Electrocatalytic hydrogenation processes at controlled potential. 3. Measurement of the catalyst potential

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ELECTROCATALYTIC HYDROGENATION PROCESSES 
AT CONTROLLED POTENTIAL—3. MEASUREMENT 
OF THE CATALYST POTENTIAL

J. F. VAN DER PLAS and E. BARENDRECHT
Laboratory for Electrochemistry, University of Technology, P.O. Box 513, 
Eindhoven, The Netherlands

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Abstract – To study the implications of the theory, part 2, to the response of measuring probes, we used a potential decay technique. It is found that for hydrogenation reactions in acidic media, silver is the best material for a measuring probe, due to its low exchange current density for the hydrogen evolution reaction. The influence of the rotation speed in the slurry cell on the response of the measuring probe is discussed.

1. INTRODUCTION
To control the potential of an electron-conducting catalyst present as a slurry in a reactor, it is necessary to measure this potential reproducibly and accurately. The method used is to let the catalyst particles collide with a small metal electrode (e.g. gold), assuming that the measured potential of the electrode is the same as the mean potential of the catalyst particles [1].

The accuracy of the method has as yet not been questioned because in most cases particle and probe were of the same material [2]. In these cases one may assume that the frequent collisions will equalize the potentials of both particles and probe.

However, when a catalyst is used, supported by another material, it becomes difficult to make a probe of the same material as the supported catalyst. For instance, to make a probe of an active carbon supported catalyst, the carbon can only be "glued" together by means of a polymeric material, like PTFE. This, however, makes the probe different from the actual catalyst, because of the hydrophobic character of PTFE.

During our experiments with the electrocatalytic hydrogenation of nitric acid [3], substantial differences were measured between probes of different material in the case of the nitric acid reduction. Therefore, a study has been made of the parameters determining the potential of a measuring probe.

2. EXPERIMENTAL
Procedures and instrumentation
In order to study the response of a measuring probe to charge transfer processes with both the reactants and the particles, potential decay experiments were carried out. A measuring probe was given a potential \( E_m \), relative to the steady-state potential of the probe in the solution. Then the probe was disconnected from the potentiostat and the relaxation of the probe potential to its steady-state value was recorded. These measurements were carried out with the redox couple \( \text{H}_2 - \text{H}^+ \) in a 0.5 M \( \text{H}_2\text{SO}_4 \) solution and with Pt–C catalyst concentrations ranging from 0 to 33 g/l. To describe mass transfer in the solution, rotating disc electrodes were used, together with the instrumentation sketched in Fig. 1. The potential was set on the probe by means of a Wenking potentiostat, type 68 FR 0.5. The connections of the potentiostat to the electrodes are made by a relay. To disconnect the potentiostat from the measuring cell, the relay was driven by a h.p.-function generator, type 3310 B. The potential-time decay curve was recorded, after the cell was disconnected from the potentiostat, with a Data-lab transient recorder, type DL 901, synchronized with the function generator. The decay curve could also be recorded on a Tektronix storage oscilloscope, type 5103 N, or via the transient recorder on a h.p. X(t)-Y-Y'-recorder, type 7046 A. The working (measuring) electrode was pretreated before with a positive and a negative going potential pulse of 5 V, delivered by a Wenking double pulse generator, type DPC 72, also synchronized by the function generator. The potential–time relationships at different points in the instrument arrangement are shown in Fig. 2.

The measuring cell and the construction of the disc electrodes are as described [4]. As reference a hydrogen electrode, in the same solution as in the cell, was used. The measurements were performed at different rotation speeds and with different set potentials.

3. RESULTS
Potential–time relationships have been recorded for different starting potentials, rotation speeds and catalyst concentrations. The probe materials used were selected for their difference in exchange current density for the hydrogen oxidation reaction (e.g. platinum vs silver) and in contact resistance (e.g. metal vs carbon). To compare the curves obtained with an equal starting potential and rotation speed but with different catalyst concentration, a relaxation time \( \tau \), is defined, being the time necessary for the potential to reach a value of one fifth of the starting potential vs rhe. This definition of the relaxation time is used, because the potential decay curves were not simply exponential or logarithmic, so that for these measurements the relaxation time has no definite meaning. Therefore a more practical definition
Fig. 1. Scheme of the instrumentation and the potential variations at different points.

Fig. 2. Potential–time relationships for the different insets in Fig. 1.

Table 1. Relaxation time, τr, in msec for a starting potential of 50 mV vs rHE; ω = 40 Hz; 0.5 M H₂SO₄ solution, hydrogen saturated

<table>
<thead>
<tr>
<th>Catalyst Pt–C, g/l</th>
<th>0</th>
<th>1.33</th>
<th>6.67</th>
<th>33.33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td>19</td>
<td>90</td>
<td>31</td>
<td>50</td>
</tr>
<tr>
<td>Gold</td>
<td>11</td>
<td>62</td>
<td>26</td>
<td>37</td>
</tr>
<tr>
<td>Silver</td>
<td>&gt;10⁵</td>
<td>127</td>
<td>63</td>
<td>52</td>
</tr>
<tr>
<td>Iridium</td>
<td>14</td>
<td>78</td>
<td>31</td>
<td>28</td>
</tr>
<tr>
<td>Rhodium</td>
<td>14</td>
<td>112</td>
<td>36</td>
<td>54</td>
</tr>
<tr>
<td>Glassy carbon</td>
<td>&gt;10⁵</td>
<td>38</td>
<td>&gt;10⁵</td>
<td>20</td>
</tr>
</tbody>
</table>

is used which we believe to be more representative for the potential decay curve. These relaxation times are shown in Table 1 for the different electrode materials.

