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The electrocatalytic oxidation of ethanol studied on a molecular scale

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CHAPTER 2

EXPERIMENTAL TECHNIQUES

This chapter gives a short overview of the experimental setup and techniques employed in the research described in this thesis. Both electrochemical techniques and in situ characterization techniques are discussed briefly.

2.1 Electrochemical methods

2.1.1 Electrochemical set-up

The set-up used for the electrochemical experiments is shown in Figure 2.1. The set-up consists of a three-electrode electrochemical cell connected to a PC-controlled potentiostat. The electrochemical cell is a single-compartment glass cell, which was cleaned extensively before each experiment. In the electrochemical cell, the current of the reaction under investigation passes between the working electrode (the electrode of interest) and the counter (or auxiliary) electrode. The counter electrode was chosen to be an electrode that does not produce substances that may interfere with the reaction at the working electrode. In most cases in this thesis, the counter electrode consisted of a wire or sheet of the same metal as the working electrode, with a surface area larger than the surface electrode. The reference electrode, an electrode of known potential, was placed in a Luggin-Haber capillary, immersed in the same electrolyte as the working electrode.

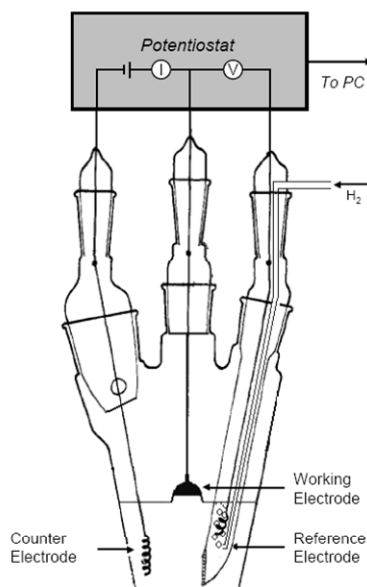


Figure 2.1: Schematic drawing of a three-electrode electrochemical cell. Adapted from Ref 1

In the potentiostat, the working electrode and the reference electrode are connected through a circuit with a high impedance, so that a negligible current passes through the reference electrode. Consequently, its potential remains constant. In essence, a potentiostat controls the potential difference between the working and reference electrodes and measures the current passing through the working (and counter) electrode.

2.1.2 Cyclic voltammetry

Cyclic voltammetry is an electrochemical technique that can be considered the electrochemical analogue of gas phase temperature programmed techniques, such as temperature programmed desorption (TPD), oxidation (TPO) or reduction (TPR)². In cyclic voltammetry, the potential of the working electrode is varied linearly in time with a certain scan rate (in V s^{-1}) between two potential limits, while the currents are measured, resulting in current vs. potential (I - E) plots. During the voltammetric sweep, the measured current consists of a Faradaic and a non-Faradaic contribution. A Faradaic process is a reaction which occurs at the electrode surface and results in a charge (*e.g.* electrons) transfer across the electrode-electrolyte interface. Such reactions are governed by Faraday's law:

$$I_F = \frac{dQ}{dt} = n_e F \frac{dN}{dt} = n_e F A \nu$$

In other words, the charge Q related to a Faradaic process which passes through the working electrode equals the amount of reactant (N) converted multiplied by the number of electrons exchanged (n_e) in the process and the Faraday constant (F). As a result, the current I_F can be directly related to the reaction rate ν (in $\text{mol s}^{-1} \text{m}^{-2}$) for a given surface area A .

Although generally the Faradaic processes are the main interest of an electrochemical investigation, the effect of non-Faradaic processes, *i.e.* processes that give rise to a current without charge being transferred across the interface, must be taken into account as well. An important non-Faradaic process is the (dis)charging of the electrochemical double layer, which can be envisioned as follows: as the electrode-electrolyte interface can be described by a charged (metal) plane on the electrode side and a layer of ions of opposing charge on the electrolyte side, the solid-solution interface acts as a capacitor,

called the electrochemical double layer. Therefore, a change in the potential of the electrode will lead to a charging of the double layer, which is given by the following equation:

$$I_{DL} = AC_{DL} \frac{dE}{dt}$$

From this equation, it follows that the double layer current I_{DL} is proportional to the surface area of the electrode A , the capacitance of the double layer C_{DL} and the scan rate (dE/dt). The double layer current should be so low that it does not interfere with the analysis of the current associated with Faradaic processes.

