds) (Chen and Lasia 1991; Spataru et al 1996; Notoya 1997). In the present study, the alloy electrode consists of Ni as the major element, and therefore the following mechanism is assumed to be valid for HER.

$$\begin{align*}
\text{H}_2\text{O} + \text{M} + e^- &\xrightarrow[k_1]{k_{-1}} \text{MH}_\text{s} + \text{OH}^- , \tag{9} \\
\text{MH}_\text{s} + \text{H}_2\text{O} + e^- &\xrightarrow[k_{-2}]{k_2} \text{H}_2 + \text{M} + \text{OH}^- . \tag{7}
\end{align*}$$

Reaction (9) with a single arrow indicates an irreversible rds and it differs from reaction (6) which suggests an equilibrium process of fast reaction. Under the Tafel conditions (i.e. $(E - E') \gg RT/F$), the kinetic equation can be rewritten as:

$$i = i_0 \exp[-\alpha f |\eta|] , \tag{10}$$

where $i$ is current density corresponding to overpotential.
\( \eta (= E - E') \), \( E \) the electrode potential, \( E' \) the reversible potential of HER, \( i_0 \) the exchange-current density and \( \alpha \) the energy-transfer coefficient. By extrapolation of HER Tafel line (figure 2) to \( E' (\sim -0.93 \text{ V vs MMO}) \), \( i_0 \) is evaluated, and from the Tafel slope (b) the value of \( \alpha \) is obtained. The values of \( i_0, b \) and \( \alpha \) obtained for HER in KOH electrolytes of varying concentrations are given in Table 1. The values of these parameters are nearly constant in all solutions suggesting a negligible influence of concentration of KOH on the kinetics of HER at \( \text{Zr}0.5\text{Ti}0.5\text{V}0.6\text{Cr}0.2\text{Ni}1.2 \) alloy. The value of \( i_0 \) is similar in magnitude to the reported values for HER at several electrodes in KOH electrolytes (Chen and Lasia 1991; Spataru et al. 1996; Notoya 1997). Although the Tafel slope (b) is expected to be \( \sim 120 \text{ mV} \) assuming \( \alpha = 0.5 \), large deviations from this value are reported in the literature (Appleby et al. 1973). In the present study also, the values of \( b \) obtained are higher than 120 mV (Table 1). Accordingly, the values of \( \alpha \) (Table 1) are marginally lesser than 0.5.

Since the alloy electrode has been proven for its hydrogen absorbing capability as reported previously by studying battery grade laboratory scale electrodes, cells and battery (Ganesh Kumar et al. 1998, 1999, 2000; Rodrigues et al. 1998, 1999), it was polarized cathodically at a current density of \( 2 \text{ mA cm}^{-2} \) for absorption of hydrogen, which resulted in vigorous evolution of gas at the electrode surface. During the course of electrolysis, the passage of current was intermittently terminated and open-circuit potential of the electrode was measured. A shift in open-circuit potential from \( E_{\text{oc}} \) to the theoretical reversible hydrogen evolution reaction potential (\( -0.93 \text{ V vs MMO} \)) was taken to be the indication for absorption of the atomic hydrogen by the alloy electrode. It was found that considerable length of polarization was required to activate the electrode and to realize a potential value of \( -0.93 \text{ V vs MMO} \). Subsequent to its activation, the potential was stable around \( -0.93 \text{ V vs MMO} \) and it did not return to \( E_{\text{oc}} \) even after the electrode was left under open-circuit condition for a prolonged time.

For the purpose of kinetic studies of HER, the activated alloy electrode was subjected to Tafel and a.c. impedance measurements in KOH electrolytes with varying concentrations. Although the alloy behaves as a reversible hydrogen electrode, oxidation of hydrogen is not studied. This is due to the reason that the quantity of absorbed hydrogen in the alloy is so small that the electrode becomes deactivated within a few minutes under anodic conditions. Hence, the polarization as well as the a.c. impedance studies, which require large overpotential range and a long duration of the experiments could not be performed. For a battery grade electrode, which requires storage of a larger charge, the alloy was finely powdered.

