EXAMINING A POTENTIAL FUEL CELL POISON: A VOLTAMMETRY STUDY OF THE INFLUENCE OF CARBON DIOXIDE ON THE HYDROGEN OXIDATION CAPABILITY OF CARBON SUPPORTED PT AND PTRU ANODES

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Abstract

Polymer electrolyte fuel cells being operated on reformed fossil fuels are exposed to large quantities of carbon dioxide. In order to elucidate the extent of the reverse water gas shift of CO$_2$ on hydrogen covered fuel cell anodes to CO, an extensive cyclic voltammetry study has been done on Pt and PtRu electrodes in sulfuric acid with varying hydrogen coverage. The electrodes used are representative of those being used in PEM fuel cells. The reverse shift reaction is facile on Pt/C, but with the surface not poisoned to the same extent as it does by exposure to CO saturated solutions. The reaction product is oxidized in a similar fashion to formic acid and methanol on platinum. The results indicate the formation of a stable adlayer, consisting of linear, bridge and multibonded CO in accordance to what has been proposed for unsupported platinum electrodes. PtRu/C fuel cell anodes are expected to be considerably more tolerant towards carbon dioxide than Pt/C anodes, with both the reaction suppressed and the adsorbate oxidation occurring at a lower potential.
Introduction

While studies of reformate tolerance in PEM fuel cells mainly address CO poisoning, carbon dioxide has also been shown to affect anode performance [1-4]. The effects on Pt anodes are modest, compared to CO, but at the level CO₂ is present in reformate under PEMFC conditions (up to 25%), losses are significantly greater than can be expected by dilution alone. The prevalent route for poisoning involves the reduction of carbon dioxide. The standard reduction potential for CO₂ is – 0.2 V [5], meaning that at a typical fuel cell anode operating near +50 mV, the chemical pathway will be dominant over the electrochemical pathway.

The first step of the reaction on Pt electrodes, in acidic solutions, is the electroadsorption of hydrogen adatoms, followed by their reaction with carbon dioxide:

\[ \text{H}^+ \rightarrow \text{H}_{\text{ads}} \]  \hspace{1cm} (1)

\[ \text{CO}_2 + 2 \text{H}_{\text{ads}} \rightarrow \text{CO} + \text{H}_2\text{O} \]  \hspace{1cm} (2)

CO₂ reduction on Pt by Pt hydrides, in acidic solution, was first reported by Giner [6], who postulated CO or a COOH radical being a main product in the reaction as in the case of HCOOH adsorption [7]. Since then the exact nature of the reduction product has been the subject of some controversy. The formation of CO [8], COOH [9,10] and COH [11,12] has been proposed. Different “reduced” CO₂ adsorbates on Pt have been described as ensembles of CO₂, CO, H and H₂O [13,14]. More conclusively, IR spectroscopy has revealed the characteristics of reduced CO₂ on polycrystalline and low index single-crystal Pt electrodes, where linear, bridged and triply bonded CO molecules were identified [14-19]. Apart from CO, the presence of COH and COOH was also detected [19].
Platinum is used in the hydrogen fed PEM fuel cells owing to its superior hydrogen oxidation capabilities. When reformed fuels as natural gas or gasoline are fed, the anodes are, besides hydrogen, also exposed to CO and CO₂. PtRu is generally used in these, as CO poisons the hydrogen oxidation capability less on PtRu than on Pt. For this reason they are called CO tolerant, albeit the fact that tolerance is not quantitatively a well-defined concept. The tolerance is attributed to CO adsorption inhibition due to electronic effects and to the bifunctional character of PtRu in the electro-oxidation of CO: nucleation of oxygen containing species (OHₐd) on Ru atoms, at low potentials, which then interact with adsorbed carbon monoxide on neighboring atom sites. Performance losses of fuel cells with PtRu anodes due to carbon dioxide have been reported to be minimal [2-4]. Since CO was not tolerated to the same extent, the improved performance was attributed to the reduction of CO₂ to CO being suppressed, rather than the improved elimination of CO, meaning basically that PtRu should be a poor CO₂ reduction catalyst.

