Assessment of CO-tolerance for different Pt-alloy anode catalysts in a polymer electrolyte fuel cell using ac impedance spectroscopy

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Abstract

Assessment of CO-tolerance for different anode catalysts (Pt/C, PtRu/C and PtSn/C) at 50 °C and PtRu/C at different operating temperatures in the polymer electrolyte fuel cell (PEFC) was evaluated using ac impedance spectroscopy. Impedance measurements for the oxidation of a H₂/CO₂ mixture reported that at a critical potential (referred to as the onset potential), ‘pseudo-inductive’ behavior appears, the value of which is different for different anode catalysts (0.70, 0.45 and 0.30 V for Pt/C, PtRu/C and PtSn/C at 50 °C, respectively) and strongly dependent upon working temperatures (0.50, 0.45 and 0.40 V for PtRu/C at 25, 50 and 70 °C, respectively). Based on that, we proposed that this onset potential for the ‘pseudo-inductive’ behavior can be used as a new criterion for the evaluation of CO-tolerance for different anode catalysts at different operating temperatures. © 2002 Published by Elsevier Science B.V.

Keywords: Electrocatalysis; Ac impedance; Fuel cell; Anodic oxidation; Cyclic voltammetry

1. Introduction

The development and commercialization of the polymer electrolyte fuel cell (PEFC) have attracted much attention for transportation applications due to its high efficiency and low pollutant emission level. H₂ is the most suitable fuel for PEFC system, yet its fuel infrastructure and the necessary safety measures may take many years to establish [1]. In recent years fuel cell developers and major automobile companies have been looking for alternative solutions. One near-term strategy is to generate H₂ on demand by converting low cost liquid hydrocarbons through an on-board reformer. However, thus generated H₂ could contain some CO that will deactivate the surface catalytic site of Pt based electro-catalysts. Consequently, it is imperative to develop alternative catalysts that can tolerate a higher CO concentration.

A lot of research work has been done in this area to identify and synthesize CO-tolerant electrocatalysts for working temperatures below 100 °C, suitable for PEFC operation. The Pt–Ru alloy catalyst with a 50% Ru atomic composition is one of the most popular CO-tolerant electrocatalysts known to date [2]. Other binary catalysts such as PtSn [3], PtFe [4,5], PtMo [6,7] and PtRe [8] have emerged as promising candidates with a performance close to, or even better than that of PtRu. As many suitable CO-tolerant catalytic materials are identified, a consistent, simple and reliable technique will have to be established to allow systematic evaluation and characterization of the activity and performance of the newly found electrocatalysts. For this purpose, three electrochemical methods including polarization measurement [6–8], cyclic voltammetry [6,8] and stripping voltammetry [3,8] have been commonly employed in the fuel cell community.

An electrochemical impedance spectroscopy (EIS) based technique, unlike the above-mentioned methods, offers possibilities of unraveling different surface processes in the frequency domain, suitable for studying
anodic oxidation processes on the catalyst surface. Although EIS has been widely used in monitoring the corrosion process and characterizing intercalating materials in lithium ion batteries, it has only just gained a footing in the fuel cell research in recent years [9–12]. In particular, there have been studies reporting the monitoring of the impedance changes of the anode caused by the gradual loss of catalytic activity due to CO poisoning [13–16]. An impedance theory based model recently established in our group has improved understanding of the complex impedance patterns developed in the anodic oxidation of H2+CO mixtures and enabled a quantitative assessment of the effect of applied potentials on the oxidation kinetics [17].

In this study, we will report the EIS based diagnostics of the capability for CO-tolerance for different anode electrocatalysts at different operating temperatures. Specifically, we will describe how the ‘onset potential’ for the pseudo-inductive behavior observed in the complex impedance plot can be used as a new criterion for the evaluation of CO-tolerance. Moreover, comparisons of the diagnostic results obtained in the impedance spectroscopy and other traditional electrochemical methods will be discussed.