When no catalyst is present, the τr-values obtained are indicative only for the electrochemical process. Upon adding catalyst, τr increases except with the silver and glassy carbon electrode. However, when glass particles are used instead of the catalyst particles, the relaxation time is not influenced. Measurement of τr with a silver electrode is only possible in the presence of the catalyst.

When no catalyst is present, the silver dissolves and the potential does not relax to the hydrogen redox potential. Measurements at a glassy carbon electrode were strongly dependent on the pretreatment of this electrode and were not possible if no hydrogen redox potential could be established at the electrode.

The relaxation time has a minimum value in the medium catalyst concentration range. The same behaviour is found for other starting potentials.

The dependence of the relaxation time on the rotation speed ω of the electrode has been calculated by plotting log τr vs log ω. In most cases linear curves were obtained (see Fig. 3). The slopes measured with different electrode materials and with different catalyst concentration are shown in Table 2.

In general, the dependence of the relaxation time on the rotation speed decreases when the start potential increases. The influence of the catalyst concentration is rather small. Again, the behaviour of the silver electrode is remarkable. Without catalyst no measurements can be made, but in the presence of catalyst its behaviour is comparable with that of the other metals. The same applies for glassy carbon.
4. DISCUSSION

The increase of the relaxation time, when catalyst is added to the solution, is unexpected. For, it is to be imagined that the presence of a catalyst would add a charge transfer process to the electrochemical reaction occurring at the measuring probe, and thus would lower the relaxation time. This is also confirmed by the response of the measuring probe as a function of $\alpha$ as calculated from theoretical considerations (part 2). From these calculations it was deduced that an increasing charge transfer between particle and measuring probe resulted in a faster response of the measuring probe[5]. The increase in time, as found in practice, however, may be due to a disturbance of the hydrodynamic and diffusion boundary layer by the particles. From the experiment with the glass particles it can be concluded that the mere presence of particles is not the cause, but that the behaviour observed must be associated with the catalytic action of the catalyst particles. The catalyst particles adsorb so much of the dissolved hydrogen, that the hydrogen concentration in the solution is lowered, which leads to an increase in relaxation time.

The contribution of the particles to the charge transfer can be concluded from the decrease in relaxation time with increasing catalyst concentration. The apparent minimum in relaxation time at a medium catalyst concentration can then be ascribed to the fact that at a certain catalyst concentration the collisions of particles with the measuring electrode are optimal: higher concentrations cannot contribute anymore to the total charge transferred. To the contrary, clogging of particles at the electrode surface may then occur, which means that colliding particles must transfer their charge via other particles to the probe. Thus the contact resistance will become larger and therefore the relaxation time will increase.

The behaviour of silver and glassy carbon in the absence of catalyst is due to their low exchange current density for the hydrogen oxidation reaction, which makes it difficult to build up a $H_2 - H^+$ redox potential at the electrode. However, the behaviour in the presence of catalyst shows that they are very useful to measure a catalyst potential. The somewhat unpredictable behaviour of the glassy carbon electrode and the higher specific resistivity of the material compared to silver makes the glassy carbon electrode less efficient than the silver electrode. Therefore, silver seems to be the best material to be used as a measuring probe in a hydrogen saturated solution, because its potential is solely determined by the catalyst particles.

The dependence of the relaxation time on the rotation speed of the electrode is different for the starting potentials applied. With a small starting potential (25 mV), the slope of the log $\tau_r$-log $\omega$ curve is $-1$, indicating that $\omega \tau_r = constant$. This means physically that the relaxation time depends on the relaxation of the diffusion layer at the electrode surface. At higher starting potentials (eg 100 mV), the

Table 2. $-\log \tau_r -\log \omega$ values for the potential decay measurements with the $H_2-H^+$ redox couple at different starting potentials and catalysts concentrations. Hydrogen saturated, 0.5 M $H_2SO_4$ solution

<table>
<thead>
<tr>
<th>Pt-C Catalyst concentration</th>
<th>0 g/l</th>
<th>1.33 g/l</th>
<th>6.67 g/l</th>
<th>33.33 g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>50</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>Starting potential mV</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td>0.96</td>
<td>0.79</td>
<td>0.60</td>
<td>0.87</td>
</tr>
<tr>
<td>Gold</td>
<td>1.07</td>
<td>0.90</td>
<td>0.61</td>
<td>0.90</td>
</tr>
<tr>
<td>Silver</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.16</td>
</tr>
<tr>
<td>Tridium</td>
<td>1.06</td>
<td>0.88</td>
<td>0.62</td>
<td>0.91</td>
</tr>
<tr>
<td>Rhodium</td>
<td>0.98</td>
<td>0.89</td>
<td>0.80</td>
<td>0.77</td>
</tr>
<tr>
<td>Glassy carbon</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.86</td>
</tr>
</tbody>
</table>
slope tends to a value of $-0.5$. Now, $\tau_1$ depends on the limiting diffusion current at the electrode surface which varies, according to the Levich equation[6], with the square-root of the rotation speed.

Generally, it is supposed, that the difference between the potential of the measuring probe used and the catalyst potential is small. In that case, $\tau_1$ is reciprocal proportional to the rotation speed. So, high rotation speeds of the electrode or high fluid velocities past the measuring probe improve the response.

5. CONCLUSIONS

It can be concluded from the above mentioned results, that silver is a suitable material for a measuring probe in hydrogenation reactions. It has a low exchange current density for the oxidation of hydrogen and is thus hardly influenced by this electrochemical reaction. The unpredictable behaviour of the glassy carbon electrode makes it, in spite of its low exchange current density, in practice less suitable than silver.

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5. J. F. van der Plas and E. Barendrecht, 25, 1471–1475.