# CO-stripping Technique

EC-MS Application Note #11

Why Do a CO-strip?

The CO-strip technique is based on the electrochemical oxidation of an adsorbed layer of CO from a sample surface of interest. The technique is often used to quantify the active surface area of the sample and can provide insight on crystalline facets and binding energies of the adsorbed species. Furthermore, the CO_2 mass spectrometer (MS) signal of the EC-MS may be calibrated via the CO-strip technique.

$$*CO + H_2O \longrightarrow CO_2 + 2\,H^+ + 2\,e^- \tag{1}$$
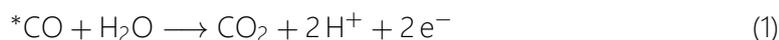
The overall reaction is given by eq. (1), where a CO molecule adsorbed on a surface site (*CO) is oxidized to CO_2 with a net transfer of two electrons. Thereby the total charge passed during a CO-strip is a direct measure of the total number of sites present on the studied surface. At the same time, the released CO_2 is detected in the MS. Again according to eq. (1), the amount of CO_2 released in the strip can be related to the total charge passed during the CO strip, which can be used to calibrate the CO_2 signal. This application note will demonstrate how to perform a CO-strip experiment using the EC-MS system and the key steps of the data treatment procedure.

Experimental Procedure for CO-strip

To successfully carry out a CO-strip experiment, the sample studied should bind CO sufficiently strong, e.g. Pt or Pt-group metals. The general experimental procedure follows three main steps (i-iii).

(i) Reference measurement

(ii) CO-poisoning

(iii) CO-stripping

First, a stable CV under inert gas saturation should be obtained as a reference measurement (i) for verification and as a baseline. Next, the gas is changed to CO, which poisons the sample surface (ii) while the potential is held constant at a value where CO is not oxidized.

CO-stripping Technique | EC-MS Application Note #11 | v. 1.0

The inert gas is switched back on and remaining non-adsorbed CO is purged out. Then, the CO is stripped of (iii) in an anodic-going sweep in a CV, giving rise to a faradaic current. Finally, the reference measurement from step (i) is repeated. There are many parameters which may influence the CO-strip experiment, such as electrode material, surface structure, electrolyte, adsorption potential, scan speed etc. In the following example a typical CO-strip experiment using a polycrystalline Pt disk in 0.5 M H_2SO_4 is shown, using parameters that are suitable for this system. The parameters used here might not be optimal for other systems.

First, a few points regarding safety and preparation of the experiment are discussed. Next, the experimental procedure with the EC-MS is described, followed by the data treatment procedure.

Safety & Experimental Considerations

Before starting a CO-strip, make sure that a completely dry and rigorously cleaned cell is available, a chip is installed in the setup, and electrolyte, sample and other accessories are prepared. Furthermore, a make-up gas line (e.g. He) and a CO line need to be connected to the EC-MS. Always pump down and purge newly installed gas lines several times to minimize contamination of gas supply and the EC-MS.

Precautions need to be taken when working with CO and other toxic, flammable or otherwise hazardous compounds. Avoid any leak or outlet of CO and ensure proper ventilation of the work area. The use of a gas alarm or a handheld CO-detector is advisable. During experiments, the gas outlet of the EC-MS setup (roughing pump outlet) should be led into a ventilation point to avoid the release of CO in the work area. Prepare a risk assessment according to your institution's rules before starting any experiment involving CO.

Metal (e.g. Ni, Fe) carbonyls may form by exposing a metal (e.g. steel) to CO at a high pressure. The decomposition of the metal carbonyl at the electrode can lead to contamination and may cause unwanted effects in experiments. Several steps can be taken to minimize the effect:

- Keep the pressure in the CO supply line low to minimize the driving force towards forming metal carbonyls

- Install a carbonyl filter at the end of the CO line just before entering the EC-MS

- Avoid nickel containing fittings and tubing to the extent possible

- Flush the CO line to remove stagnant gas before starting an experiment

Reference Measurement

Start by setting up experimental parameters in Zilien and EC-lab. The experimental procedure in EC-lab should contain a CVA technique followed by a loop. Choose suitable values

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CO-stripping Technique | EC-MS Application Note #11 | v. 1.0

of parameters such as current range, bandwidth, scan rate etc. depending on the experiment and system studied. For further detail on EC parameters consult the EC-lab manual and application notes, as well as *EC-MS application note #3*. Pump down the chip and start the Zilien experiment. Set a flow of 1 mL/min inert make-up gas (e.g. He) on **line #1** via **MFC1**. Prior to starting EC experiments, perform a breath test and a drop test to verify that the EC-MS is fully operational. Mount cell with sample, inject electrolyte and connect glass pipes and electrode connections. For more details on preparation steps above, see the *EC-MS manual*. Make a reference measurement:

(i) Trigger the EC experiment from Zilien and wait to obtain a stable CV. Use the same set of parameters in EC-lab that will be used during the CO-strip for comparison (scan speed, potential limits etc.).