### Table 2. Electrode kinetic data for the HER occurring on the Zr0.5Ti0.5V0.6Cr0.2Ni1.2 electrode subsequent to its activation in KOH electrolytes.

<table>
<thead>
<tr>
<th>( C_{\text{KOH}} ) (M)</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel slope (V)</td>
<td>0.188</td>
<td>0.172</td>
<td>0.152</td>
<td>0.175</td>
<td>0.153</td>
<td>0.150</td>
<td>0.169</td>
<td>0.155</td>
<td>0.162</td>
<td>0.170</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.319</td>
<td>0.348</td>
<td>0.394</td>
<td>0.341</td>
<td>0.392</td>
<td>0.400</td>
<td>0.354</td>
<td>0.385</td>
<td>0.370</td>
<td>0.352</td>
</tr>
<tr>
<td>( i_0 \times 10^5 ) (A cm(^{-2} ))</td>
<td>8.13</td>
<td>8.75</td>
<td>4.38</td>
<td>12.5</td>
<td>15.6</td>
<td>8.13</td>
<td>32.5</td>
<td>26.25</td>
<td>21.87</td>
<td>12.20</td>
</tr>
</tbody>
</table>

### Table 3. Impedance parameters for the Zr0.5Ti0.5V0.6Cr0.2Ni1.2 alloy electrode in 6 M KOH subsequent to its activation (see the text for symbols).

<table>
<thead>
<tr>
<th>( E ) vs MMO (V)</th>
<th>-0.936</th>
<th>-0.971</th>
<th>-1.03</th>
<th>-1.074</th>
<th>-1.17</th>
<th>-1.229</th>
<th>-1.28</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_\Omega ) (( \Omega ))</td>
<td>1.338 ± 0.026</td>
<td>1.256 ± 0.021</td>
<td>1.433 ± 0.028</td>
<td>1.195 ± 0.025</td>
<td>1.27 ± 0.027</td>
<td>1.31 ± 0.027</td>
<td>1.58 ± 0.032</td>
</tr>
<tr>
<td>( R_1 ) (( \Omega ))</td>
<td>1.244 ± 0.293</td>
<td>1.257 ± 0.248</td>
<td>1.462 ± 0.350</td>
<td>2.306 ± 0.392</td>
<td>2.23 ± 0.624</td>
<td>1.49 ± 0.624</td>
<td>0.97 ± 0.569</td>
</tr>
<tr>
<td>( Q ) × 10(^{4} ) (C cm(^{-2} ))</td>
<td>4.99 ± 3.5</td>
<td>5.67 ± 3.17</td>
<td>4.62 ± 3.00</td>
<td>4.33 ± 1.68</td>
<td>4.63 ± 2.03</td>
<td>2.69 ± 1.77</td>
<td>2.01 ± 1.88</td>
</tr>
<tr>
<td>( n )</td>
<td>0.856 ± 0.081</td>
<td>0.847 ± 0.064</td>
<td>0.845 ± 0.075</td>
<td>0.812 ± 0.045</td>
<td>0.81 ± 0.055</td>
<td>0.86 ± 0.085</td>
<td>0.90 ± 0.122</td>
</tr>
<tr>
<td>( R_\infty ) × 10(^2 ) (( \Omega ))</td>
<td>4.69 ± 0.101</td>
<td>3.99 ± 0.053</td>
<td>2.28 ± 0.038</td>
<td>1.49 ± 0.021</td>
<td>4.31 ± 0.085</td>
<td>2.23 ± 0.089</td>
<td>8.67 ± 0.085</td>
</tr>
<tr>
<td>( Q_\infty ) × 10(^4 ) (C cm(^{-2} ))</td>
<td>9.29 ± 0.235</td>
<td>8.79 ± 0.167</td>
<td>8.22 ± 0.263</td>
<td>7.45 ± 0.254</td>
<td>6.39 ± 0.342</td>
<td>5.64 ± 0.559</td>
<td>6.79 ± 0.085</td>
</tr>
<tr>
<td>( n_2 )</td>
<td>0.717 ± 0.006</td>
<td>0.716 ± 0.005</td>
<td>0.722 ± 0.008</td>
<td>0.735 ± 0.008</td>
<td>0.76 ± 0.015</td>
<td>0.76 ± 0.024</td>
<td>0.78 ± 0.048</td>
</tr>
</tbody>
</table>