2. Experimental

PCT-2000 fuel cell test station (ElectroChem, USA) and Autolab potentiostat (Eco-Chemie, Netherlands) with built-in frequency analyzer were used for electrochemical measurement (including impedance) of anodic H2+CO oxidation. A 5 cm² membrane electrode assembly (MEA) was prepared following the procedure reported previously [18]. In the MEA, a 20 wt% Pt/C, 20 wt% PtRu(1:1)/C or 20 wt% PtSn (3:1)/C electrode with a total metal loading of ~0.1 mg cm⁻² was used as the anode (working electrode). A Nafion® 117 membrane and an E-TEK Pt/C electrode (0.35 mg cm⁻²) were used as electrolyte and cathode (counter electrode), respectively. The working electrode chamber of the cell was fed with the H2+2% CO mixture, and the counter electrode chamber was supplied with pure H2. Because of the negligible overpotential at the counter electrode for the hydrogen oxidation, it also served satisfactorily as a reference electrode [19,20]. All the measured potentials shown in this paper are reported versus the reference hydrogen electrode (RHE). To minimize the mass transfer resistance, the flow-rate of the gases was fixed at 90 ml min⁻¹, well above the stoichiometry. The temperature of the cell was 50 °C, and the gas streams were humidified at 70 °C. Alternatively, experiments were made with the cell temperature at 25 and 70 °C, and gas humidification at 45 and 90 °C, respectively.

Prior to experiments, 20 cyclic voltammetric scans were carried out to clean the electrode surface. Then the system was given 15 min to reach a pseudo steady state at each specific potential before collecting electrochemical data (current and impedance, respectively). Impedance spectra were recorded at 10 points per decade by superimposing an ac signal on the cell in the constant dc voltage mode. The frequency of the ac signal applied was in the range of 0.01 Hz to 10 kHz and the amplitude of the ac signal was fixed at 10 mV to minimize the signal noise. The measured impedance data were checked by Kramers–Kronig (K–K) transform software provided by the equipment manufacturer Autolab (Ecochemie), at which one component Z’ or Z” of the measured data points was fitted to a special model circuit expression and then the other component Z” or Z’ was calculated based on the extracted circuit parameters. If the measured data for the other component agree with the transformed data, (i.e. data reconstructed from the model circuit), then the data set should satisfy K–K assumptions implicitly because the passive circuit always satisfies the four criteria for K–K transforms. Expressed mathematically, this is that the sum of the squares of the relative residuals between the transformed data and the corresponding experimental data should be as small as possible. The results show that the relative residuals are lower than 10⁻³. Therefore, all the data are validated.

For the CO-stripping voltammetry experiment, the electrode was kept at 0.025 V versus RHE for 30 min in a H2+2% CO gas flow and subsequently purged with pure N2 for 30 min, then the measurement was conducted at a scan rate of 20 mV s⁻¹.

3. Results and discussion

To provide a systematic strategy to evaluate the CO-tolerance for different anode catalysts at different operating temperatures, we first describe the results using typical voltammetric methods before discussing in detail the impedance-based evaluation. Finally, we will demonstrate that the onset potential observed in the oxidation impedance can be used as an effective criterion for evaluating the capability for CO-tolerance among different electrocatalysts.

3.1. Evaluation of CO-tolerance of anode electrocatalysts using cyclic voltammetry and stripping voltammetry

The cyclic voltammetry for the oxidation of the H2+2% CO mixture and the stripping voltammetry for the oxidation of adsorbed CO (COads) on Pt/C, PtRu/C and PtSn/C electrodes at 50 °C are presented in Figs. 1 and 2, respectively. As is shown in the cyclic voltammetry (Fig. 1), at a low potential region no significant current flow is observed for the Pt/C. Although H2 can be oxidized at low potentials (below 0.6 V) on the Pt/C, its
The reaction is often hindered by the competition of CO adsorption, which forms a dense CO adlayer and blocks the active site for H\(_2\) adsorption and the subsequent oxidation. Similarly, the stripping voltammetry (Fig. 2) showed that the CO ads cannot be oxidized on the Pt/C in the low potential region. Consequently, the observed current on Pt/C at this region is primarily generated by H\(_2\) adsorption, followed by the oxidation on the vacant sites of Pt in the adlayer of adsorbed CO [21].

As the potential reaches the ignition potential where CO ads oxidation on the Pt/C starts to kick in, available active surface sites are increased and thus the oxidation of H\(_2\) accelerates as shown by the sharp surge of the current flow.

For the PtRu/C and PtSn/C, similar patterns are observed. However, the ignition potentials of the oxidation of the H\(_2\)+2\% CO mixture and the stripping voltammetry (Fig. 2) showed that the CO ads cannot be oxidized on the PtSn/C surface [22], the CO ads can be removed at a potential lower than that of the PtRu. The addition of Sn is known to play a significant role in modifying the catalytic surface property and lowering the activation energy for CO ads oxidation. The Sn surface site is not responsible for the chemisorption of CO as is concluded from the result that the total oxidation charge for the PtSn/C is smaller than that for Pt/C and PtRu/C. The Sn dopant serves as a surface modifier. Crabb et al. [22] have demonstrated that a small amount of Sn dopant will be enough to produce the effect. Any further increase in the Sn concentration will decrease the total oxidation charge.