(ii) Obtain the reference measurement: First, end the CV with a potential hold at +0.05 V vs. RHE for 10 min.

(iii) Then start cycling the potential again (using the loop to restart the CVA technique). The first cycle can be used as a baseline for background subtraction during data treatment.

## Gas Exchange to Induce CO-poisoning

Next, CO is introduced to the cell to induce CO-poisoning. Keep the same Zilien and EC-lab measurements running that were used for the baseline measurement. Before switching gases, ensure the inlet valve on the CO line is open (i.e. **V9** when **line #2** is used for CO) and the **MFC2** mode is *normal*. Now perform the gas exchange:

(i) End the CV with a potential hold at +0.05 V vs. RHE)

(ii) *Write* 10 ml/min in the **MFC2** setpoint field but do not press enter or click outside the field.

(iii) In quick succession click **V8** and write and enter 0 mL/min in the **MFC1** setpoint field. This connects **line #2** to the chip while initializing a 10 ml/min flow of CO, while **line #1** is closed and the He flow is stopped. Now CO enters the chip and saturates the electrolyte. The M28 signal seen in the MID will promptly increase while M4 decreases, as seen in the top panel of Fig. 1a. Simultaneously, a peak is observed in the current (red trace, bottom panel) due to CO displacing adsorbed hydrogen on the Pt electrode.

(iv) When the M28 signal stabilizes at a maximum, the make-up gas can be switched back to the inert gas: *write* but do not enter 10 mL/min in the **MFC1** setpoint field. In quick succession click on **V8** and write and enter 0 mL/min in the **MFC2** setpoint field.

(v) Keep an eye on the pressure at **P3** when running gas flows at 10 mL/min. If **P3** is higher than expected, the gas ballast on the scroll pump should be used. After a few minutes the He flow can be turned down to 1 mL/min.

(vi) If the CO gas is no longer required in this measurement the **MFC2** mode can be set to *Flow Off* and the inlet valve closed (e.g. **V9** when **line #2** is used for CO). If instead

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CO-stripping Technique **|** EC-MS Application Note #11 **|** v. 1.0

a different gas is desired on **line #2**, the entire line (all the way through **MFC2**) should be pumped via the gas manifold.
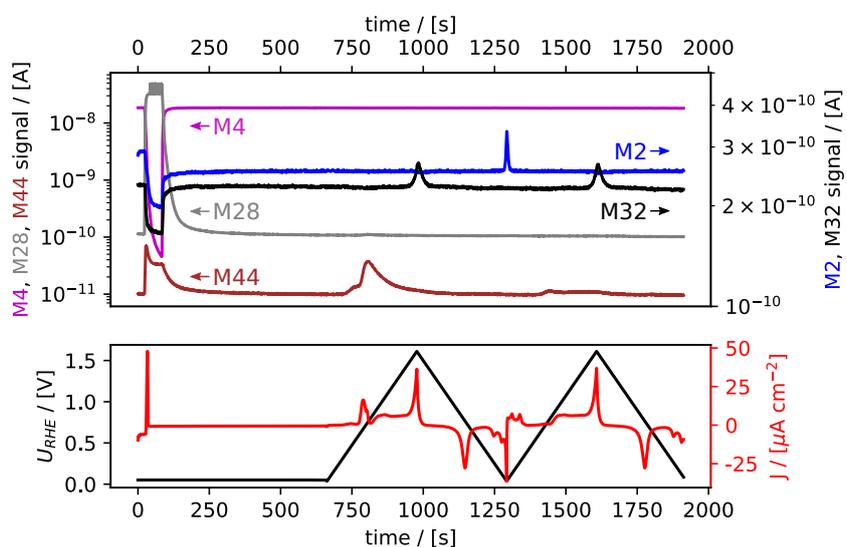
(a) EC-MS plot during gas exchange and CO-strip as a function of time
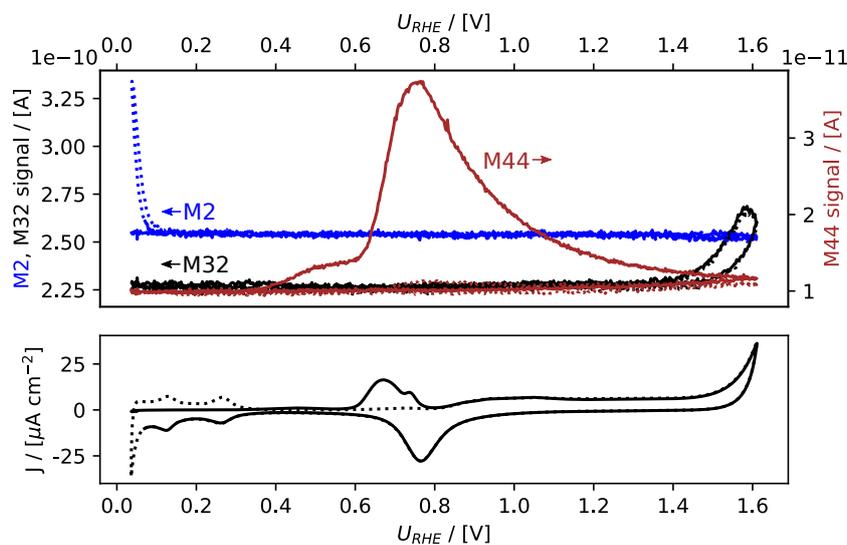
(b) CO stripping CVs as a function of potential.

