Determination of the Electrochemically Active Surface Area of Metal-Oxide Supported Platinum Catalyst

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The electrochemically active surface area (ECSA) of metal-oxide supported platinum catalysts as obtained from hydrogen underpotential deposition ($H_{\text{upd}}$) and from carbon monoxide stripping experiments was investigated. It was demonstrated that both methods fail to give meaningful values of the ECSA if they are performed in the conventional way as known for pure Pt and carbon supported Pt catalysts, respectively. For both methods, the reason for this failure is the lack of a correct baseline for the integration of the associated charges. It was found that the cyclic voltammogram recorded in CO saturated electrolyte gives an improved baseline for the $H_{\text{upd}}$ analysis. For CO stripping, a novel baseline method was developed by performing a “CO stripping simulation” (COSS) experiment in CO-free electrolyte. The first cycle of this COSS-experiment is an improved baseline for the integration of the CO stripping peak, since possible support reduction/oxidation currents can be accounted for. With these modifications, $H_{\text{upd}}$ and CO stripping voltammetry can be used for metal-oxide supported platinum to yield true, reproducible and consistent values for the ECSA.

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Experimental

Catalyst preparation and electrochemical set-up.— In this study, we investigated the ECSA measurement methodology on two different metal-oxide supported Pt catalysts: Pt nanoparticles supported on a mixed iridium-titanium oxide and Pt nanoparticles supported on antimony-doped tin dioxide. The Ir$_{0.8}$Ti$_{0.2}$O$_2$ powder, and the Pt/Ir$_{0.8}$Ti$_{0.2}$O$_2$ catalyst were supplied by Umicore AG & Co KG. For the Pt/Ir$_{0.8}$Ti$_{0.2}$O$_2$ catalyst powder, the oxide support is loaded with 8.8 wt-% Pt nanoparticles. Thin-film electrodes were prepared from a suspension made from 5 mg of the catalyst/oxide powder, 1 mL ultrapure Milli-Q water, 4 mL isopropanol, and 20 μL Nafion as a binder. 40 μL of the suspension were dropped and then dried on glassy carbon disks with a 5 mm diameter (geometric surface area $A_{\text{geo}} = 0.196$ cm$^2$), resulting in a Pt loading of 18 μg cm$^{-2}$.

For the second catalyst, thin porous layers of home-made Pt at-% Sb-doped SnO$_2$ were prepared in a similar manner as described above. Then, Pt was sputtered onto the porous Sb-SnO$_2$ film resulting in a Pt loading of 20 μg cm$^{-2}$. For experimental details of the sputtering process, we refer to our previous publications. For comparison with a standard Pt/C catalyst, a 47 wt-% Pt/HSAC (high surface area carbon, TDK) was used for reference thin-film electrodes with a Pt loading of 24 μg cm$^{-2}$.

The electrodes were immersed under potential control inside a three electrode glass cell in 0.1 M HClO$_4$ electrolyte, prepared from Suprapur 70% perchloric acid (Merck KGaA) and ultrapure Milli-Q water. All electrochemical measurements were performed at room temperature. A saturated Hg/Hg$_2$SO$_4$ electrode (ALS Co., Ltd) served as reference calibrated versus a reversible hydrogen electrode (RHE) in the same electrolyte to yield a reference potential of (721 ± 1) mV vs. RHE. A platinum counter electrode was used for measurements with the supported Pt catalysts. The measurements with the bare metal-oxide supports were performed using a gold counter electrode in order to avoid any possible contamination from platinum. The potentiostat used was a Metrohm Autolab PGSTAT 128N.

Experimental methodology.— For the $H_{\text{upd}}$ analysis, we performed cyclic voltammetry (CV) at 50 mV s$^{-1}$ in N$_2$ (N5.0) saturated electrolyte. The upper potential was chosen at 1.0 V vs. RHE, and the lower potential was chosen between 0.0 V and 0.05 V vs. RHE to see the onset of hydrogen evolution in the CV. As discussed below, we performed the same CV also in CO saturated electrolyte with the electrode rotating at 1600 rpm.

