

Ethanol Stripping in Alkaline Medium: A DEMS Study

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In this study, the adsorption of ethanol on platinum in alkaline medium is investigated by stripping voltammetry in combination with differential electrochemical mass spectrometry (DEMS). It is shown that the amount of adsorbed ethanol depends on the adsorption potential. Adsorbed ethanol can be oxidized to carbon dioxide in two different potential regions: one below 0.9 V vs. RHE and the other above 0.9 V vs. RHE. Furthermore, adsorbed ethanol can be reduced to methane below 0.2 V vs. RHE when the stripping voltammogram is started in cathodic direction from the adsorption potential. The number of electrons transferred per molecule of carbon dioxide evolved is calculated and found to be two in the potential region below 0.9 V vs. RHE, independent of the adsorption potential. A larger number of electrons is found in the potential region above 0.9 V vs. RHE. Based on the findings, a preliminary reaction scheme is presented.

Introduction

Liquid-fed direct alcohol fuel cells show a high potential for future power supply. Being the major renewable bio-fuel, ethanol is an interesting alternative to the extensively studied methanol (1). Aside from the fact that ethanol can be produced in large quantities from renewable resources fairly easily, it is less toxic, its boiling point and theoretical mass energy density (ethanol: 8 kWh/kg, methanol: 6 kWh/kg) are relatively higher compared to methanol (2, 3). Also, ethanol in its denatured form is already widely available (4). On the other hand, by moving from the C₁-alcohol methanol to the C₂-alcohol ethanol, the challenge of C-C bond breaking arises in order to achieve complete oxidation of the fuel. Therefore, in acidic medium, methanol exhibits superior reaction kinetics compared to ethanol on platinum based catalysts, and ethanol oxidation is associated with the formation of several unwanted byproducts like acetaldehyde and acetic acid (3).

Compared to the acidic medium, the kinetics of the electro-oxidation of aliphatic alcohols is significantly improved. This fact is ascribed to the higher coverage of the electrode with adsorbed hydroxyl, playing a key role in the removal of electrode poisoning species (5, 6). In fact, the electro-oxidation of ethanol in alkaline medium is specifically interesting, as the increase in the kinetics of the ethanol oxidation reaction is so strong that it becomes faster than the kinetics of the methanol oxidation reaction at the same electrode under the same conditions (7). Furthermore, in alkaline medium base metals can be used as catalyst instead of precious noble metals, significantly lowering the overall cost of a fuel cell system (8, 9).

It is known from literature that voltammetric stripping of pre-adsorbed ethanol in acidic medium leads to carbon dioxide and methane as predominant products. Carbon dioxide is formed by the oxidation of adsorbates and methane is generated by their reduction in the low potential region of the first negative going potential sweep. Various C₁ and C₂-species are discussed as adsorbates of the ethanol adsorption (10, 11). However, the reaction mechanism and the adsorbed intermediates of ethanol in alkaline medium remain widely unclear.

In the present study the adsorption of ethanol in alkaline medium on platinum as model catalyst is investigated dependent on the adsorption potential. In order to find out more about the nature and formation of adsorbates, electrochemical stripping voltammetry in combination with differential electrochemical mass spectrometry (DEMS) is performed.

Experimental

Stripping voltammetry in combination with DEMS is a powerful tool to detect and identify adsorbates. In the present case, the stripping voltammetry is conducted at the working electrode of a DEMS flow cell arrangement, in principle described elsewhere (7). The cell is equipped with an inert body made from PCTFE and a PTFE membrane (60 μm thickness, 0.02 μm average pore size, 50 % porosity) supplied by Gore, sputter deposited with platinum (approximately 60 nm), serving as working electrode and vacuum inlet of the mass spectrometer. A platinum foil was used as counter electrode, separated from the working electrode compartment by a glass frit. A freshly prepared reversible hydrogen electrode (RHE) in a separate compartment was employed as reference electrode. The connection to the working electrode compartment was established by a capillary. Electrolyte was kept flowing from the reference electrode compartment to the cell in order to avoid blocking by gas bubbles. The potential of the working electrode in the DEMS cell was controlled with a Gamry Reference 600 potentiostat operated by a custom made LabVIEW software, simultaneously controlling the mass spectrometer Balzers QMS 200.

The measurements are conducted, starting with a potentiostatic step in base electrolyte followed by the exchange of the base electrolyte (0.1 M KOH, prepared from Merck Titrisol[®]) by an ethanol containing solution (0.1 M ethanol (analytical grade purity, Merck) / 0.1 M KOH). The potential is kept constant for a certain adsorption time before the electrolyte is again changed to base electrolyte. Afterwards, a stripping voltammogram is started, beginning at the adsorption potential. The stripping voltammogram is started in either anodic or cathodic direction, respectively. All measurements are conducted at ambient temperature (22 °C ± 1 °C).

Calibration of the Mass Spectrometer

In order to quantify a certain volatile product, the mass spectrometric ion current signal of a fragment specific for this product has to be correlated to the Faradaic current signal. Such a calibration is possible when using a known chemical reaction (12, 13). In the present case, the oxidation of adsorbed carbon monoxide to carbon dioxide is used to calibrate the mass spectrometer (equation [1]).