Figure 1: EC-MS plot during gas exchange and CO-strip. Mass spectrometer signals are shown in the top panels, electrochemical potential vs. RHE and current density in the bottom panels. (a) Initially, the potential is held at +50 mV vs. RHE while the make-up gas is changed from He to CO, as seen in the M4 and M28 signals. A sharp peak in the current density (red) is observed immediately, due to CO displacing adsorbed hydrogen on the Pt sample. The potential is held constant while switching the make-up gas back to He until all non-adsorbed CO is purged out. Upon sweeping the potential (5 mV/s scan rate) anodically, a peak in the electrochemical current and the M44 signal are observed, indicating the oxidation of adsorbed CO to CO_2. (b) shows the CVs as a function of potential. The second cycle from (a) is shown as baseline (dotted).

CO-stripping Technique | EC-MS Application Note #11 | v. 1.0

CO Strip

After switching back to inert make-up gas (e.g. He), wait for the M28 signal to drop back to baseline level, to ensure that all non-adsorbed CO has been removed from the gas lines and the sample volume. The total duration of the potential hold period should be the same as for the reference measurement. Then continue the CV in EC-lab, in the same manner as for the reference measurement. This time, an oxidation peak can be observed in the electrochemical measurement, concurrently with a peak in M44, see Figs. 1a and 1b. Choose a low scanrate (e.g. 5 mV/s or lower) for optimal time response of the MS signal.

Data Treatment

The following section illustrates the key steps of data analysis. Note that there is a vast amount of scientific literature discussing how to use CO-stripping to determine surface area. The analysis shown below serves as an example in the context of EC-MS, and we refer the reader to the scientific literature for further details[1–3]. Using CO-stripping for MS calibration, is of course limited to the calibration of the CO_2 signal.

Surface Area Determination

Assuming ideal behavior, adsorbed CO forms a monolayer coverage on the surface. The faradaic current passed when oxidizing this monolayer can therefore be used to determine the number of surface sites available for CO adsorption, which gives an estimate for the electrochemically active surface area (ECSA). As the density of atoms on the surface depends on the exposed facet, and the coverage is not always a full monolayer, usually conversion factors from the literature are used to convert the faradaic charge to surface area. Here, we use a factor of 340 $\mu C\,cm^{-2}$ for polycrystalline Pt. The faradaic charge is determined by integrating the stripping current with respect to time, between 0.4 and 0.9 V vs. RHE. As the oxidation of CO occurs in a similar potential range, as the onset of Pt surface oxidation, the charge determined from a reference measurement in the absence of CO is subtracted, see eq. 2 and Fig. 2.

$$\text{ECSA} = \frac{(Q_{\text{CO-strip}} - Q_{\text{ref}})\,[\mu C]}{340\,[\mu C\,cm^{-2}]} \tag{2}$$

In the measurement shown in Fig. 2, using the second cycle as reference, an ECSA of 0.208 cm^2 was determined, or 0.193 cm^2 when using the baseline cycle determined in the reference measurement. For comparison, the geometric surface area of the electrode used is 0.196 cm^2.