CO stripping experiments were done according to the following protocol: First, CO was purged for 10 min in the electrolyte with the electrode potential kept at 0.1 V vs. RHE. Then the gas was switched to...
N₂ for 30 min in order to remove the CO from the electrolyte with the electrode potential still kept at 0.1 V vs. RHE. Subsequently, the CO monolayer on the Pt surface was stripped off by performing a CV at 20 mV s⁻¹, starting at 0.1 V vs. RHE to an upper potential of 1.0 V vs. RHE. CO stripping simulation experiments were performed according to the same protocol with the only difference that the electrolyte was always saturated with N₂. Here, the potential was first kept at 0.1 V for 40 min in N₂ saturated electrolyte, followed by a CV at 20 mV s⁻¹. In the following, we will use the abbreviation COSS-experiment for “CO stripping simulation” experiment. It should be emphasized that the word simulation does not refer to any kind of computer simulation. However, it expresses that fact that in the COSS-experiment, the same protocol as in a CO stripping experiment is followed with the difference that CO is never present in the electrolyte in the course of the COSS-experiment.

The experiments on each specific electrode were organized as follows: First, the electrolyte was saturated with N₂ and the COSS-experiment was performed. Then the CV at 50 mV s⁻¹ for the Hupd analysis was recorded. After that the purging gas was switched to CO, and the CV at 50 mV s⁻¹ for the Hupd baseline was done. The final step was the true CO stripping experiment. The reason for this organization was that, once introduced into the electrolyte, the CO gas is extremely difficult to be entirely removed, and interferences from oxidation of residual CO are possible. Therefore, we suggest performing all experiments in N₂ saturated electrolyte before the experiments in CO purged electrolyte. At least three independent electrodes of each catalyst were analyzed in order to check the reproducibility of the results and to get an estimate of the experimental errors on the numerical ECSA values obtained.

Results

Platinum on carbon support.— In this section, we will carefully analyze the ECSA values from Hupd and from CO stripping obtained for the Pt/C catalyst. Following Ref. 13, the ECSA values from both methods agree better for such high surface area Pt/C catalysts if the Hupd area is corrected for a baseline obtained from a CV in O₂ saturated electrolyte, rather than applying the standard baseline correction with the capacitive currents from the double layer region.

Figure 1a plots the CVs of the Pt/C catalyst once obtained in N₂ saturated (deaerated) electrolyte and once obtained in CO saturated electrolyte. In the CO saturated electrolyte, the current is almost constant and purely capacitive below 0.4 V vs. RHE (Figure 1b), which shows that the whole Pt surface is blocked by adsorbed CO. However, these capacitive currents in CO saturated electrolyte are smaller than the capacitive currents in the double layer region (0.4 V – 0.5 V vs. RHE) in N₂ saturated electrolyte, which are extrapolated in Figure 1b by the horizontal dashed lines into the Hupd region. This can be explained by the different structure of the electrochemical double layer on a free Pt surface and on a CO covered Pt surface resulting in different specific double layer capacitances.

In a commonly used Hupd analysis (see e.g. 15), the capacitive currents from the double layer region in deaerated electrolyte are extrapolated into the potential region <0.4 V vs. RHE (horizontal dashed lines in Figure 1b) and taken as subtraction baseline for the hydrogen adsorption/desorption peaks. We will denote in the following this baseline as “standard baseline”. The lower potential limit for the integration of the charges is chosen at the minimum of the cathodic baseline as “standard baseline”. The lower potential limit for the integration of the charges is chosen at the minimum of the cathodic baseline as “standard baseline”. The vertical dashed line indicates the lower limit of the Hupd region.