2.1.3 Chronoamperometry

While voltammetry yields information about the response of an electrochemical system to an ever-changing potential, it is somewhat less suited for kinetic analysis, as the system is constantly changing. A suitable electrochemical technique to study the kinetics of a system is chronoamperometry. In chronoamperometry, the potential is stepped instantaneously from one potential (generally a potential where the studied reactions do not take place) to the potential of interest. The current response of the electrochemical system on the perturbing potential step is followed over time, resulting in current vs. time ($I-t$) plots. Similar to voltammetric experiments, double layer (dis)charging should be taken into account when analyzing chronoamperometric transients. As only a single potential step is made, the double layer (dis)charging can be given by the following equation:

$$I(t) = AE_s e^{(-t/R_s C_{DL})}$$

As a typical electrolyte resistance (R_s) is 10-100 Ω and a typical double layer capacitance (C_{DL}) is 10-100 μF , the double layer charging current should be negligible after the first 50 ms after a potential step E_s . Therefore, this current mainly impacts very fast processes. After the initial 50 ms, the currents can be attributed to Faradaic processes. A detailed analysis of the current evolution with time can yield kinetic insights into these processes.

2.1.4 Rotating disk electrode

As an electrochemical reaction occurs, the concentrations of reactants and products near the electrode will deviate from the concentrations in the bulk of the solution. More particularly, the reaction causes the local concentration of the reactants to drop and of the products to increase near the electrode, both of which might affect the reaction rate. In addition, the concentration of reaction intermediates might also build up near the electrode surface, increasing the probability of re-adsorption and further reaction³. As a result, the conditions near the electrode surface, the region which is probed through electrochemical measurements, might differ significantly from the well-defined bulk solution. One way to circumvent these issues is to introduce forced convection to an electrochemical system. An electrochemical technique to introduce convection is to employ a rotating disk electrode (RDE). The principle of a RDE is shown in Figure 2.2.

In a rotating disk electrode set-up, the working electrode is embedded in a chemically inert shroud. The shroud is attached to a motor and rotated at a certain frequency. The spinning disk drags the solution at its surface along with

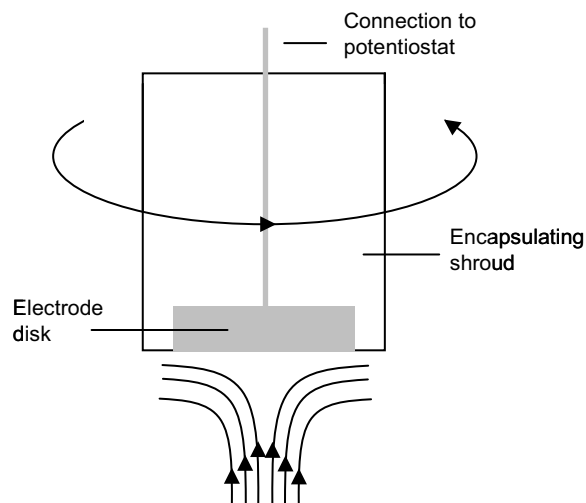


Figure 2.2: Schematic drawing of a rotating disk electrode (RDE) and the resultant stream lines.

it, flinging it outward due to the centrifugal force. The solution at the surface is replenished by flow normal to the electrode surface. An important property of a RDE set-up is that the hydrodynamic equations and the convective-diffusion equation can be solved rigorously. The main advantage of a RDE set-up is that by varying the rotation rate, the kinetic (reaction limited) and diffusional (mass transport limited) current can be separated, as given by the Koutecký-Levich equation:

$$\frac{1}{I} = \frac{1}{I_K} + \frac{1}{I_l} = \frac{1}{I_K} \pm \frac{1}{0.62n_e F A D^{2/3} \nu^{-1/6} \omega^{-1/2} C^{bulk}}$$

Here, I_K represents the current in the absence of mass transfer effects. In other words, I_K is the current if the reaction rate is relatively slow compared to diffusion, therefore keeping the reactant concentration at the reaction equal to the bulk concentration regardless of the electrode reaction. The second term represents the mass transfer contribution to the total current. As can be seen, this is dependent on the number of electrons being transferred (n_e), the Faraday constant (F), the area of the electrode (A), the diffusion coefficient of the reactant (D), the kinematic viscosity (ν), the rotation frequency (ω) and the bulk concentration of the reactant (C^{bulk}). The main implication of the Koutecký-Levich is that the current is independent of the rotation rate if the current is purely reaction limited, while the current is inversely proportional to the square root of the rotation rate if reaction is purely under diffusional control.

