In order to achieve reliable data regarding high temperature polymer electrolyte fuel cell (HT-PEFC) electrode degradation novel diagnostic techniques for the determination of the electrochemically active surface area (ECSA) were developed. Cyclic voltammetric CO-monolayer oxidation (CO stripping) charge measurements were combined with real-time CO2 exhaust gas analysis. Different evaluating methods were developed to overcome the problem of side reactions during CO stripping. Furthermore, a calibration curve for absolute ECSA determination via CO stripping was established, eliminating the temperature dependency of CO adsorption. In addition, these methods were successfully extended and implemented to locally resolved ECSA measurements. In summary, this paper introduces novel fundamental HT-PEFC electrode diagnostics for improved understanding of degradation phenomena.

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gas was detected in real-time. The amount of measured CO₂ was subsequently used to calculate the ECSA \((ECSA_{CO2})\).

**Experimental**

All experiments were carried out with BASF Celtec membrane electrode assemblies. Those MEAs consist of a H₃PO₄ doped PBI membrane and carbon paper gas diffusion electrodes (Pt/Vulcan XC-72, 1 mgPt/cm² of around 50–75 μm thickness) on anode and cathode, respectively. The MEA was operated at ambient pressure and was supplied with dry process gases with stoichiometries of 1.2 for hydrogen and 2.0 for air.

The CV measurements were carried out in the fuel cell using a two-electrode arrangement, i.e., the fuel cell anode (hydrogen electrode) was used as reference and counter electrode, whereas the fuel cell cathode (air electrode) was used as the working electrode (WE). During the CV measurements nitrogen at the WE side was humidified at room temperature. Compared to the setup in the foregoing publication, CO₂ concentrations were determined using a gas sensor based on infrared absorption with a higher detection range of up to 10000 ppmCO₂ (California Analytical Instruments Model 601). The CVs were recorded using a BioLogic SP-300 potentiostat.

**Method Development**

The three different ECSA determination methods can be divided into two categories. All three methods yield the amount of charge needed to oxidize the adsorbed CO. The first category is based on the integration of the CO oxidation currents in the recorded CVs. For each method three CVs were recorded (cf. Table I). The first CV can be considered as a cleaning step. For the second CV, which is called the reference, all parameters are kept identical compared to the CO stripping CV, except that instead of CO nitrogen was introduced. The third CV is the actual CO stripping measurement (for parameters see below). For both CV based methods it is necessary to define a baseline in order to calculate the CO oxidation charge. This is an important and sensitive requirement to achieve reproducible and diagnostically conclusive results. Accordingly, two potentials need to be specified as lower and upper limit, respectively. In the following, two different methods were evaluated to define those potentials and the baseline.

**ECSA_{CV vs. sec. cycle}** — The potentials at the current density minimum before and after the CO oxidation peak were used as integration boundaries. The second cycle of the same CO stripping CV is used as a baseline between the two potentials. In this method the reference CV is not needed for the charge calculation (cf. gray area in Figure 2a).

**ECSA_{CV vs. ref. CV}** — The reference CV simulates the CO stripping experiment without the adsorption of CO in order to obtain a correct integration baseline. This is necessary to avoid possible contributions to the overall stripping charge from sources other than CO oxidation which need to be corrected for. The integration boundaries are defined according to the potentials at the intersection between the reference and the CO stripping CV in the first cycle. The reference CV peak is used as a baseline (cf. orange hatched area in Figure 2a).

The second ECSA determination category is based on the measurement of CO₂ in the WE exhaust gas during the measurement of the CO stripping CV. One method was implemented according to the following routine.

**ECSA_{CO2}** — In Figure 2b the CO₂ concentration in the WE exhaust gas during the first two potential cycles of the CO stripping CV can be seen. The main area of the first peak can be attributed to the CO oxidation during the first CO stripping potential cycle. However, one cannot integrate the entire peak in order to estimate the \(ECSA_{CO2}\). Small amounts of CO₂, which are not related to CO monolayer oxidation, can be measured in the exhaust gas during the second

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**Table I. ECSA overall measuring process.**