As shown in Figure 2, the experimental Hupd area is corrected for a baseline obtained from a CV in CO saturated electrolyte, which is extrapolated in Figure 1b by the horizontal dashed lines into the Hupd region. This can be explained by the different structure of the electrochemical double layer on a free Pt surface and on a CO covered Pt surface resulting in different specific double layer capacitances.

In a commonly used Hupd analysis (see e.g. 15), the capacitive currents from the double layer region in deaerated electrolyte are extrapolated into the potential region <0.4 V vs. RHE (horizontal dashed lines in Figure 1b) and taken as subtraction baseline for the hydrogen adsorption/desorption peaks. We will denote in the following this baseline as “standard baseline”. The lower potential limit for the integration of the charges is chosen at the minimum of the cathodic current before the onset of hydrogen evolution (vertical dashed line in Figure 1b). For improving the Hupd analysis, Mayrhofer et al. 13 suggested to subtract the CV currents obtained in CO saturated electrolyte from the Hupd signal instead of the standard baseline currents. This leads to the net Hupd currents shown in Figure 2. However, as mentioned above, the difference in the structure of the electrochemical double layer adjacent to a CO blocked Pt surface compared with a free Pt surface leads to the fact that even after this COSS-baseline subtraction, a small double layer remains visible in the potential region 0.4 V – 0.5 V vs. RHE. Thus, for a careful ECSA analysis these remaining capacitive currents have to be removed by applying the standard baseline correction after the CO-baseline subtraction.

Figure 1. (Color online) (a): CV of the Pt/C catalyst in N₂ and in CO saturated 0.1 M HClO₄ at 50 mV s⁻¹. The CV in CO saturated electrolyte is recorded with the electrode rotating at 1600 rpm. The currents are normalized to the geometrical surface area (geo). (b): The Hupd region of the CV's from (a). The horizontal dashed lines indicate the capacitive double layer currents used as the standard baseline. The vertical dashed line indicates the lower limit of the Hupd region.

Figure 2. (Color online) Net Hupd currents after subtraction of the CV in CO saturated electrolyte from the CV in N₂ saturated electrolyte, see Figure 1.
The ECSA value obtained from the hydrogen adsorption in the cathodic scan must agree with the value obtained from the hydrogen desorption in the anodic scan. After applying the CO-baseline correction, we found a ratio of \( \text{ECSA}_{\text{ads}} / \text{ECSA}_{\text{des}} = (0.93 \pm 0.04) \). The reason for the slightly smaller hydrogen adsorption charge is the small amount of molecular hydrogen formed at potentials close to 0.0 V vs. RHE. This hydrogen will be in solution in the electrolyte adjacent to the Pt surface, so that it can be oxidized when the potential is increased in the anodic scan. This small hydrogen oxidation current therefore is superimposed to the hydrogen desorption current from \( H_{\text{upd}} \), thus giving a slightly larger apparent desorption charge and \( \text{ECSA}_{\text{des}} \) value. In the following, we will call the average value of \( \text{ECSA}_{\text{ads}} \) and \( \text{ECSA}_{\text{des}} \) the “ECSA\(_{\text{Hupd}}" \) value. The question arises whether the CO-baseline correction yields ECSA\(_{\text{Hupd}}" \) values that are significantly different from the values obtained with the standard baseline correction. We compared both ECSA\(_{\text{Hupd}}" \) values, and found a ratio ECSA\(_{\text{Hupd}}" \) / CO-baseline / ECSA\(_{\text{Hupd}}" \) / standard = (1.06 ± 0.06). This shows that for the carbon supported Pt catalyst, the CO-baseline correction is actually not necessary, since the standard baseline correction yields, within the experimental error, the same value for the ECSA.