In the present study, the reduction of carbon dioxide is examined, by cyclic voltammetry in H₂SO₄, on Pt and PtRu, supported on high-surface area carbon, doped with Nafion. Thus the actual catalysts used in the PEMFC are investigated. In such a way the effects of both support, finite metal particle size and solid polymer electrolyte (Nafion) are studied on the process and a good understanding of how and if carbon dioxide poses a serious threat on the anode, in the PEMFC, is obtained.

**Experimental**

The catalysts used in the experiments were E-TEK Pt and PtRu (1:1) supported on carbon Vulcan XC-72 with a 40% metal loading, from which propanol based catalyst inks were prepared with Nafion (5%, EW 1100). Cyclic voltammetry
experiments were conducted in 1N \( \text{H}_2\text{SO}_4 \) (Merck) prepared with Millipore super Q water. The setup consisted of a standard electrochemical cell, with the usual three electrode arrangement, on a computer controlled Autolab PGSTAT 20 potentiostat / galvanostat (Ecochemie). Platinum and platinized Pt square foils (1.5 cm\(^2\)) were used for the working and counter electrodes respectively. The catalyst ink was applied on both sides of the working electrode. \( \text{Hg} / \text{Hg}_2\text{SO}_4 \) (\( \text{K}_2\text{SO}_4 \) saturated) was used as a reference electrode, which has a potential of \( E = +0.658 \text{ V} \) versus the Reversible Hydrogen Electrode (RHE) and all potentials were referred to the RHE. All voltammograms were collected between 18 mV (starting potential) and 1.26 V with a scan rate of 5 mV / s, in the temperature range of 25 – 75 \( ^\circ \text{C} \).

The samples were electrochemically cleaned in solution by continuous cycling, and nitrogen purging with the voltammogram of the clean surface being reproducible. CO and CO\(_2\), both 10% in Argon, gases were employed. The solution was saturated with the gas, in each case, while the electrode was held at the adsorption potential, which was 18 mV versus RHE unless otherwise stated. For both CO and CO\(_2\) experiments, monitoring the reduction current in chronoamperometry ensured solution saturation, which occurred after 40 minutes for carbon dioxide. After each dose the solution was cleaned of any contaminants by bubbling nitrogen through it. No adsorbate oxidation was monitored during the second scan. Formic acid and methanol adsorption experiments were conducted by adding several drops of \( \text{HCOOH} \) and \( \text{CH}_3\text{OH} \) (Merck 98-100% p.a.) respectively to the solution, while keeping the anode potential at 18 mV for 30 sec.
**Results and Discussion**

*Pt / C.* - The voltammetry profiles of the Pt/C electrode in the supporting electrolyte with and without saturation amounts of CO or CO$_2$, at room temperature (25 °C), are depicted in Figure 1. For the clean surface, the profile resembles that observed from polycrystalline platinum, with the hydrogen region, from 0 to ~0.37 V vs. RHE, corresponding to the reductive adsorption of protons in the cathodic scan and the subsequent oxidation of the hydrogen adatoms in the anodic scan [20]. Two oxidation peaks are observed, in the anodic stripping voltammogram of CO$_{ads}$, with a main peak at 744 mV and a pre-wave peak at 658 mV, attributed to ‘strongly’ and ‘weakly’ adsorbed CO respectively [21]. For CO$_2$ a relatively broad distribution is seen, which basically consists of two overlapping peaks, with the major one at 624 mV. This corresponds to what has been observed on smooth and electrodispersed platinum electrodes [10, 13, 14 and 16], although a comparison of CO and CO$_2$ found the main peaks to coincide [10, 16], which is not the case in the present study.

At the adsorption potential of 18 mV the coverage of adsorbed hydrogen is unity. Upon CO saturation of the solution, CO displaces almost all the hydrogen from the surface, as seen by the significant suppression of the hydrogen adsorption-desorption charges. In the case of CO$_2$ the expulsion of atomic hydrogen is not as complete, since as seen in the voltammogram, an amount of adsorbed hydrogen is still left behind. Evaluating the charges $Q_H$ in each case, gives the amount of surface atoms covered:

$$\theta_{CO/reducedCO_2} = \frac{Q_H^O - Q_H^A}{Q_H^O}$$

(3)
where $Q^0_H$ and $Q^A_H$ represent that charge transferred during hydrogen oxidation before and after CO adsorption / CO$_2$ reduction respectively. The values are listed in Table 1. The presence of reduced CO$_2$ leaves 22% of the Pt surface sites vacant for hydrogen adatom adsorption, in contrast to CO where practically the whole surface (98%) is saturated. Also listed are the number of electrons involved in the oxidation of the adsorbate per single adsorption / reduction site (eps), which is defined as:

