Second Cycle Is Dead: Advanced Electrode Diagnostics for High-Temperature Polymer Electrolyte Fuel Cells

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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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“People all over the world, we need to solve the climate crisis. It’s not a political issue, it’s a moral issue.”¹

Besides the moral claim it is specifically a question and challenge of 21st century science to counter the climatic change.² A significant role is played by a stable, affordable and most of all sustainable electricity supply as an incitement for a global progress. Therefore, it is necessary to demonstrate technological pathways which are in line with a constantly increasing economy and a healthy environment.³ Fuel cells can be part of those very much needed new pathways. Based on renewable hydrogen, generated for example via biogas steam reforming⁴–⁶ or electrolysis,⁷–⁹ fuel cells can provide thermal and electrical energy in a large power range¹⁰–¹¹ in efficient manner and without greenhouse gas emission.

High temperature polymer electrolyte fuel cells based on phosphoric acid doped polybenzimidazole (PBI) membranes as a gel-type proton transport medium benefit in several different ways from operating at elevated temperatures of around 160°C.¹² First of all, they can be combined effectively with heating systems due to a high working temperatures above 100°C; note this is the typical way to perform this experiment in LT-PEFC). The second method requires potentials than the HER.²⁷ Nevertheless, CO adsorption is strongly dependent, see, e.g., the CO adsorption isotherms in the references.²⁸–³¹ Therefore, it is necessary to introduce a calibration curve, which allows the calculation of the absolute ECSA based on one monolayer of adsorbed CO (ECSA_{mono}). Additionally, side reactions, which are not related to CO monolayer oxidation, may influence the ECSA determination at elevated temperatures (e.g., surface oxidation, anion adsorption, cf. Figure 1).

In this manuscript two different CO stripping evaluation techniques based on CO oxidation currents are evaluated in order to investigate and overcome the highlighted issues. This first method uses the current of the second potential sweep as a baseline to determine the CO related oxidation peak (ECSA_{CV vs. sec. cycle}; note this is the typical way to perform this experiment in LT-PEFC). The second method requires the measurement of an additional CV called the reference CV. The current response of the first potential sweep serves as the baseline for the stripping peak charge (ECSA_{CV vs. ref. cv}). A similar method in the context of ECSA determination of oxide supported Pt catalysts at low temperatures was recently applied.²²

In addition, a novel, third way of ECSA measurement, which is not based on the CV itself, was developed and evaluated. During the CO stripping measurements the CO₂ content of the electrode’s exhaust...
gas was detected in real-time. The amount of measured CO₂ was subsequently used to calculate the ECSA (ECSA₃⁴).

Experimental

All experiments were carried out with BASF Celtec membrane electrode assemblies. Those MEAs consist of a H₃PO₄ doped PBI XC-72, 1 mgPt/cm² of around 50–75 μm including a membrane thickness of around 50–75 μm. The cells (active area 45.15 cm²) were operated at ambient pressure and were 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 as lower and upper limit, respectively. In the following, two different methods were evaluated to define those potentials and the baseline. 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.

Table I. ECSA overall measuring process.

| Start → | CV_clean | Purge | Conditioning | Purge | CV_ref | Purge | CO adsorption | Purge | CV_clean |
|---------|----------|-------|--------------|-------|--------|-------|--------------|-------|----------|
| Flow rate / L h⁻¹ | 72 | 10 | 72 | 27 | 72 | 10 | 72 | 27 | 72 | 10 |
| Potential / mV | OCP | cycling | OCP | 150 | 150 | cycling | OCP | 150 | 150 | cycling |
| Duration / min | - | - | 10 | 5 | 30 | - | 10 | 5 | 30 | - |
| Gas type | N₂ | N₂ | N₂ | N₂ | N₂ | N₂ | CO | N₂ | N₂ | N₂ |

A second crucial parameter is the optimal amount of CO introduced to the electrode for catalyst poisoning and the subsequent amount of N₂ for purging residual gas-phase CO out of the system. Therefore, experiments with different values for flow rate and time were carried out. In ref. 33 it was shown that with an increasing dose of N₂ after CO adsorption the deviation in the estimated ECSA becomes smaller. The dose is calculated by the product of the molar flow rate and the flow time divided by the electrode area. It is assumed that a certain amount of N₂ is needed to purge the residual, non-adsorbed CO from the WE and its porous structures because it could adsorb on unblocked electrochemically active surface areas which have already oxidized its initial CO molecules. Insufficient N₂ purging doses would therefore lead to an overestimation of the ECSA. Due to those results all further experiments were carried out with doses of 21.9 μmolCO cm⁻² WE and 351 mmolN₂ cm⁻² WE.