CO_2 Calibration

As mentioned, the faradaic current observed during the CO-strip is related to the number of molecules of CO being oxidized according to Faraday's law of electrolysis, where Q is the total charge, z the number of electrons in the reaction (z=2 in the case of CO oxidation) and $\mathcal{F}$ the Faraday constant:
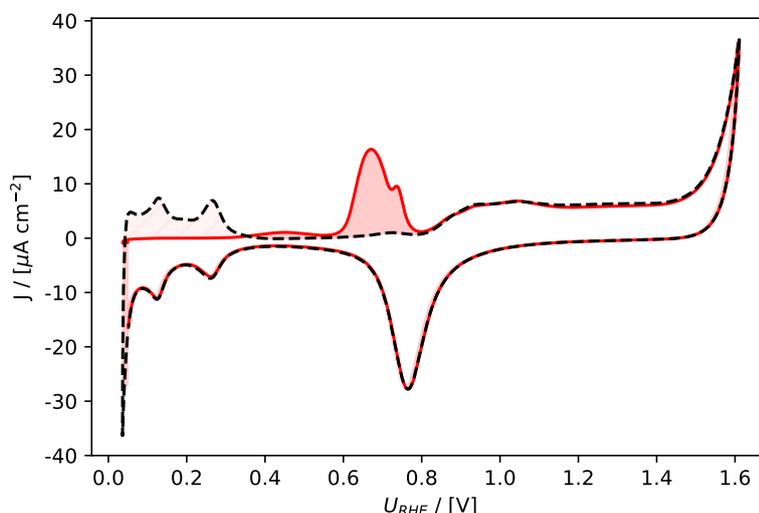

Figure 2: Electrochemical current vs. potential: The red, full line shows the CO stripping cycle, the black, dashed line the second cycle used as reference cycle. Both cycles were integrated in the potential range from 0.4 to 0.9 V vs. RHE on the anodic scan, the difference is highlighted by the darker red shading in the figure.

$$n_{CO_2,EC} = \frac{Q}{z\mathcal{F}} \tag{3}$$

Due to the design of the EC-MS chip, all CO_2 formed during the CO strip will be observed in the MS, which means that the faradaic current can be used to calibrate the MS signal of CO_2 to convert from detector current I_{MS} in [A] to molecular flux $\dot{n}_{CO_2}$ in [mol/s]:

$$\dot{n}_{CO_2} \text{ [mol/s]} = \frac{I_{MS} \text{ [A]}}{F_{CO_2,M44} \text{ [C/mol]}} \tag{4}$$

Where $F_{CO_2,M44}$ is the calibration factor for CO_2 measured at m/z=44 (M44), according to eq. 5:

$$F_{CO_2,M44} \text{ [C/mol]} = \frac{Q_{M44} \text{ [A s]}}{n_{CO_2,EC} \text{ [mol]}} \tag{5}$$

The integrated M44 signal is shown in Fig. 3. Also in this case it is important to subtract a background signal, both when determining the amount of CO_2 released from the faradaic current, and when integrating the M44 signal from the MS. Either a separate measurement without introducing CO, or the CO_2 released in the second cycle after dosing CO can be used as such a background signal. In either case, trace carbon contamination might contribute to the M44 background. In the example shown here, a calibration factor $F_{CO_2,M44}$ of 5.1 C/mol was determined when using the baseline measurement without CO as a reference. Note that this calibration factor depends on the tuning of the MS and which detector is being used (Faraday cup or electron multiplier) and therefore needs to be determined regularly and can deviate from the value stated here.
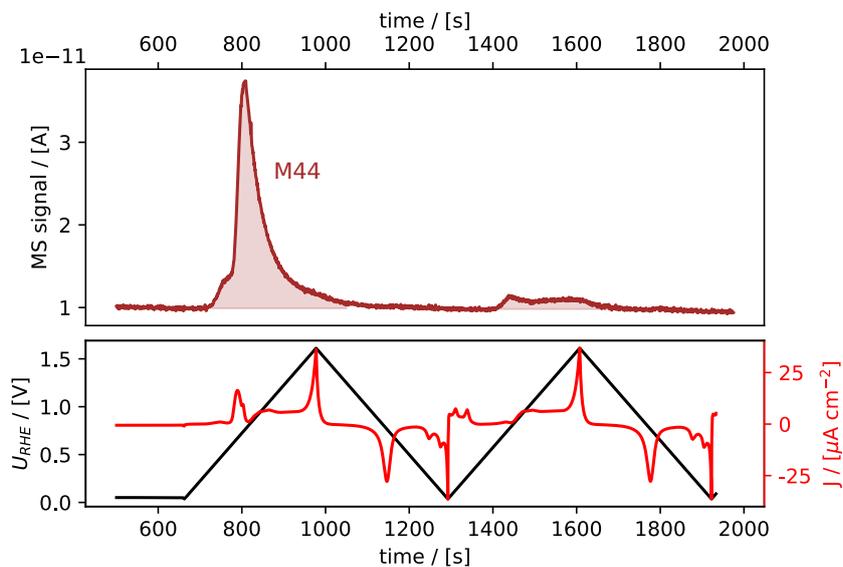