$$eps = \frac{Q_{ox}}{Q^0_H - Q^A_H}$$

A H-Pt ratio of 1 is assumed for the Pt site open to hydrogen adsorption. For CO the value of eps is 2 meaning that it possesses a linear form, occupying an atop position, since two electrons are required for the oxidation of one molecule of CO. A value of one would have implied bridge bonding. Prevalent atop bonding has been suggested for single crystalline Pt, under electrochemical conditions, with bridge bonded CO being identified at saturation coverage [22]. Hollow site preference also has been recently predicted [23]. Eps values between one and two were found for platinized Pt [10,24,25], indicating a mixture of linear, bridge and multi-bonded CO. On carbon supported platinum, the limited particle size was found to favor the formation of the linear bond [26].

The finite particle size, which for the catalysts presently used is on average 39 Å [27], has been held responsible for the CO oxidation coverage dependence seen on Pt/C, with the peak potential shifting to higher values with increasing coverage [26]. It has been established that CO forms relatively compact islands on Pt [28]. It is less
probable that at low coverage these islands are formed on the small particles of the supported catalyst. As the coverage though increases, islands will start to grow, resulting in slower oxidation, since water molecules can only attack carbon monoxide on the edges, and thus in a shift of $E_p$ to higher values. Figure 2 shows a comparison of reduced CO$_2$ oxidation and of preadsorbed CO at the same relative coverage (0.78). In both cases the same amount of hydrogen adsorption sites are blocked, but only the high potential shoulder of reduced CO$_2$ corresponds to that of preadsorbed CO. The difference in peak shape and potential alludes to a different adsorbate or structure involved in each case. The difference in eps values supports this. The CO$_2$ reduction product gives an eps value of 1.4, clearly indicating a combination of products, which corroborates the existence of the two peaks in the oxidation profile.

The anodic stripping voltammogram after a small amount of either HCOOH or CH$_3$OH was added to the solution is shown in Figure 3, alongside that of CO$_2$ (saturation). The concurrence of peaks, observed as well on unsupported Pt [7,9], points to the involvement of a similar product in the oxidation of methanol, formic acid and the reduction of carbon dioxide. The electro-oxidation of HCOOH on Pt has been well documented and exhibits a dual reaction pathway [29]. Direct 2e$^-$ dehydrogenation reaction proceeds parallel to dehydration to CO which is a stable intermediate acting as a site blocking poison. Both reactions yield CO$_2$ (and H$^+$) as the final product [30], with COOH$_{ads}$ acting as the reactive intermediate in dehydrogenation [31]. For methanol, CO has been mainly identified as the adsorbed intermediate formed on carbon supported Pt [26,32], with the existence of COH on platinized Pt at low coverage being suggested as well [24]. It should be noted that both formic acid and methanol, at these coverages at least, preferentially block sites otherwise occupied by strongly bonded hydrogen, as evident in the anodic stripping.
The interaction of carbon dioxide with the platinum particles leads to the creation of a stable CO adlayer, whose oxidation characteristics differ from those of preadsorbed CO. The reduction product is more easily oxidized, for the same surface coverage, owing to a difference in the adlayer structure. As has been stated previously, preadsorbed CO tends to form islands on platinum, with oxidation initiated on the perimeter of these islands, shifting the peak potential to higher values. For the reduction of CO₂, the lower saturation coverage can be explained in terms of an ensemble size requirement. That is, since hydrogen adatoms directly participate in the reaction, more sites would be required for the reduction to proceed on the surface. Assuming a uniform distribution is logical and would lead to faster oxidation kinetics. Also while preadsorbed CO bonds linearly on to the Pt catalyst, CO₂ reduction leads to both linear, bridge and/or multibonded CO, as deducted by the eps value being between one and two and in accordance to spectroelectrochemical data on unsupported platinum electrodes [14-19]. Condensed islands of linearly bonded CO are probably formed too, resulting in the high potential shoulder in the oxidation profile. In addition to carbon monoxide, the presence of either COH and /or COOH, both with calculated eps values of one [26], is possible.