A second method frequently used to determine the ECSA is CO stripping voltammetry. Conventionally, the second cycle of the CO stripping CV is used as baseline for the CO stripping peak in the first cycle. For reasons that will become apparent in the following section, we developed a novel method to find a suitable baseline by performing a “CO stripping simulation” (COSS) experiment in purely N\(_2\)-purged electrolyte,\(^1\) where the potential is kept at 0.1 V vs. RHE in N\(_2\)-saturated electrolyte for the same time as the total time spent for CO and N\(_2\) purging in the course of the true CO stripping experiment. The first cycle of this COSS-experiment can then be used as a baseline for the integration of the CO stripping peak. In the following, we will call this the “N\(_2\)"-baseline” for CO stripping. We also performed this novel baseline method on the Pt/C catalyst and compared it with the results from the standard baseline.

Figure 3a illustrates the first and the second cycle of the true CO stripping experiment, and the first cycle of the COSS-experiment. From the close-up of the CO stripping potential region in Figure 3b, it can clearly be deduced that the difference between the first cycle of the COSS-experiment and the second cycle of the CO stripping experiment is negligible. This can be also seen from the ECSA values obtained with the two different baselines. The ratio is \( \text{ECSA}_{\text{COSS}} / \text{N}_2\text{-baseline} / \text{ECSA}_{\text{COSS}} / \text{standard} = (0.96 \pm 0.01) \). Thus, in order to determine the ECSA of Pt/C the N\(_2\)-baseline method is not required. The question remains how to choose the correct integration limits for the CO stripping peak. In the potential region 0.5 V – 0.75 V vs. RHE, the currents of the first CO stripping cycle are smaller than the baseline currents, which can be explained with the blocking of the Pt surface by the adsorbed CO layer. The adsorption of OH\(^-\) from water on the Pt surface is prevented until the oxidative removal of the CO adlayer starts. In the potential region >0.95 V vs. RHE, all curves coincide, which shows that after removal of the CO layer the electrochemical state of the Pt surface is identical with the state in the baseline. Thus, the Pt oxidation charge which is missing on the Pt blocked surface is recovered during the removal of the CO layer. As a consequence, part of the charge of the CO stripping peak actually does not originate from the CO oxidation but from the delayed Pt surface oxidation/OH\(^-\) adsorption. This can be taken into account in the analysis by integrating the charge between CO stripping cycle and baseline from the double layer region at \( \approx 0.5 \) V vs. RHE up to the potential where CO stripping cycle and the baseline merge (\( \approx 0.95 \) V vs. RHE).

The ECSA can be calculated from this net CO stripping charge by using a specific charge of 420 \( \mu \text{C cm}^{-2} \text{specific} \) for a monolayer of adsorbed CO. A comparison of this ECSA\(_{\text{COSS}}" \) value with the value obtained from \( H_{\text{upd}} \) yields the ratio ECSA\(_{\text{COSS}}" \) / CO-baseline / ECSA\(_{\text{Hupd}}" \) / CO-baseline = (0.85 ± 0.05). The smaller ECSA value from CO stripping compared to \( H_{\text{upd}} \) points to the fact that no full CO monolayer is formed, similar to previous observations for Pt/Vulcan\(^1\) for the low index Pt single crystal surfaces.\(^2\) This leads to a systematic underestimation of the ECSA. Consequently, for catalyst systems similar to the one studied in the present work the ECSA value from \( H_{\text{upd}} \) can be considered more reliable. Table I summarizes the ECSA values obtained from hydrogen adsorption and desorption in \( H_{\text{upd}} \), and from CO stripping with N\(_2\)-baseline.

**Figure 3.** (Color online) (a): CO stripping CV and COSS-CV of the Pt/C catalyst in 0.1 M HClO\(_4\) at 20 mV s\(^{-1}\). The COSS-CV is performed after holding the potential at 0.1 V vs. RHE for 40 min in N\(_2\) purged electrolyte. (b): Close-up of the CO stripping region of the CVs from (a).