---

**Figure 5.** Tafel plot of a Zr0.5Ti0.5V0.6Cr0.2Ni1.2 alloy electrode in 6 M KOH in the potential range between -0.90 V and -1.4 V vs MMO. Area of the electrode: 0.16 cm\(^2\).
as reported elsewhere (Ganesh Kumar et al 1998, 1999, 2000; Rodrigues et al 1999a). A typical cathodic Tafel plot of the alloy electrode in 6 M KOH is shown in figure 5. The presence of linearity of the data over about two orders of magnitude of current suggests that reaction (5) occurs under charge-transfer control. Similar data were obtained in KOH electrolytes of varying concentrations. The values of $i_0$, $b$ and $a$ obtained in KOH electrolytes for HER at $\text{Zr}_{0.5}\text{Ti}_{0.5}\text{V}_{0.6}\text{Cr}_{0.2}\text{Ni}_{1.2}$ alloy electrode subsequent to its activation are shown in table 2. Akin to the values of the parameters before activation (table 1), the values after activation (table 2) do not show a strong dependence on the concentration of the electrolyte, although there is some scatter in the values. On an average, the Tafel slope remains the same before and after activation. However, the exchange-current density values are marginally only higher after activation of the electrode than before activation.

A.c. impedance spectra of $\text{Zr}_{0.5}\text{Ti}_{0.5}\text{V}_{0.6}\text{Cr}_{0.2}\text{Ni}_{1.2}$ alloy electrode in 6 M KOH recorded at $–0.93$ V vs MMO and at cathodic overpotentials in HER region are shown in figures 6 and 7 in Nyquist and Bode plots, respectively. The data in a Nyquist plot take the shape of a distorted semicircle suggesting the presence of overlapped semicircles. A study of literature on the impedance of HER in alkaline media revealed the presence of two semicircles (Chen and Lasia 1991; Dumont et al 1993). The high-frequency small semicircle was not clearly understood and it was attributed to the geometry of the electrodes schematically by a resistance and a capacitance in parallel.
Hydrogen evolution reaction kinetics on Zr$_{0.5}$Ti$_{0.5}$V$_{0.6}$Cr$_{0.2}$Ni$_{1.2}$ alloy (Chen and Lasia 1991; Dumont et al 1993). The low-frequency semicircle was due to a parallel arrangement of charge-transfer resistance ($R_{ct}$) of HER and double-layer capacitance ($C_{dl}$). The impedance data of the present study are also considered to consist of two semicircles which overlap due to similarity in magnitude of the respective time constants. Since the two semicircles are distorted, an equivalent circuit (figure 8) consisting of constant phase-elements (CPE) in the place of capacitance is considered similar to the studies reported (Munichandraiah et al 1998; Rodrigues et al 1999a, b). In the equivalent circuit (figure 8), $R_0$ represents the solution resistance, $R_1$ and $Q_1$ represents resistance and constant phase-element of high frequency small semicircle respectively, $R_{ct}$ and $Q_{dl}$ correspond to charge-transfer resistance of HER and CPE in place of double-layer capacitance ($C_{dl}$), respectively. The admittance representation of CPE is given by:

$$Y^*(\omega) = Y_0(\omega)^n.$$

For $n = 0$, it represents a resistance with $R = Y_0^{-1}$; for $n = 1$, a capacitance with $C = Y_0$; for $n = 0.5$, a Warburg; and for $n = -1$ an inductance with $L = Y_0^{-1}$ (Boukamp 1989).