Arvia and coworkers [13,14] have suggested the involvement of two distinguishable adsorbates, with a CO₂-H₂O clathrate type structure, depending on whether the reaction occurs via weakly or strongly bound hydrogen. The adsorbate from the reaction with the strongly bonded hydrogen species was found to be the most stable and was suggested to undergo a rather slow intra-conversion reaction leading to an adsorbed ensemble consisting of linear bonded CO, surrounded by adsorbed water molecules, hydroxyl and hydrogen species [14]. These conclusions would tie in well with the results presented here, but the same sort of CO₂ based intermediates being
involved in both the formic acid and methanol reaction as well seems rather unlikely. It is possible that different types of adsorbed CO form ensembles with hydrogen and water.

The effect of strongly and weakly bonded hydrogen on the reduction process can be examined by looking at the adsorption potential dependence, as seen in Figure 4. As expected, only negligible reduction is observed upon saturation at 378 mV, well above hydrogen adsorption, since the presence of hydrogen is imperative for the reaction to proceed. Only a minute amount of CO\textsubscript{2}, or CO contaminant, is adsorbed and oxidized at the higher potential which leads to the blocking of sites available for molecular hydrogen adsorption, as manifested by the drop in current of the middle peak in the hydrogen region. At 168 mV only strongly bonded hydrogen exists and eventually less CO\textsubscript{2} is allowed to react. But what is interesting is that the peak shape is qualitatively identical with the one for adsorption at 18 mV, with no peaks disappearing due to the lack of the weakly bonded hydrogen, and that the two states of hydrogen are not distinguishable in the anodic scan.

With increasing temperature the peak shifts negatively, becoming sharper, as shown in Figure 5, retaining the relative ratio between the products to a certain extent. The values for the peak potentials and relative coverages are given in Table 2. An almost linear dependence of $E_p$ on temperature is observed for both reduction product and CO, the values of the later given in Table 2 as well for comparison. This is common for CO on Pt [33], with the electro-oxidation rate increasing with increasing temperature [34]. Similarly, the oxidation of reduced CO\textsubscript{2} becomes more effective at higher temperature. What is interesting though, is the fact that the reduction itself becomes slightly more effective, as seen in the increase of the relative surface coverage. Maier et. al. [35] have suggested the formation of different types of
intermediates by the adsorption of CO$_2$ on polycrystalline Pt, by time and temperature
dependent surface reactions, with CO being the most stable at 20 °C and COOH
dominating at 70 °C. This strong selectivity dependence is not observed in the present
study. Both overlapping peaks shift uniformly (Figure 4), with the peak at lower
potential showing only a small increase in current compared to the higher one,
indicating a slight selectivity dependence. The eps maintains its original value.

One of the characteristics of the catalysts studied is that it has been
impregnated with Nafion, a copolymer consisting of a polytetrafluoroethylene (PTFE)
backbone and perfluorosulfonic groups. Huang and Feguy studied the reduction of
carbon dioxide on reticulated vitreous carbon (RVC) electrodes modified with
platinum black affixed to the substrate with a Nafion film and found that these
electrodes were not poisoned by the reduced species under the same conditions that
completely block unmodified Pt [36]. Apart from the special physical and chemical
features of the RVC electrode, Nafion was suggested as a possible contributor through
its anion-exchange capacity. The inclusion of Nafion does not seem to affect the
chemical reactivity of the currently studied catalysts in any way. Interactions between
the platinum particles and the conductive carbon support do not appear to inhibit the
reaction either. Carbon dioxide reduction is facile on Pt/C anodes, which renders its
consideration as a poison in PEM fuel cells necessary.

$\text{PtRu} / \text{C}$. –The cyclic voltammograms for fuel-cell-grade carbon supported PtRu in
CO and CO$_2$ saturated 1N H$_2$SO$_4$ are shown in Figure 6. For CO, the peak is clearly
shifted to a lower potential (420 mV) compared to platinum, which is a result of a
weakening of the CO-Pt bond [37] and the bifunctional character of the alloy which
lies in the fact that oxygen-like species adsorb easily on Ru. The onset of adsorption
would occur at potentials as low as 0.2 V [38] coinciding with hydrogen desorption, making a quantitative evaluation of surface coverage by desorption charges rather ambiguous. So while it is apparent that the surface is not fully saturated by carbon monoxide, absolute numbers deducted from hydrogen sites left unaffected is not precise.