**Platinum on iridium-titanium oxide support.**—The first metal-oxide supported catalyst which was investigated in this study consists of Pt nanoparticles supported on \( \text{Ir}_0.8\text{Ti}_0.2\text{O}_2 \). Figure 4a plots the CVs of the catalyst in N\(_2\) and in CO saturated electrolyte, respectively. The shape of the CV in N\(_2\) purged electrolyte differs very much from the conventional “platinum CV” as shown in Figure 1 for the Pt/C catalyst. The reason for this difference is the \( \text{Ir}_0.8\text{Ti}_0.2\text{O}_2 \) support, which gives a much larger contribution to the currents than a conventional carbon support. This has a drastic influence on the shape of the CV in the \( H_{\text{upd}} \) region shown in Figure 4b. The horizontal dashed lines indicate the standard baselines from the capacitive currents in the double layer region. These baselines obviously fail in this case, because the areas of hydrogen adsorption and hydrogen desorption as indicated by the dashed lines differ significantly. Furthermore, the hydrogen desorption area would not even start at the lower limit indicated by the vertical dashed line. However, instead of the standard method, the CV recorded in CO saturated electrolyte serves as a well suited baseline for the \( H_{\text{upd}} \) signals. This is drastically different from the situation of a carbon supported Pt catalyst, where we found that both baseline methods yield coinciding ECSA values. In the case of the \( \text{Ir}_0.8\text{Ti}_0.2\text{O}_2 \) supported Pt, the only correct baseline is the CV in CO saturated electrolyte.

Figure 5a shows the net \( H_{\text{upd}} \) currents obtained after subtracting the CO-baseline from the CV in N\(_2\) purged electrolyte. A comparison with Figure 2 shows that the well-known platinum \( H_{\text{upd}} \) shape can be recovered with this CO-baseline method. A further confirmation of the
Table I. Summary of the roughness factors $r = \frac{\text{ECSA}}{\text{Ageo}}$ as determined from Hupd and from CO stripping. Also given are the ratios of the ECSA values obtained from Hupd adsorption over desorption, and the ratios of the ECSA values obtained from the N$_2$-baseline CO stripping method over the CO-baseline Hupd method for the three different catalysts.

| Catalyst            | $r$ (Hupd)     | $r$ (CO stripping) | $\frac{\text{Hupd}}{\text{ECSA}_{\text{ads}}/\text{ECSA}_{\text{des}}}$ | $\frac{\text{ECSA}_{\text{COstrip}}/\text{ECSA}_{\text{Hupd}}}$ |
|---------------------|----------------|-------------------|-------------------------------------------------|-----------------------------|
| Pt/C                | 19.9 ± 2.0     | 16.8 ± 1.5        | 0.93 ± 0.04                                     | 0.85 ± 0.05                 |
| Pt/Ir$_{0.8}$Ti$_{0.2}$O$_2$ | 6.4 ± 1.0     | 6.1 ± 1.0         | 0.98 ± 0.08                                     | 0.93 ± 0.05                 |
| Pt/Sb-SnO$_2$       | 2.24 ± 0.05    | 2.40 ± 0.40       | 0.98 ± 0.03                                     | 1.08 ± 0.19                 |

validity of this method comes from a comparison of the ECSA values obtained from the hydrogen adsorption and hydrogen desorption. We find that both values agree very well with a ratio of ECSA$_{\text{ads}}$/ECSA$_{\text{des}}$ = (0.98 ± 0.08). Figure 5b plots the same CVs as Figure 4a but for the bare Ir$_{0.8}$Ti$_{0.2}$O$_2$. The presence of CO in the electrolyte clearly has no influence on the CV of the bare metal-oxide support.