<table>
<thead>
<tr>
<th>Start</th>
<th>CV_clean</th>
<th>Purge</th>
<th>Conditioning</th>
<th>Purge</th>
<th>CV_ref</th>
<th>Purge</th>
<th>CO adsorption</th>
<th>Purge</th>
<th>CV_mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate / Lnh⁻¹</td>
<td>72</td>
<td>10</td>
<td>72</td>
<td>27</td>
<td>72</td>
<td>10</td>
<td>72</td>
<td>27</td>
<td>72</td>
</tr>
<tr>
<td>Potential / mV</td>
<td>OCP</td>
<td>cycling</td>
<td>OCP</td>
<td>150</td>
<td>150</td>
<td>cycling</td>
<td>OCP</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Duration / min</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Gas type</td>
<td>N₂</td>
<td>N₂</td>
<td>N₂</td>
<td>N₂</td>
<td>N₂</td>
<td>N₂</td>
<td>CO</td>
<td>N₂</td>
<td>N₂</td>
</tr>
</tbody>
</table>

Figure 1. CO stripping CV at 180°C with small H₃PO₄ region and high HER currents. Further known issues concerning ECSA determination are indicated.
electron oxidation mechanism (cf. Equations 3 to 5), was used for rate during the measurements. Moreover, Equation 1, based on a two-electron oxidation step. For each measured mole of CO₂ two electrons were needed for the oxidation.

\[ n_{CO_2} = \frac{pV}{RT} \times A_{CO_2} \]  

where \( p \) and \( T \) are the ambient pressure and temperature, respectively, \( R \) is the universal gas constant, and \( V \) is the actual volume gas flow rate during the measurements. Moreover, Equation 1, based on a two-electron oxidation mechanism (cf. Equations 3 to 5), was used for the calculation of the oxidation charge \( Q_{CO_2} \).

\[ Q_{CO_2} = 2 \times N_A e \times n_{CO_2} = 2 \times F \times n_{CO_2} \]  

where \( N_A \) is the Avogadro constant, \( e \) the elementary charge and \( F \) the Faraday constant. The factor of two is the result of the two-electron oxidation step. For each measured mole of CO₂ two electrons were needed for the oxidation.

\[ Pt + CO_2 \leftrightarrow Pt - CO_{ad} \]  

The overall measuring process including all timings, potentials and flow rates is highlighted in Table I. The essential experimental setup is shown in Figure 3a.

![Figure 2](image1.png)  

**Figure 2.** a) Reference and CO stripping CVs. The gray area is related to the ECSA calculation method. The orange hatched area indicates the charge for the ECSA vs. ref. CV method. Measuring conditions: 160 °C, 10 mVs⁻¹, 10 Lₜₒ₉⁻¹ N₂, 4.5 Lₜₒ₉⁻¹ H₂, 1 mol.% CO in N₂. b) Real-time CO₂ signal at the fuel cell WE exhaust during the first two CO stripping potential cycles. The peak area of the second potential cycle is subtracted from the area of the first one. The resulting orange hatched area is used for the ECSA calculations. Note that it is not possible to exactly synchronize the CV measurement with CV vs. ref. CV.

![Figure 3](image2.png)  

**Figure 3.** a) Setup for CV and CO₂ measurements. b) S++ measuring device for locally resolved CO stripping CVs. c) Flow field with PEEK inlay.

\[ Pt + H_2O \rightarrow Pt - OH_{ad} + H^+ + e^- \]  

\[ Pt + CO_{ad} + Pt - OH_{ad} \rightarrow 2Pt + CO_2 + H^+ + e^- \]  

For all three methods a specific charge of 420 μCcm⁻²Pt⁻¹ and an active electrode area of 45.15 cm² were used for the ECSA calculations (cf. Equation 6).

\[ ECSA_{sec/ref/CO2} = \frac{Q_{sec/ref/CO2}}{420 \frac{μC}{cm^2} \times 45.15 \text{ cm}^2} \]  

**Results and Discussion**

CO stripping measurements at different temperatures were performed in order to understand the temperature dependency of CO adsorption and to establish a calibration curve. As one can see in Figure 4a, the CVs differ in various aspects. First of all, the Hupd area (in the cycles following the initial CO stripping sweep) increases with lower temperatures pointing to the aforementioned temperature dependency of Hupd formation. Secondly, the main CO oxidation peak shifts from lower to higher potentials with decreasing temperatures, in agreement with the known temperature dependence of reactions 3 to 5 (see above). An interesting feature appears at around 0.5 V after the first potential cycle. With increasing temperature a peak appears at this potential (cf. Figure 4b, for clarity, only the data for 40 °C and 180 °C are plotted). To clarify whether this peak is related to residual CO or highlights a different oxidation process a control measurement was carried out. A CV was recorded with the same parameters but without the initial CO adsorption. Again, a peak in the CV appeared at higher temperatures (see orange lines in Figure 4b). This finding indicates that there is not only...
Figure 4. a) First CO stripping CV cycle at different temperatures b) First (solid line) and second (dashed line) potential sweep of the reference CV at 40°C and 180°C, respectively. Measuring conditions: 10 mVs⁻¹, 10 Lnh⁻¹ N₂, 4.5 Lnh⁻¹ H₂, 1 mol.% CO in N₂.