The impedance data of HER were subjected to NLLS fitting, the impedance parameters obtained are given in table 3 and the theoretical curves are shown as solid lines in figures 6 and 7. The theoretical curves agree well with the experimental data. Charge-transfer resistance ($R_{ct}$) measured at overpotentials is approximately related to $i_0$ and $\alpha$ of HER as described below (Elumalai et al 1999).

Figure 7. Electrochemical a.c. impedance spectra in Bode form of a Zr$_{0.5}$Ti$_{0.5}$V$_{0.6}$Cr$_{0.2}$Ni$_{1.2}$ alloy electrode in 6 M KOH at different potentials ($E$ vs MMO). The experimental data are shown as symbols and the theoretical data obtained from NLLS fit results are shown as solid curves.
Equation (10) is rewritten as,
\[ \eta = (\ln i_0 - \ln i)/\alpha f. \]  \hspace{1cm} (12)

By differentiating with respect to \( i \), we obtain,
\[ (d\eta/di)|_{\eta=0} = R_{ct} = -1/\alpha f. \]  \hspace{1cm} (13)

By substituting for \( i \) from (10), we get
\[ R_a = e^{\alpha/\eta}(\alpha f i_0), \]  \hspace{1cm} (14)

or, \( \ln R_a + \ln(\alpha f i_0) = \alpha f \eta. \)  \hspace{1cm} (15)

A plot of \( \ln R_a \) against \( \eta \) thus results in a straight line with a slope of \( (\alpha f) \) and an intercept of \( \ln(\alpha f i_0)^{-1} \). It is thus possible to evaluate the values of \( \alpha \) and \( i_0 \) from the impedance spectra of \( \text{Zr}_0.5\text{Ti}_0.5\text{V}_{0.5}\text{Cr}_{0.5}\text{Ni}_{1.2} \) alloy electrode recorded at several potentials in HER regime. The variation in resistance \( R_{ct} \) of HER as a function of potential is shown in figure 9. The \( i_0 \) and \( \alpha \) values derived are \( 5.9 \times 10^{-4} \text{ A cm}^{-2} \) and \( 0.343 \) respectively, which are nearly similar to those obtained from the Tafel polarization experiments (table 2).

An examination of the impedance parameters listed in table 3 suggests that the ohmic resistance \( (R_0) \) is nearly invariant in the range 1.1–1.6 U with overpotential. The magnitude of \( R_1 \) is small and it does not vary with overpotential in a systematic manner. A similar non-variance of this parameter is reported in the literature for HER at nickel electrodes (Chen and Lasia 1992; Dumont et al 1993). The value of \( n_1 \), corresponding to \( Q_1 \), is close to unity, thus reflecting capacitive behaviour of this constant phase element. On the other hand, the value of \( n_2 \) (corresponding to \( Q_{dl} \)) is \( \approx 0.7 \), which deviates substantially from unity. Therefore, the constant phase element \( Q_{dl} \) could not be equated to \( C_{dl} \) of the electrode.

4. Conclusions

The study suggests that \( \text{Zr}_{0.5}\text{Ti}_{0.5}\text{V}_{0.5}\text{Cr}_{0.5}\text{Ni}_{1.2} \) alloy ingot has the tendency to undergo corrosion in alkaline medium prior to its activation. But subsequent to the hydride forma-

References

Boukamp B A 1989 Equivalent circuit, Users manual (The Netherlands: University of Twente)
Ganesh Kumar V 1999 Studies on nickel/metal–hydride, lithium–ion and valve regulated lead/acid batteries, Ph.D. Thesis, Indian Institute of Science, Bangalore
Ganesh Kumar V, Shaju K M, Munichandraiah N and Shukla A K 1998 J. Power Sources 76 106
Munichandraiah N, Scanlon L G and Marsh R A 1998 J. Power Sources 72 203
Notoya R 1997 Electrochim. Acta 42 899