Figure 6a shows the results of a CO stripping experiment on the Pt/Ir$_{0.8}$Ti$_{0.2}$O$_2$ catalyst. The first and the second cycle of the true CO stripping experiment are plotted, as well as the first cycle of the COSS-experiment. The CO stripping potential region is shown in more detail in Figure 6b. The second cycle of the CO stripping CV clearly fails as a baseline for the CO stripping peak in the first cycle, because the anodic currents of the first cycle have a positive offset with respect to the second cycle. The reason for that is shown in Figure 7, which shows the results of the same experiments performed on the bare Ir$_{0.8}$Ti$_{0.2}$O$_2$ support. Also here, the first cycle has a strong positive offset with respect to the second cycle. This can be explained with the reduction of the Ir$_{0.8}$Ti$_{0.2}$O$_2$ oxide: At 0.1 V vs. RHE a reduced state (valency $<+4$V) of iridium is thermodynamically preferred. Thus, the metal-oxide is partially reduced during the 40 min when the potential is held at 0.1 V vs. RHE prior to the CV. This reduction is followed by a reoxidation during the anodic scan of the first cycle, leading to the observed positive offset of the oxidation currents.

Similar to the case of Hupd, a better baseline for the CO stripping peak thus has to be found. This is accomplished by the first cycle of the COSS-experiment. As shown in Figure 7, the first cycles of the true CO stripping experiment on the bare Ir$_{0.8}$Ti$_{0.2}$O$_2$ support and the COSS-experiment coincide with negligible difference. This proves on the one hand that the Ir$_{0.8}$Ti$_{0.2}$O$_2$ support does not show any CO adsorption/CO stripping properties, and on the other hand that the reoxidation currents in the first cycle are reproducible. Thus, the first cycle of a COSS-experiment on the Pt/Ir$_{0.8}$Ti$_{0.2}$O$_2$ catalyst can serve as a reliable baseline, which we call the “N$_2$-baseline”.

The close-up of the CO stripping region in Figure 6b shows that this N$_2$-baseline even reveals the suppressed oxidation of the CO blocked Pt surface in the first cycle of the true CO stripping experiment, similar to the findings for the Pt/C catalyst. Following the discussion for the case of the Pt/C catalyst, the charge between CO stripping cycle and baseline has to be integrated from the double layer region at $\approx 0.5$ V vs. RHE up to the potential where CO stripping cycle and the baseline

![Figure 4](image-url)  
**Figure 4.** (Color online) (a): CV of the Pt/Ir$_{0.8}$Ti$_{0.2}$O$_2$ catalyst in N$_2$ and in CO saturated 0.1 M HClO$_4$ at 50 mV s$^{-1}$. The CV in CO saturated electrolyte is recorded with the electrode rotating at 1600 rpm. (b): The Hupd region of the CVs from (a). The horizontal dashed lines indicate the capacitive double layer currents used as the standard baseline. The vertical dashed line indicates the conventional lower limit of the Hupd region.

![Figure 5](image-url)  
**Figure 5.** (Color online) (a): Net Hupd currents after subtraction of the CV in CO saturated electrolyte from the CV in N$_2$ saturated electrolyte, see Figure 4. (b): CV of the bare Ir$_{0.8}$Ti$_{0.2}$O$_2$ support in N$_2$ and in CO saturated 0.1 M HClO$_4$ at 50 mV s$^{-1}$. Same current density scale as in Figure 4a.
coincide (≈ 0.95 V vs. RHE). A comparison of the ECSA value from the N₂-baseline CO stripping method with the value from the CO-baseline Hupd method yields the ratio ECSA_{CO-strip}/ECSA_{Hupd} = (0.93 ± 0.05). The same explanation given for the Pt/C catalyst can be also applied for the Pt/metal-oxide systems leading to ECSA values from CO stripping that are systematically smaller than those obtained from Hupd analysis. A similar COSS-experiment was considered to overcome baseline problems in CO stripping voltammetry in the context of high-temperature PEFCs.²⁶