CO oxidation taking place during the CO stripping in the relevant potential range. It is assumed that two distinct processes are the origins of this behavior. Firstly, surface functionalities of the high surface area support (Vulcan XC-72; cf. Figure 5) might be oxidized. The oxidation of those functionalities is triggered by temperature and potential.

Secondly, the oxidation of phosphorous acid impurities may also contribute to the initial oxidation peak (cf. Equation 7) as outlined in ref. 41, 42.

$$\text{H}_3\text{PO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 2\text{H}^+ + 2\text{e}^- \quad [7]$$

A further interesting finding is the small shoulder at around 0.7 V, recorded at 40°C. Relating to literature, this feature is known as the CO stripping pre-peak (or pre-oxidation wave) which only appears in the case of CO adlayers with high coverage. Therefore, we use the ECSA results at 40°C as reference for one monolayer of adsorbed CO, i.e., each CO molecule is bonded to a Pt surface atom in linear fashion (‘on-top’ configuration).

In Figure 6 the CO₂ signals measured with the IR-sensor during the CO stripping CV at three different temperatures are shown. The amplitude of the main CO₂ peak during the first potential cycle decreases with increasing temperatures. In contrast, the CO₂ peaks related to the second cycle slightly increase with elevated temperatures. This second CO₂ source is not associated to the main CO oxidation peak. It is reasonable to assume a second CO₂ source resulting from oxidation of different carbonaceous species (e.g., oxidation of the carbon support). The CO oxidation pre-peak at 40°C is also slightly visible in the CO₂ signal. At higher temperatures a small peak forms after the main peak, which is certainly related to carbon corrosions at elevated potentials and temperatures. For all three techniques the apparent ECSA decreases with elevated temperatures (cf. Figure 7), which is in good agreement with the assumption that the CO desorption rate (backward reaction in Equation 3) is more pronounced at higher temperatures.

The CO₂ and the CO stripping vs. reference CV methods are in

![Figure 5. Oxidation/reduction of carbon surface functionalities, e.g. hydroquinone/quinone type redox reactions.](image)

Figure 6. CO₂ signals during CO stripping voltammetry at different temperatures. The first peak indicates the first potential cycle whereas the second one indicates the second cycle. Measuring conditions: 10 mVs⁻¹, 10 Lnh⁻¹ N₂, 4.5 Lnh⁻¹ H₂, 1 mol.% CO in N₂.

Figure 7. Measured apparent ECSA trend at different temperatures determined via the three introduced methods. The gray line is used to establish a calibration curve.

<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>CO stripping vs. second cycle</th>
<th>CO stripping vs. reference CV</th>
<th>CO₂ method</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>394</td>
<td>386</td>
<td>392</td>
</tr>
<tr>
<td>60</td>
<td>376</td>
<td>365</td>
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<td>90</td>
<td>349</td>
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<td>120</td>
<td>322</td>
<td>278</td>
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<td>305</td>
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<tr>
<td>160</td>
<td>268</td>
<td>126</td>
<td>123</td>
</tr>
<tr>
<td>180</td>
<td>203</td>
<td>23.4</td>
<td>50.6</td>
</tr>
</tbody>
</table>
The slope of the curve (cf. Equation 11). This correlation allows the calculation of the adsorption equilibrium, an equation was deduced from the calibration and yields an apparent CO adsorption enthalpy of \( \Delta H^\circ = (53.5 \pm 5.6) \text{ kJmol}^{-1} \).

The missing equilibrium constant can be deduced from Equation 10, which expresses the mentioned Langmuir isostere.

The gray points indicate the surface coverage and the equilibrium constant. The coverage is calculated via locally resolved ECSA measurements.