2.2 Vibrational spectroscopy

Vibrational spectroscopy is a widespread tool to study molecules adsorbed on (metal) surfaces, owing to its non-invasive character. By following a reaction with a vibrational spectroscopic technique, molecular level information can be obtained on the intermediates and products of the reaction. The vibrational spectroscopic techniques described in this section, Fourier transform infrared spectroscopy (FTIR) and surface enhanced Raman spectroscopy (SERS), are based on probing molecular vibrations. These techniques are based on the following principle (Figure 2.3): molecules possess discrete levels of vibrational energy. When a molecule is hit by a photon of a certain wavelength

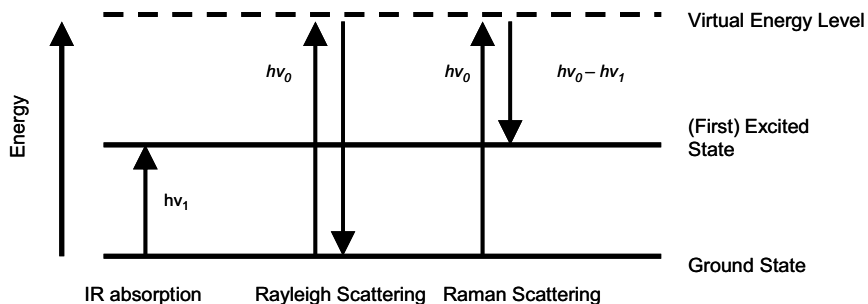


Figure 2.3: Schematic energy diagram of the vibrational transitions in infrared spectroscopy and Raman spectroscopy (only Stokes scattering).

corresponding to one of the energy transitions in the molecule, the light may be absorbed. By following the photons which are transmitted over a range of wavelengths, information on the transitions between different vibrational energy level can be obtained. These energy transitions are characteristic for the composition of the species. In addition, the characteristic frequencies (group frequencies) assignable to particular moieties are relatively independent of the other groups in the molecule, although a small dependence on the environment of the studied species can usually be observed. Examples of environmental parameters which can influence these transitions include the nature of the adsorption site, the electrode potential and the surface coverage of the species.

2.2.1 Fourier transform infrared spectroscopy

In Fourier transform infrared spectroscopy (FTIR), a molecule absorbs photons with the same frequency as the energy gap between the vibrational levels of an allowed transition. Generally, a photon is absorbed to excite the ground state of a molecular vibration to its first excited state (Figure 2.3). In order for a transition to be infrared active, it must be associated with a change in the dipole moment of the vibration. Therefore, the vibrations of polar molecular bonds generally correspond with strong infrared bands. Due to the low transparency of metal electrodes, FTIR measurements in an electrochemical system are usually performed in reflection geometry, which gives rise to another selection rule. Since metallic substrates are conductive, a dipole change of adsorbed molecule will invoke an image dipole on the substrate (Figure 2.4). If a molecule is

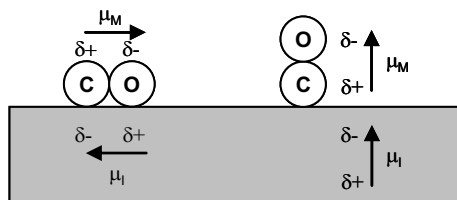


Figure 2.4: Illustration of the surface selection rule with adsorbed CO for infrared spectroscopy. In the case of a molecule adsorbed parallel to the surface, the molecular dipole and image dipole cancel each other, while in the case of a molecule adsorbed perpendicular to the surface the molecular and image dipole enhance each other.

adsorbed parallel to the surface, the resulting molecular dipole and image dipole cancel each other. As a result, the molecule will be infrared inactive. If a molecule is adsorbed perpendicular to the surface, the dipoles sum up and the molecule is infrared active. Therefore, only the contribution of a dipole that is perpendicular to the surface is visible in FTIR.