Platinum on antimony-doped tin dioxide support.— After the successful application of the improved Hupd and CO stripping methods on the iridium-titanium oxide supported Pt catalyst, the question arises whether these methods can be also used for Pt catalyst on other metal-oxide supports. For this reason, a second metal-oxide supported Pt catalyst was investigated, which was prepared by sputtering Pt onto a porous, conductive Sb-doped SnO₂ electrode. The CVs of this catalyst in N₂ saturated electrolyte and in CO saturated electrolyte are shown in Figure 8a. As in the case of the Ir_{0.8}Ti_{0.2}O₂ support, the CV in N₂ saturated electrolyte does not clearly resolve the typical features of a platinum CV. For this reason, the standard baseline method for the Hupd analysis also fails for this metal-oxide supported Pt catalyst, as shown in Figure 8b. However, the CV recorded in CO saturated electrolyte again constitutes a suitable baseline for the Hupd region. The net Hupd currents obtained after subtracting this CO-baseline from the CV in N₂ purged electrolyte are plotted in Figure 9a. Again, the well-known platinum Hupd signal can be recovered with this CO-baseline method. However, the early onset of CO oxidation on the Pt/Sb-SnO₂ catalyst (as discussed below) leads to the fact that after subtraction of the CO-baseline, the currents bend downwards in the Pt double layer region between 0.4 V – 0.5 V vs. RHE. Therefore, the determination of the capacitive double layer currents becomes ambiguous. We have determined the capacitive currents at the potential where the cathodic current is minimal (at ≈ 0.4 V vs. RHE) before the beginning of the Hupd region. For the ratio of the ECSA values obtained from the hydrogen adsorption and hydrogen desorption currents, we find ECSA_{ads}/ECSA_{des} = (0.98 ± 0.03), which is in very good agreement with the respective values obtained for the Pt/C and the Pt/Ir_{0.8}Ti_{0.2}O₂ catalysts. A further support for the validity of the CO-baseline Hupd method is the reproducibility of the absolute ECSA values obtained for the three different Pt/Sb-SnO₂ electrodes. The Pt sputtering process can be expected to yield very reproducible Pt loadings on the electrodes. This is confirmed by the fact that the absolute
Figure 9. (Color online) (a): Net Hupd currents after subtraction of the CV in CO saturated electrolyte from the CV in N2 saturated electrolyte, see Figure 8. (b): CV of the bare Sb-SnO2 support in N2 and in CO saturated 0.1 M HClO4 at 50 mV s\(^{-1}\). The current density scale is the same as in Figure 8a.

ECSA\(_{\text{Hupd}}\) values of the different electrodes agree within 5% (see Table I). The same CVs as in Figure 8a but for the bare Sb-SnO2 support are plotted in Figure 9b. No influence of the CO on the CV of the bare metal-oxide support can be seen.

A comparison of the CVs recorded in CO saturated electrolyte which are plotted in Figures 1a, 4a and 8a reveals another important detail of the Hupd with CO-baseline method: The Pt/Sb-SnO2 catalyst has a very high activity toward CO oxidation. The onset potential lies in the platinum double layer region between 0.4 V – 0.5 V vs. RHE. However, this is only true if the electrode is rotated at 1600 rpm. Without rotation, the onset potential is even lower, below 0.4 V vs. RHE, so that the CO oxidation overlaps with the Hupd region. This is shown in Figure 10, which compares the CVs recorded in CO saturated electrolyte with and without rotation. The shift of the CO oxidation toward higher potentials due to the rotation of the electrode is a consequence of the negative reaction order of CO oxidation on a platinum surface.\(^{27,28}\) Thus, rotating the electrode during the CV in CO purged electrolyte can help to separate the potential range of CO oxidation from the potential range of hydrogen underpotential deposition. This separation is a prerequisite for the applicability of the CO-baseline method for Hupd analysis.