Compared also to the results attained for Pt, described in the previous section, CO\textsubscript{2} reduction is suppressed on PtRu. About 85% of the surface has been left unaffected, after saturation at 18 mV, with the broad peak shifted to 440 mV, just slightly higher than what is seen for CO. Reduction product and CO oxidation occur in the same region, in contrast to what was seen on platinum. This is reasonable, if one assumes CO as the main reduction product and takes into account the fact that whereas on Pt CO island formation inhibits oxidation, a loose adlayer has been observed at the alloy [28]. Thus, the best distribution of CO\textsubscript{ads} / OH\textsubscript{ads} reactive pairs is offered which has a positive effect on the rate of oxidative adsorption.

Based on the discussion in the previous section one can expect the formation of CO by CO\textsubscript{2} on platinum atoms with carbon monoxide adsorbing on both Pt and Ru in the alloy. It is unclear though how carbon dioxide reacts with the Ru atoms. Ru is a known catalyst for the gas phase conversion of carbon dioxide to methane [39], which has also been detected as an electrochemical reduction product, alongside CO and CH\textsubscript{3}OH, on Ru electrodes [40]. Elsewhere, it was found that CO\textsubscript{2} chemisorbed particles were produced on platinum and rhodium with neither reductional chemisorption nor interactions of CO\textsubscript{2} with adsorbed hydrogen being observed for ruthenium [41]. If this were so, it would explain the low reduction efficiency observed on PtRu in the present study.
A comparison to formic acid and methanol on PtRu is interesting; their anodic stripping voltammograms being depicted in Figure 7. In the case of formic acid, the reaction product evolves in the same region as the one from carbon dioxide, but for methanol the peak comes at a much higher value (645 mV). Formic acid dehydration on PtRu leads to the formation of CO, with both Pt and Ru sites active in the process, the oxidation of which is observed in the stripping voltammogram. For methanol the situation is different. CO again is the dehydrogenation product, but adsorption in electrolyte does not occur on Ru, at least for low temperatures and for potentials up to 750 mV [42]. This results in a strong decrease in methanol dehydrogenation currents for increasing ruthenium concentrations in PtRu since the available surface area for adsorption is effectively reduced. Dehydrogenation (adsorption) does not occur when the surface is saturated with hydrogen, and as seen from Figure 7, proceeds at potentials higher than CO oxidation, which is not the rate-determining step in the reaction.

The dependence of the CO$_2$ reduction product on potential and temperature are shown in Figures 8 and 9, respectively. As expected, no reduction takes place above the hydrogen region. Similarly to Pt, reduction becomes more effective with the oxidation of the product shifting to lower potentials with increasing temperature. Temperature has a greater impact in activating the reaction than it does for Pt, with the coverage more than doubled at 75 °C. The main peak potentials for CO and reduced CO$_2$ are given in Table 3. The peak difference for the two is within 20 mV, with oxidation occurring in about the same region. Small differences could be due to differences in the configuration of the product relative to preadsorbed CO rather than to the oxidation of a different product altogether.
It should be noted that based on voltammetry alone, direct assignment of the reduction product on PtRu is speculative. Although for formic acid and methanol, carbon monoxide is the main product, in accordance to what has been seen on platinum, a detailed spectroscopic study is clearly necessary. It is still unclear though how the ruthenium atoms react to carbon dioxide, apart from the fact that oxidation of the product is more facile on the alloy, which is in accordance to its bifunctional character. What is of great importance, is that the reaction is suppressed to a great extent in comparison to platinum, implying that PtRu exhibits both CO and CO₂ tolerance.