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 CvOx_conv 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 CvOx_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 category.

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electron oxidation mechanism (cf. Equations 3 to 5), was used for the 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.

\[ \text{Pt} + \text{CO} \leftrightarrow \text{Pt} - \text{CO}_2 \text{ad} \]  

Potential cycle. Therefore, 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 other than CO. Based on this area, the charge for the oxidation of carbonaceous species other than CO.

\[ n_{\text{CO}_2} = \frac{p V}{RT} \times A_{\text{CO}_2} \]  

Equation 1 was used to calculate the total molar amount of CO2 (\( n_{\text{CO}_2} \)), which is now only related to the oxidation of carbonaceous species other than CO.

![Figure 2](image)

**Figure 2.** a) Reference and CO stripping CVs. The gray area is related to the ECSA vs. ref. CV method. The orange hatched area indicates the charge for the ECSA vs. sec. CV method. Measuring conditions: 160°C, 10 mVs⁻¹, 10 Lh⁻¹ N₂, 4.5 Lh⁻¹ H₂, 1 mol.% CO in N₂.

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.

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 \( \text{Hupd} \) 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 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

\[ \text{Pt} + \text{H}_2\text{O} \rightarrow \text{Pt} - \text{OH}_\text{ad} + \text{H}^+ + e^- \quad [4] \]

\[ \text{Pt} + \text{CO}_\text{ad} + \text{Pt} - \text{OH}_\text{ad} \rightarrow 2\text{Pt} + \text{CO}_2 + \text{H}^+ + e^- \quad [5] \]

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

\[ \text{ECSA}_{\text{sec/ref}/\text{CO}_2} = \frac{Q_{\text{sec/ref}/\text{CO}_2}}{420 \frac{\mu\text{C}}{\text{cm}^2} \times 45.15 \text{ cm}^2} \]  

![Figure 3](image)

**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.

The locally resolved measurements were carried out with the commercially available S++ current scan device. It is based on internal shunt resistors and provides a resolution of 100 segments (10 × 10). The device is placed between the back side of the WE flow field and the fuel cell current collector plate. The flow field plate is 4 mm thick in order to reduce leak currents and contains a recess at the gas in- and outlet for two inlays made of polyether ether ketone (PEEK). Those inlays are necessary to prevent the S++ coating from degrading due to the presence of phosphoric acid in the hot exhaust gas stream (cf. Figure 3b and 3c).
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\(^{37–39}\) is triggered by temperature and potential\(^{40}\).

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

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

Equation 7

A further interesting finding is the small shoulder at around 0.7 V, recorded at 40°C. Relating to literature\(^43\), 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 CO\(_2\) signals measured with the IR-sensor during the CO stripping CV at three different temperatures are shown. The amplitude of the main CO\(_2\) peak during the first potential cycle decreases with increasing temperatures. In contrast, the CO\(_2\) peaks related to the second cycle slightly increase with elevated temperatures. This second CO\(_2\) source is not associated to the CO oxidation peak. It is reasonable to assume a second CO\(_2\) 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 CO\(_2\) 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\(^{38}\).

The CO\(_2\) and the CO stripping vs. reference CV methods are in agreement with the apparent ECSA trend at different temperatures determined via the three introduced methods. The gray line is used to establish a calibration curve.