The results of CO stripping on the Pt/Sb-SnO2 catalyst are shown in Figure 11. The close-up of the CO stripping region in Figure 11b shows that the second cycle of the CO stripping CV fails as a baseline for the CO stripping peak, similar to the case of the Ir\(_{0.8}\)Ti\(_{0.2}\)O2 supported catalyst. However, for the Pt/Sb-SnO2 the novel N2-baseline (first cycle of the COSS-experiment) also fails, which can be seen from the fact that the curves do not merge in the potential range >0.8 V vs. RHE, after the CO monolayer has been stripped off, and as a consequence, no clear definition of the integration limits can be given.

This behavior cannot be explained taking into account the electrochemical properties of the Sb-SnO2 support alone. Figure 12 plots the results of a CO stripping experiment on the bare Sb-SnO2 support. As shown in Figure 12a, the second cycle of the CO stripping experiment has smaller anodic oxidation currents than the first cycle. This can be explained with a reduction/reoxidation behavior of the Sb-SnO2 support similar to case of the Ir\(_{0.8}\)Ti\(_{0.2}\)O2 support. However, as shown in Figure 12b, this difference is negligible on the current density scale of Figure 11a. Therefore, the failure of both CO stripping baselines in the case of the Pt/Sb-SnO2 catalyst is not a mere effect of the Sb-SnO2 support, but it must be induced by interactions between the Pt catalyst...
0.1 V vs. RHE in N₂ saturated electrolyte for the same time as in the true CO stripping experiment. The first cycle of the subsequent CV can be used as a baseline for the CO stripping peak. This N₂-baseline method was successfully applied for the Pt/Ir₀.₈Ti₀.₂O₂ catalyst. However, for the Pt/Sb-SnO₂ catalyst the N₂-baseline CO stripping method fails most likely due to an interaction between Pt and the support, which leads to a non-reproducibility of the first CV cycle after potential hold at 0.1 V.

The two methods investigated in this study manifest a beautiful complementarity between CO purged and N₂ purged electrolyte: For Hupd analysis, the signal is taken in N₂ saturated electrolyte, and the baseline is recorded in CO saturated electrolyte. Vice versa, for CO stripping the signal is taken after adsorbing CO on the Pt surface, and the baseline is taken in N₂ purged electrolyte.

We strongly suggest the use of Hupd analysis with CO-baseline for the determination of the ECSA of metal-oxide supported Pt catalysts. CO stripping is less recommended for two reasons: First, even though an improved baseline can be found from a COSS-experiment, this N₂-baseline can fail for certain metal-oxide supports. Second, in the course of a CO stripping experiment the potential must be held at a low value for a long time. The metal-oxide support can be partially reduced during that time, which potentially leads to a degradation of the catalyst.

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Conclusions

- Two different experimental techniques to determine the ECSA of Pt catalyst on different supports have been compared: Hupd analysis and CO stripping voltammetry.
- On carbon support, the standard methods of baseline correction give meaningful and consistent ECSA values.
- For the metal-oxide supported Pt catalysts – Pt/Ir₀.₈Ti₀.₂O₂ and Pt/Sb-SnO₂ – the standard baselines both for Hupd and for CO stripping fail. The common reason is the contribution of the metal-oxide support to the overall CV currents.
- The Hupd method can be adapted to metal-oxide supported Pt by using a CV recorded in CO saturated electrolyte as a baseline for the Hupd signal. With this CO-baseline, a meaningful Hupd analysis can be performed on metal-oxide supported Pt catalysts.
- A novel method to obtain a baseline for the CO stripping peak was proposed. For this purpose, a “CO stripping simulation” (COSS) experiment was performed by holding the potential at

![Figure 12](image_url)

Figure 12. (Color online) (a): CO stripping CV and COSS-CV of the bare Sb-SnO₂ support in 0.1 M HClO₄ at 20 mV s⁻¹. The COSS-CV is performed after holding the potential at 0.1 V vs. RHE for 40 min in N₂ purged electrolyte. (b): Same CVs as in (a) but with the current density scale of Figure 11a.

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