In the literature, the ignition potential is often used as a tool for the evaluation of CO-tolerance of alloy catalysts prepared by different alloy compositions or operated at different temperatures and CO concentrations [3,6–8]. From the viewpoint of the ignition potential, the CO-tolerance of catalysts evaluated in this study increases in the order of Pt/C < PtRu/C < PtSn/C.

The cyclic voltammetry for the oxidation of the H\(_2\)+2\% CO mixture and the stripping voltammetry for the oxidation of the adsorbed CO (CO ads) on the PtRu/C electrode at different operating temperatures are presented in Figs. 3 and 4, respectively. It can be seen from the stripping voltammetry (Fig. 4) that with the increase of the working temperature from 25 to 70 °C, the ignition potential of the adsorbed CO (CO ads) oxidation on the PtRu/C decreases, indicating that the CO-tolerance can be improved by increasing the temperature. Similarly, the cyclic voltammogram (Fig. 3) also showed that the CO-tolerance increases with an increase of the operating temperature.

Although the voltammetric techniques allow the assessment of the CO-tolerance for different electrocatalysts through the comparison of the ignition potential, such studies will not be practical for the diagnostics

![Fig. 1. The cyclic voltammograms of the oxidation of a H\(_2\)+2\% CO mixture on Pt/C (0.10 mg cm\(^{-2}\) Pt), PtRu(1:1)/C (0.09 mg cm\(^{-2}\) PtRu) and PtSn(3:1)/C (0.12 mg cm\(^{-2}\) PtSn) electrodes at 50 °C.](image1)

![Fig. 2. The stripping voltammograms of the oxidation of adsorbed CO on Pt/C (0.10 mg cm\(^{-2}\) Pt), PtRu(1:1)/C (0.09 mg cm\(^{-2}\) PtRu) and PtSn(3:1)/C (0.12 mg cm\(^{-2}\) PtSn) electrodes at 50 °C.](image2)

![Fig. 3. The cyclic voltammograms of the oxidation of a H\(_2\)+2\% CO mixture on PtRu(1:1)/C (0.09 mg cm\(^{-2}\) PtRu) electrodes at different operating temperatures.](image3)
of the electrocatalysts in the real operation since the stripping voltammetry can provide information for the oxidation of adsorbed CO only in an inert atmosphere, but not for the dynamic equilibrium occurring in the mixed H₂ + CO gas flow, where CO can compete with the H₂ oxidation and re-adsorb on sites liberated by the oxidation [14]. Moreover, as the ignition potential is defined as the potential value at which a sudden increase in the current flow is seen, it is difficult to determine the accurate value of ignition potentials from the stripping and cyclic voltammograms. In particular, the ignition potential can often be misinterpreted when the axis-scale of the current flow in the current versus potential plot is changed. On the other hand, electrochemical impedance measurements, although more time-consuming experimentally, provide more information than that of the voltammetric techniques. Conversely to the stripping and cyclic voltammetry, not only can the onset potential (described in the next section) be identified in the impedance spectra, but also kinetic information involving multiple surface processes can be found by impedance measurements. For example, in the case of electrocatalytic oxidation involving two adsorbed species, interesting impedance patterns that switch from the 1st to the 2nd or 3rd quadrant can often be identified [23]. This impedance pattern reversal signals the change of the rate determining step in the electrode reaction, information on which will not be obtainable from voltammetric measurements. In the next section, we will describe how the ‘onset potential’ for the pseudo-inductive behavior observed in the complex impedance plot can be used to evaluate the CO-tolerance capability for different electrocatalysts.

3.2. Evaluation of CO-tolerance of different anode electrocatalysts using the impedance spectroscopy

In this section, the EIS technique was used to investigate the catalytic activity for the CO oxidation, i.e. the CO-tolerance, at different anode electrocatalyst surfaces. The potential dependence of the impedance changes of three electrocatalysts, Pt/C, PtRu/C and PtSn/C, is shown in Figs. 5–7, respectively. Similar impedance trends are observed; nonetheless the potential value where the impedance pattern starts to change is different for different electrocatalysts.

For the three electrocatalysts studied, a large open impedance arc is observed at the low potential value (V₀ = 0.70, 0.45 and 0.30 V for Pt/C, PtRu/C and PtSn/C, respectively and hereafter called the onset potential), the so-called ‘pseudo-inductive’ behavior [13] in the complex impedance plot begins to emerge. The onset potential, in this study, for the pseudo-inductive behavior is defined as the potential value (at the experimental frequencies of 0.01 Hz to 10 kHz) at which a large positive loop at higher frequencies is accompanied by a low frequency negative semicircle
loop in the 4th quadrant (Figs. 5a, 6a, and 7a). The appearance of the 4th quadrant impedance loop signals that the coverage of adsorbed CO starts to decrease with an increase of the potential.