### Table II. ECSA estimation at different temperatures via the introduced CO\(_2\) and CV methods.

| Temperature (°C) | CO stripping vs. second cycle | CO stripping vs. reference CV | CO\(_2\) method |
|-----------------|-----------------------------|-------------------------------|-----------------|
| 40              | 394                         | 386                           | 392             |
| 60              | 376                         | 365                           | 361             |
| 90              | 349                         | 332                           | 332             |
| 120             | 322                         | 278                           | 281             |
| 140             | 305                         | 201                           | 209             |
| 160             | 268                         | 126                           | 123             |
| 180             | 203                         | 23.4                          | 50.6            |

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\(^{-1}\) N\(_2\), 4.5 Lnh\(^{-1}\) H\(_2\), 1 mol.% CO in N\(_2\).

Figure 5. Oxidation/reduction of carbon surface functionalities, e.g. hydroquinone/quinone type redox reactions.

Figure 6. CO\(_2\) 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\(^{-1}\) N\(_2\), 4.5 Lnh\(^{-1}\) H\(_2\), 1 mol.% CO in N\(_2\).

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.
excellent 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 CO2 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.

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.44 The introduced ECSA detection method was empirically developed but is now supported by a fundamental physio-chemical model.

$$\theta(T) = \frac{ECSA(T)}{ECSA_{mono}} \quad [8]$$

Due to the good agreement with the LANGMUIR model, the results were applied to the VAN’THOFF equation.44 The slope of the VAN’THOFF 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 Reference 10, which expresses the mentioned Langmuir isostere, where p is the partial pressure of CO.

The VAN’THOFF fit in Figure 8b is in good experimental agreement and yields an apparent CO adsorption enthalpy of \((-53.5 \pm 5.6) \text{ kJmol}^{-1}\). Values within a similar range have been reported in the literature,45 which is further evidence for supporting the developed ECSA estimation method.

$$\left( \frac{\partial \ln K}{\partial T^{-1}} \right)_p = -\frac{\Delta H^\circ}{R} \quad [9]$$

$$K(T) = \frac{1}{p} \frac{\theta(T)}{1 - \theta(T)} \quad [10]$$

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 $ECSA_{mono}$ based on a monolayer of adsorbed CO for any measured

$$ECSA_{CV vs. ref. CV} \text{ at temperatures } \theta \text{ between 40 and 180°C.}$$

$$ECSA_{mono} = ECSA_{CV vs. ref. CV} \ast (1.01 - 5.32 \ast 10^{-7} \ast \theta^{2.7})^{-1} \quad [11]$$

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 $ECSA_{mono}$ 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 $ECSA_{mono}$ based on all segments equals to (244 ± 55.2) cm²Ptcm⁻²WE. This value is in excellent agreement with the globally recorded and calculated $ECSA_{mono}$ of 256 cm²Ptcm⁻²WE. Therefore, the introduced method for determination of the true WE ECSA in HT-PEFCs represents an excellent tool for detailed, locally resolved degradation diagnostics.

**Figure 8.** The gray points indicate the surface coverage and the equilibrium constant, respectively, deduced from the CO stripping experiments via the reference method. a) The dash dotted line represents a LANGMUIR fit of the surface coverage. b) The dashed line represents a VAN’THOFF fit of the equilibrium constant.

**Figure 9.** Locally resolved CO stripping CVs. Measuring conditions: 160°C, 10 mVs⁻¹, 10 Lₐh⁻¹ N₂, 4.5 Lₐh⁻¹ H₂, 1 mol.% CO in N₂.

**Figure 10.** Locally resolved $ECSA_{mono}$, calculated with the CO stripping vs. reference CV method and Equation 11. Measuring conditions: 160°C, 10 mVs⁻¹, 10 Lₐh⁻¹ N₂, 4.5 Lₐh⁻¹ H₂, 1 mol.% CO in N₂.
Conclusions

In this study we presented three different ECSA measurement techniques for the HT-PEFC. The \textit{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 \textit{ECSA}_{CV vs. ref. CV} method. Furthermore, we developed the novel \textit{ECSA}_{CO} technique, which is based on CO\textsubscript{2} detection in the WE exhaust gas during CO stripping voltammetry. The \textit{ECSA}_{CV vs. ref. CV} and the \textit{ECSA}_{CO} 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 \textit{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 (\(-53.5 \pm 5.6\) kJmol\(^{-1}\)). 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 future degradation studies.

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