CO-stripping Technique | EC-MS Application Note #11 | v. 1.0

Figure 3: EC-MS plot highlighting the integrated CO_2 signal from the CO-strip shown in Fig. 1a Note that the baseline is not at 0 A, therefore a suitable baseline level should be chosen for the integration.
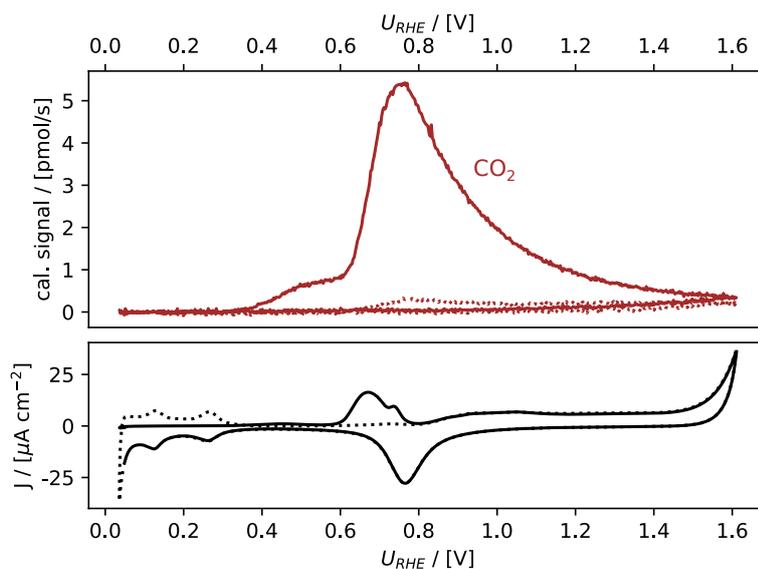

Figure 4: EC-MS plot as shown in Fig. 1b after calibration of the M44 signal to show the molecular flux of CO_2 released in CO strip. In addition to calibration, the signal was normalized to the baseline.

Using the calibration factor, the raw M44 signal can then be plotted as CO_2 flux instead, as shown in Fig. 4. This figure highlights the high sensitivity of the EC-MS, where a mass flux on the order of only a few pmol/s can be followed in real time.

CO-stripping Technique | EC-MS Application Note #11 | v. 1.0

References

[1]   S. Rudi, C. Cui, L. Gan, and P. Strasser, "Comparative Study of the Electrocatalytically Active surface areas (ECSAs) of Pt Alloy Nanoparticles Evaluated by Hupd and CO-stripping Voltammetry," *Electrocatalysis*, vol. 5, pp. 408–418, 4 2014. DOI: `10.1007/s12678-014-0205-2`.

[2]   A. Cuesta, A. Couto, A. Rincón, M. Pérez, A. López-Cudero, and C. Gutiérrez, "Potential Dependence of the Saturation CO Coverage of Pt Electrodes: The Origin of the Pre-peak in CO-stripping Voltammograms. Part 3: Pt(poly)," *Journal of Electroanalytical Chemistry*, vol. 586, pp. 184–195, 2 2006. DOI: `10.1016/j.jelechem.2005.10.006`.

[3]   T. Binninger, E. Fabbri, R. Kötz, and T. J. Schmidt, "Determination of the Electrochemically Active Surface Area of Metal-Oxide Supported Platinum Catalyst," *Journal of The Electrochemical Society*, vol. 161, H121–H128, 3 2014. DOI: `10.1149/2.055403jes`.

All data treatment and plotting in this application note was carried out using the open source Python package ixdat, available at https://github.com/ixdat/ixdat.