With increasing the bias potentials, the diameters of the two semicircles decrease rapidly and at the critical potential \(V_{\text{crit}}\) the low frequency limit of the impedance \(R_0\) approaches the smallest values and changes only slightly for a further potential increase (Figs. 5b, 6b, and 7b).

Noticeably, the onset potential for the pseudo-inductive behavior in the impedance plot is a very important parameter, of which the physical meaning depends on the understanding of pseudo-inductive behavior. The pseudo-inductive behavior means that the current signal follows a voltage perturbation with a phase delay (\(\phi = 90^\circ\) for a pure inductor). This impedance pattern is generally associated with consecutive heterogeneous reactions involving adsorption intermediates [1,24,25]. Particularly in our case, it is caused by the oxidation of adsorbed CO coupled with the subsequent \(\mathrm{H}_2\) oxidation on the surface sites freed up by the adsorbed CO. The objective of this work is to elucidate the use of impedance data for evaluating the activity and CO-tolerance of three different electrocatalysts. The detailed mechanistic modeling studies that explain the observed impedance behavior can be found in our previous publications [17,23] where the effects of applied potentials and kinetic parameters on the impedance patterns are delineated. The impedance measurement for the \(\mathrm{H}_2\) oxidation was not conducted in this study as the impedance plot of \(\mathrm{H}_2\) oxidation will simply be a small arc, the magnitude of which will be orders smaller than that of \(\mathrm{H}_2/\mathrm{CO}\) oxidation. No pseudo inductive behavior is expected in the \(\mathrm{H}_2\) oxidation system [14].

To compare the information obtained from the onset potential of the anodic \(\mathrm{H}_2/\mathrm{H}_2+2\%\mathrm{CO}\) cell with PtRu(1:1)/C anode (0.09 mg cm\(^{-2}\) PtRu) at 50 °C as a function of the bias voltage (IR-uncorrected), (a) low potential range, (b) high potential range.

Fig. 6. Complex impedance plots for a \(\mathrm{H}_2/\mathrm{H}_2+2\%\mathrm{CO}\) cell with PtRu(1:1)/C anode (0.09 mg cm\(^{-2}\) PtRu) at 50 °C as a function of the bias voltage (IR-uncorrected), (a) low potential range, (b) high potential range.

Fig. 7. Complex impedance plots for a \(\mathrm{H}_2/\mathrm{H}_2+2\%\mathrm{CO}\) cell with PtSn(3:1)/C anode (0.12 mg cm\(^{-2}\) PtSn) at 50 °C as a function of the bias voltage (IR-uncorrected), (a) low potential range, (b) high potential range.
potentiostatic curves (Fig. 8), it is found that the value of the onset potential for the ‘pseudo-inductive’ behavior agrees well with the former. Figs. 9 and 10 show the impedance plots at different bias voltages for the oxidation of the H<sub>2</sub>/CO mixture on PtRu/C at 25 and 70 °C. With increasing bias potential a similar change of the pattern of the complex impedance plots as that at 50 °C was observed for PtRu/C at 25 and 70 °C, respectively. However, impedance plots show the strong dependence of the onset potential for the ‘pseudo-inductive’ behavior on the operating temperature. With increasing temperature, the onset potential decreases in the order of PtRu/C at 25 °C (0.50 V) > PtRu/C at 50 °C (0.45 V) > PtRu/C at 70 °C (0.40 V).

Fig. 8. Polarization curves for a H<sub>2</sub>/H<sub>2</sub>/CO cell with different anodes (Pt/C, PtRu/C, and PtSn/C with total metal loading of 0.10, 0.09 and 0.12 mg cm<sup>-2</sup>, respectively) at 50 °C.

Fig. 9. Complex impedance plots for a H<sub>2</sub>/H<sub>2</sub>/CO cell with PtRu/C anode (0.09 mg cm<sup>-2</sup> PtRu) at 25 °C as a function of the bias voltage (IR-uncorrected), (a) low potential range, (b) high potential range.

Fig. 10. Complex impedance plots for a H<sub>2</sub>/H<sub>2</sub>/CO cell with PtRu/C anode (0.09 mg cm<sup>-2</sup> PtRu) at 70 °C as a function of the bias voltage (IR-uncorrected), (a) low potential range, (b) high potential range.