In this thesis, the FTIR experiments were conducted in external reflection mode. In this configuration, the infrared beam from the spectrometer is passed through an optical window and a thin layer (10-100 μm) of solution and reflected from the electrode through to solution and the optical window into a detector. Therefore species adsorbed on the electrode and species in solution are probed. Contributions from adsorbed species and solution species can be distinguished by two methods. The first method relies on the Stark-tuning: the vibrational frequencies of adsorbed species vary slightly with the external electric field. Therefore, infrared bands related to adsorbed species shift with changing electrode potential, while infrared bands of solution species remain at the same position. An alternative approach is to vary the polarization of the infrared beam. As the polarization of the light has to be parallel to the dipole transition, only *s*-polarized light (parallel to the surface) will not display infrared absorption of adsorbed species due to the surface selection rule. Therefore, *s*-polarized light only probes solution species, while *p*-polarized light (perpendicular to the surface) probes both solution and adsorbed species. By combining the results of the two different polarizations, the contribution of solution species can be distinguished from those of the adsorbed species.

Finally, it should be noted that even though the solution layer is thin, most of the infrared radiation will be adsorbed by water, complicating the analysis of FTIR spectra.

2.2.2 Surface enhanced Raman spectroscopy

Raman spectroscopy is based on the inelastic scattering of photons, which lose energy by exciting vibrations in the sample. The general principle is illustrated in Figure 2.3: rather than using (infrared) light with a frequency corresponding to the energy between two subsequent levels, Raman spectroscopy employs a monochromatic light source of lower wavelength (higher energy) to excite the molecule to a virtual state (a non-stationary state of the system). If the molecule decays to the ground state immediately, no energy is exchanged between the photon and the molecule, resulting in elastic scattering or Rayleigh scattering. Relaxation to an excited state rather than the ground state results in the emission of a photon with a different wavelength than the ingoing light. The loss in energy due to inelastic scattering is called Raman scattering (or Stokes scattering). This energy transfer, which corresponds to the energy gap between the two vibrational levels, is called the Raman effect. Alternatively, a molecule can be excited from an excited state to a virtual state, and subsequently decay from the virtual to the ground state. This photon-induced deexcitation leads to an increase in photon energy and is termed anti-Stokes scattering. However, since the fraction of vibrationally excited molecules is usually small, the anti-Stokes band has a much lower intensity than the Raman (Stokes) band. The probability of Raman scattering is quite small, as most of ingoing light will be scattered elastically.

Therefore, Raman experiments have to be conducted with intense light sources (*e.g.* lasers). In addition, further enhancement of the signal can be obtained by employing surface enhanced Raman spectroscopy (SERS).

In a SERS experiment, the Raman signals can be enhanced by a factor of 10^5 - 10^6 when the molecule is adsorbed on a roughened copper, silver or gold surface. This enhancement can be ascribed to two separate effects, the electromagnetic effect⁴ and the chemical effect⁵. The electromagnetic effect ascribes the enhancement to a local increase of the electric fields at the surface resulting from the excitation of plasmons perpendicular to the surface. Therefore, this effect is largest when the incident light corresponds with the surface plasmon frequencies, while roughened surfaces provide large hot spots

where the enhancements from perpendicular plasmons of multiple surface sites overlap. In the chemical effect, the enhancement is attributed to charge transfer transitions between the molecule and the metal. Since both effects operate only over very small distances (several nanometers), SERS is sensitive to species adsorbed on the surface or solution species in close proximity to the metal surface.

Although SERS has a much lower sensitivity than FTIR, it does offer two distinct advantages by employing visible light rather than infrared light. In infrared spectroscopy, it is difficult to measure vibrations at wavenumbers below *ca.* 900 cm^{-1} , since most optical windows absorb strongly in that frequency range. With Raman spectroscopy, however, one can measure down to 50 cm^{-1} . This allows Raman spectroscopy to probe metal-adsorbate (such metal-nitrogen, metal-carbon, metal-oxygen) vibrations, which mostly lie between 200 and 600 cm^{-1} . In addition, since water adsorbs weakly in the visible light spectrum, and the surface enhancement effects are only active over short distances, there is no need to press the metal against the optical window, circumventing the diffusion problems of a thin layer configuration.