Due to the good agreement with the Langmuir model, the results were applied to the VAN’T HOFF equation. The slope of the VAN’T HOFF equation multiplied by the universal gas constant equals the standard adsorption enthalpy, in this case, of CO on platinum nanoparticles (cf. Equation 9). The missing equilibrium constant \( K \) can be deduced from Equation 10, which expresses the mentioned Langmuir isostere, where \( p \) is the partial pressure of CO.

The VAN’T HOFF fit in Figure 8b is in good experimental agreement with the LANGMUIR model, the ECSA detection method was empirically developed and is now supported by a fundamental physio-chemical model.

In Figure 8a the electrode’s CO surface coverage curve as function of temperature is illustrated. The coverage is calculated via Equation 8 where the monolayer coverage is based on the results obtained at 40 °C. It can be fitted very well by the LANGMUIR isostere. The introduced ECSA detection method was empirically developed but is now supported by a fundamental physio-chemical model.

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In order to calibrate for the temperature dependence of the CO adsorption equilibrium, an equation was deduced from the calibration curve (cf. Equation 11). This correlation allows the calculation of the ECSA\(_{\text{mono}}\) based on a monolayer of adsorbed CO for any measured temperature and yields an apparent CO adsorption enthalpy of \( \Delta H^\circ = (53.5 \pm 5.6) \text{ kJmol}^{-1} \).

The V AN’T HOFF fit in Figure 8b is in good experimental agreement. However, the CO stripping vs. second cycle evaluation technique results in approximately ten times higher ECSA values at 180 °C (cf. Table II). This is likely to be a result of oxidation currents that are not related to the actual CO monolayer oxidation process (cf. Figure 5 and Equation 7). Those results indicate that the CO stripping vs. reference CV and the CO\(_2\) method are capable of separating and distinguishing the CO oxidation from other oxidation reactions occurring during the CV at all relevant potentials and temperatures. All further investigations were then based on the CO stripping vs. reference CV method since it features the possibility of locally resolved ECSA measurements.

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After establishing and validating the analysis routine one can now go one step further and transfer those findings to locally resolved measurements. One can see in Figure 9 that it is possible to record a homogeneous CO stripping CV for each segment with the presented setup. To the authors’ best knowledge there is no previous report on HT-PEFC which describes CV measurements with this high spatial resolution.

Following the CO stripping vs. reference CV routine and calculating the ECSA\(_{\text{mono}}\) for each segment via Equation 11, we were furthermore able to visualize the distribution of the true WE ECSA based on one monolayer of adsorbed CO (cf. Figure 10). The mean ECSA\(_{\text{mono}}\) based on all segments equals to (244 ± 10) cm\(^2\)Ptcm\(^{-2}\). This value is in excellent agreement with the globally recorded and calculated ECSA\(_{\text{mono}}\) of 256 cm\(^2\)Ptcm\(^{-2}\). Therefore, the introduced method for determination of the true WE ECSA in HT-PEFCs represents an excellent tool for detailed, locally resolved degradation diagnostics.
Conclusions

In this study we presented three different ECSA measurement techniques for the HT-PEFC. The ECSA_{CV vs. ref. CV} method cannot distinguish between CO and other oxidation currents at elevated temperatures. This circumstance results in a drastic overestimation of the ECSA and calls for alternative, more sophisticated methods. In contrast, those very side reaction currents were successfully excluded with the developed ECSA_{CV vs. ref. CV} method. Furthermore, we developed the novel ECSA_{CO2} technique, which is based on CO2 detection in the WE exhaust gas during CO stripping voltammetry. The ECSA_{CV vs. ref. CV} and the ECSA_{CO2} methods are in excellent agreement and provide reliable ECSA data. In addition, the presented CO stripping measurements showed a substantial temperature dependence, which we were able to compensate with the presented ECSA_{mono} equation. The deduced correlation provides the possibility to calculate the electrochemically active surface area based on one adsorbed CO molecule per Pt surface atom. The change in CO coverage with temperature was successfully described by the LANGMUIR model, which supports the method and yields the standard adsorption enthalpy of CO on platinum nanoparticles supported on Vulcan XC 72 in a HT-PEFC ((−53.5 ± 5.6) kJ mol⁻¹). Moreover, we could exploit those findings to establish ECSA measurements in HT-PEFC in a new range of spatial resolution. This manuscript can be seen as a fundamental but necessary basis for ECSA measurements in HT-PEFC in a new range of spatial resolution.

Acknowledgments

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References