**Conclusions**

The effect of CO₂ on commercially available Vulcan supported Pt and PtRu (E-TEK) with varying hydrogen coverage has been studied in order to examine the possibility of CO like species being formed by reverse gas shift of CO₂ with hydrogen in PEM fuel cells. A comparison has been made to existing data in the literature for smooth and platinized Pt electrodes. For Pt/C the product oxidation profile seems to coincide with that of methanol and formic acid. The results indicate the formation of a stable adlayer consisting mainly of linear, bridge and multibonded CO. On PtRu/C the reaction of CO₂ with preadsorbed hydrogen is suppressed, especially at low temperatures, and the adsorbate oxidation occurs at lower potentials, justifying its use as a reformate tolerant catalyst in polymer fuel cells.
References


Table I. Main peak potentials ($E_{\text{main peak}}$), coverages of adsorbed hydrogen ($\theta_H$), coverages of CO or reduced CO$_2$ ($\theta_{\text{(CO or reduced CO}_2)}$) and electron numbers per site (eps) of CO$_{\text{ads}}$ and reduced CO$_2$ on Pt/C at 18 mV.

<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>Reduced CO$_2$</th>
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<tbody>
<tr>
<td>$E_{\text{main peak}}$ (mV)</td>
<td>744</td>
<td>624</td>
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<tr>
<td>$\theta_{\text{(CO or reduced CO}_2)}$</td>
<td>0.98</td>
<td>0.78</td>
</tr>
<tr>
<td>$\theta_H$</td>
<td>0.02</td>
<td>0.22</td>
</tr>
<tr>
<td>eps</td>
<td>2</td>
<td>1.4</td>
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Table II. Main peak potentials ($E_{\text{main peak}}$) and coverages ($\theta$), of saturated CO and reduced CO$_2$ on Pt/C at 18 mV as a function of three different temperatures.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$E_{\text{red.CO}_2}$ (mV)</th>
<th>$E_{\text{CO}}$ (mV)</th>
<th>$\theta_{\text{(red.CO}_2)}$</th>
<th>$\theta_{\text{(CO)}}$</th>
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<tr>
<td>25</td>
<td>624</td>
<td>744</td>
<td>0.78</td>
<td>0.98</td>
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<tr>
<td>50</td>
<td>562</td>
<td>637</td>
<td>0.84</td>
<td>0.99</td>
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<td>75</td>
<td>515</td>
<td>589</td>
<td>0.85</td>
<td>0.99</td>
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Table III. Main peak potentials of saturated CO and reduced CO$_2$ on PtRu/C at 18 mV for three different temperatures.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$E_{\text{red,CO}_2}$ (mV)</th>
<th>$E_{\text{CO}}$ (mV)</th>
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<tr>
<td>25</td>
<td>440</td>
<td>420</td>
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<td>50</td>
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<td>372</td>
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<tr>
<td>75</td>
<td>330</td>
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**Figure 1.** Cyclic voltammery of clean, CO and CO\textsubscript{2} saturated carbon supported Pt in 1N H\textsubscript{2}SO\textsubscript{4}. The adsorption potential is 18 mV vs. RHE.
**Figure 2.** Anodic stripping for CO$_2$ saturation and preadsorbed CO at Pt/C in 1N H$_2$SO$_4$. The coverages correspond to an equal amount of H oxidation sites being poisoned in both cases. The adsorption potential is 18 mV vs. RHE.
Figure 3. Anodic stripping at Pt/C for CO₂ (saturation) and after small amounts of HCOOH and CH₃OH were added to 1N H₂SO₄. The adsorption potential is 18 mV vs. RHE.
Figure 4. Cyclic voltammogram for Pt/C after CO₂ saturation in 1N H₂SO₄ at 18 mV, 168 mV and 368 mV.
Figure 5. Cyclic voltammogram for Pt/C after CO₂ saturation in 1N H₂SO₄ at 25 °C, 50 °C and 75 °C. The adsorption potential is 18 mV vs. RHE.
Figure 6. Cyclic voltammetry of CO and CO$_2$ saturated carbon supported PtRu in 1N H$_2$SO$_4$. The adsorption potential is 18 mV vs. RHE.
**Figure 7.** Anodic stripping at PtRu/C for CO$_2$ (saturation) and after small amounts of HCOOH and CH$_3$OH were added to 1N H$_2$SO$_4$. The adsorption potential is 18 mV vs. RHE.
Figure 8. Cyclic voltammogram for PtRu/C after CO₂ saturation in 1N H₂SO₄ at 18 mV, 118 mV and 228 mV. The clean spectrum is also depicted for comparison.
Figure 9. Cyclic voltammogram for PtRu/C after CO₂ saturation in 1N H₂SO₄ at 25 °C, 50 °C and 75 °C. The adsorption potential is 18 mV vs. RHE.