2.3 Online electrochemical mass spectrometry

The online detection of volatile species produced in electrode reactions by mass spectrometry is a technique that has been developed in the early 1970s⁶. It is a technique which is now routinely utilized, as it can be used to probe the chemical identity of volatile products directly and allows for online quantitative determination of these products. The main challenge in electrochemical mass spectrometry lies in developing a system which is able to collect enough volatile species for the mass spectrometric measurements while preventing the large amounts of solvents (typically water) from entering the detection system. A common approach to tackle this challenge is to separate the inlet of the mass spectrometer from the working solution with a porous, hydrophobic (*e.g.* Teflon) membrane.

The online electrochemical mass spectrometry (OLEMS) set-up used in this thesis is based on the tip-based system described in Ref 7 and is shown in Figure 2.5. The set-up consists of a small Kel-F (polychlorotrifluoroethylene) inlet tip (shown in detail in Figure 2.6) of 1 mm diameter which can be placed in close proximity of the working electrode by means of a micrometer positioning

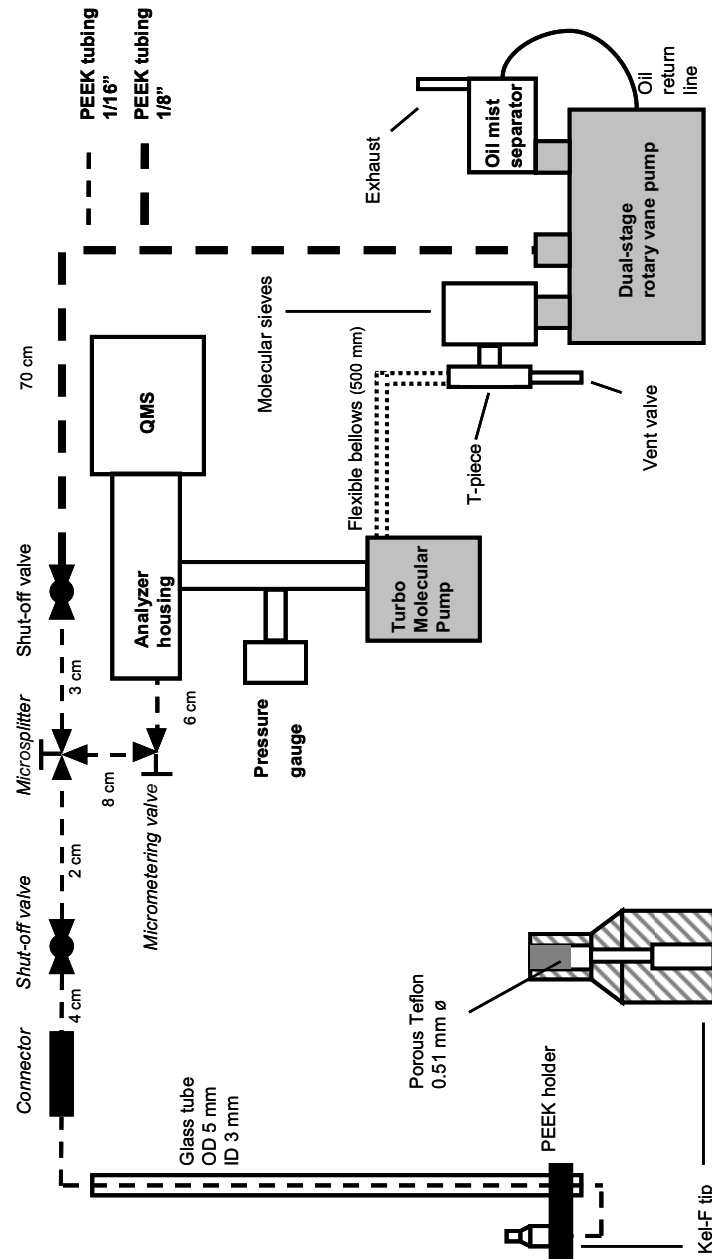


Figure 2.5: Schematic drawing of the OLEMS set-up

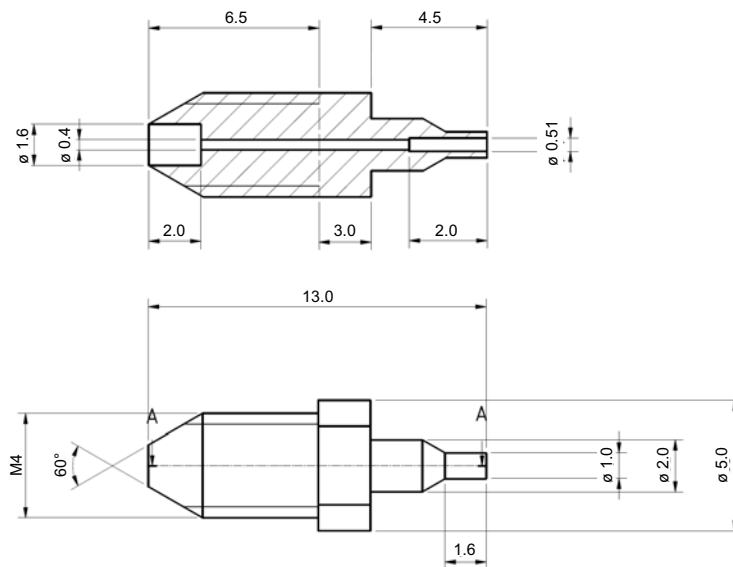


Figure 2.6: Detailed drawing of the OLEMS tip. Measures are given in millimeters.⁸

system. The inlet tip contains a small hole of 0.51 mm diameter into which a small porous Teflon (polytetrafluoroethylene) cylinder with an outer diameter of 0.60 mm is squeezed. In order to prevent leakage of the tip configuration, it is important that the Teflon cylinder is perfectly smooth and has the right porosity. In our system, the optimal porosity of the Teflon was found to be 45-55% with a pore size of 10-14 μm . The tip is connected to the quadrupole mass spectrometer (QMS) system through flexible 1/16" PEEK (polyetheretherketon) tubing. The QMS was brought to vacuum with turbo molecular pump (60 l s^{-1}) and a dual stage rotary vane