Fig. 11. Polarization curves for a H<sub>2</sub>/H<sub>2</sub>/CO cell with PtRu(1:1)/C anode (0.09 mg cm<sup>-2</sup> PtRu) at different operating temperatures.
V). Consistent results can be obtained from Fig. 11, which shows the effect of temperature on the ignition potential for the potentiostatic oxidation of a H₂ + 2% CO mixture on PtRu/C. It is concluded that an increase of the operating temperature can improve the CO-tolerance of catalysts.

To summarize the information from the previous discussion, listed in Table 1 are the critical potentials in the EIS measurement and ignition potentials from the potentiostatic measurement for the oxidation of the H₂ + 2% CO mixture. As can be seen from Table 1, the onset potential ($V_{\text{crit}}^{\text{Ia}}$) coincides with the ignition potential and the increase of operating temperature improves the CO-tolerance of the catalyst. Using the criterion of onset potential, the PtSn/C catalyst is the most efficient of the three catalysts studied in this work.

As discussed previously, at the second critical potential ($V_{\text{crit}}^{\text{II}}$) the low frequency limit of the impedance ($R_0$) approaches the smallest values and changes only slightly for any further potential increase. Calculated from the impedance modulus $|Z|$ at $f = 0.01$ Hz, this low frequency limit of the impedance can be regarded as the approximation of the polarization resistance and employed as the second parameter to evaluate the CO-tolerance of anode catalysts. Since the impedance depends on the catalyst loading, the low frequency limit of impedance ($R_0$) can be used only for qualitative comparison of catalysts with similar loading. Fig. 12a and b shows the low frequency limit of impedance ($R_0$) as a function of the bias potential for a H₂/H₂ + 2% CO cell with different anode catalysts and at different temperatures. At low bias potentials, $R_0$ is very large, which indicates the anode catalysts are fully blocked and H₂ oxidation occurs only in the holes in the CO ads dense layer. At a potential between the first critical potential ($V_{\text{crit}}^{\text{Ia}}$) and the second critical potential ($V_{\text{crit}}^{\text{II}}$), $R_0$ decreases with increasing bias potential, indicating that the surface of the catalysts is partially recovered and available for H₂ oxidation, while at very high bias potentials, $R_0$ is very small, meaning that the electrode is fully recovered. As is shown in Fig. 12a and b, at the same bias potential, $R_0$ decreases in the order of Pt/C > PtRu/C > PtSn/C at 50 °C, and PtRu/C at 25 °C > PtRu/C at 50 °C > PtRu/C at 70 °C. By examining the magnitude of $R_0$, the CO-tolerance capability among different electrocatalysts can be determined.

### Table 1

<table>
<thead>
<tr>
<th>Type of catalyst</th>
<th>Operating temperature/°C</th>
<th>$V_{\text{crit}}^{\text{Ia}}$/V</th>
<th>$V_{\text{crit}}^{\text{II}}$/V</th>
<th>Ignition potential from potentiostatic curves/V</th>
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</thead>
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<tr>
<td>PtRu/C</td>
<td>50</td>
<td>0.45</td>
<td>0.85</td>
<td>0.45</td>
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<tr>
<td>Pt/C</td>
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<td>0.70</td>
<td>0.85</td>
<td>0.70</td>
</tr>
<tr>
<td>PtSn/C</td>
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<td>0.30</td>
<td>0.85</td>
<td>0.30</td>
</tr>
<tr>
<td>PtRu/C</td>
<td>25</td>
<td>0.50</td>
<td>0.90</td>
<td>0.50</td>
</tr>
<tr>
<td>PtRu/C</td>
<td>70</td>
<td>0.40</td>
<td>0.60</td>
<td>0.40</td>
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</table>

$V_{\text{crit}}^{\text{Ia}}$: onset potential for ‘pseudo-inductive’ behavior, at which the ‘pseudo-inductive’ behavior appears, $V_{\text{crit}}^{\text{II}}$: the critical potential, at which the low frequency limit ($R_0$) approaches the smallest values.

### 4. Conclusions

The impedance pattern of the H₂ + 2% CO mixture in a PEFC on different anode catalysts (Pt/C, PtRu/C and
PtSn/C) and at different operating temperatures as a function of bias potential was investigated. It was found that, at a critical potential, ‘pseudo-inductive’ behavior appears, and the value of this potential is different for different anode catalysts. This potential was found to be coincident with the corresponding ignition potential of the H$_2$+2% CO mixture in potentiostatic curves and we believe that this onset potential for ‘pseudo-inductive’ behavior can be used as a new criterion for the evaluation of CO-tolerance of anode catalysts.

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References