pump ($2.5 \text{ m}^3 \text{ h}^{-1}$), leading to a base pressure of $3 \cdot 10^{-8}$ mbar. During measurements with the tip immersed, the pressure in the QMS is $1\text{-}5 \cdot 10^{-6}$ mbar. The pressure with the tip not immersed in air typically lies between 1 and $5 \cdot 10^{-5}$ mbar. These pressures are mainly dictated by the porosity of the tip, although it can be adjusted slightly with the microsplitter. With the microsplitter, it is possible to regulate the pressure by directing part of the sample flux towards the rotary vane pump rather than to the QMS, decreasing the working pressure. The total delay between sampling at the tip and detection at the QMS lies between 10 and 20 seconds. The main advantage of employing

this tip based set-up is that it can be modified easily to measure on electrodes in various shapes and sizes in various configurations. In particular, it allows for online mass spectroscopic measurements on single-crystal electrodes in the hanging meniscus configuration.

In the QMS, molecules are ionized by impinging it with electrons, colliding with electrons of the analyte molecule, leading to positively charged analyte ions. In addition to the molecular fragment (the ionized analyte molecule with the chemical bonds intact), ionization can cause the molecule to dissociate, leading to smaller fragments. After ionization, the fragments are separated based on mass-to-charge ratio by a quadrupole mass analyzer. By analyzing the fragmentation pattern of a molecule, its chemical identity can be deduced. In addition, identification can be facilitated by analyzing fragments with different isotopes, either through evaluating the natural abundances of the various isotopes of a certain atom, or by employing isotopically labeled compounds.

In the OLEMS experiments described in this thesis, the detector was set to follow a number of mass-to-charge ratios as a function of time during voltammetric measurements, enabling us to follow the production of gaseous products during a voltammetric measurement.

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