In order to saturate the electrode surface with carbon monoxide, the cell is flushed with carbon monoxide saturated 0.1 M potassium hydroxide solution for 5 minutes at an adsorption potential of 0.15 V vs. RHE. Afterwards, the electrolyte is exchanged to carbon monoxide free 0.1 M potassium hydroxide solution, and the electrode is held at the adsorption potential for another 15 minutes. Hereafter, the potential sweep in which the adsorbed carbon monoxide gets oxidized is started in anodic direction from the adsorption potential.

According to equation [2], the correlation of the integrated ion current for the mass to charge signal 44 ($Q_{MS,m/z\ 44}$) and the integrated Faradaic current (Q_F) results in the calibration constant K^* .

$$K^* = z * Q_{MS,m/z\ 44} / Q_F \quad [2]$$

In equation [2] z denotes the number of electrons exchanged per formula unit.

In acidic medium, integration of the Faradaic oxidation current of adsorbed carbon monoxide observed in the first potential sweep is usually done by subtraction of the background current of a subsequent potential sweep. This should in part account for double layer charging effects which amount to 20 % of the oxidation charge (12).

In the present case, in alkaline medium, the integration is done differently. Figure 1 shows the Faradaic current of the first anodic potential sweep, the difference of the first and the second anodic potential sweep and the respective mass spectrometric ion current for m/z 44 which is corrected for its background current.

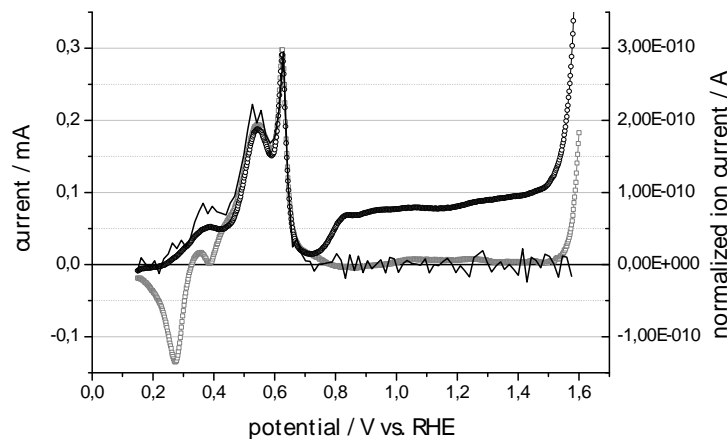


Figure 1: Oxidation of adsorbed carbon monoxide in 0.1 M KOH: Mass spectrometric ion current m/z 44, first anodic potential sweep (black line, corrected for background current), Faradaic current, first anodic potential sweep (black circles), difference between the Faradaic current of the first and second anodic potential sweep (grey squares). Adsorption potential 0.15 V vs. RHE, adsorption time 5 minutes, scan rate 10 mV / s.

From figure 1 it can be seen that the carbon monoxide oxidation in alkaline medium starts at about 0.24 V vs. RHE, which is well within the hydrogen desorption region. In fact, if the second anodic potential sweep is subtracted from the first one to correct the carbon monoxide oxidation current for the background current, the large hydrogen desorption wave, centered at approximately 0.27 V vs. RHE, will appear (fig. 1, grey squares). So if the positive current difference between the first and second anodic potential sweep was integrated, the integration would start at about 0.33 V vs. RHE. Effectively, compared to the mass spectrometric signal, this would lead to an underestimation of the integrated Faradaic current by omitting the contribution of the carbon monoxide being oxidized between 0.24 V vs. RHE and 0.33 V vs. RHE.

In order to eliminate this underestimation, in the present work, the first anodic potential sweep of the Faradaic current is integrated, beginning at the onset of the oxidation current (0.24 V vs. RHE) which coincides with the onset of the mass spectrometric m/z 44 signal, and ending at the minimum after the oxidation peak (0.73 V vs. RHE), just before the formation of the platinum oxide formation starts.

The integration of the Faradaic current is evaluated in terms of the real surface area of the electrode calculated from the integrated Faradaic current, taking into account the factor of $420 \mu\text{C} / \text{cm}^2$ for the oxidation of a complete monolayer of carbon monoxide on polycrystalline platinum and a monolayer density of 0.7 molecules of carbon monoxide per surface site. These values are compared with the real surface area determined by hydrogen adsorption at the same electrode in 0.5 M sulphuric acid according to the method of *Biegler* (14). Table I shows that the surface area calculated from the first anodic potential sweep is in good agreement with the one determined according to the method of *Biegler*, while the area calculated from the integration of the Faradaic current difference of the first and the second anodic potential sweep is somewhat smaller.

TABLE I. Comparison of the Calculated Surface Area Determined by Different Methods.

| Method | Integration (V vs. RHE) | Calculated Surface Area (cm^2) |
|---|----------------------------|--|
| Hydrogen adsorption (0.5 M H_2SO_4 , <i>Biegler</i>) | 0.45 to 0.08 | 14.0 |
| Integration first potential sweep (0.1 M KOH) | 0.24 to 0.73 | 13.5 |
| Integration difference first – second potential sweep (0.1 M KOH) | 0.33 to 0.79 | 12.7 |

Taking into account that integration of the Faradaic current in the first anodic potential sweep does not account for differences in double layer charging, this method is used for calibration of the mass spectrometer. As it is known that porous sputter deposited electrodes tend to degrade with time, the calibration is regularly repeated.

In case of the ethanol adsorbate oxidation, the oxidation charge below 0.9 V vs. RHE is integrated from the first anodic potential sweep as shown above, and the one above 0.9 V vs. RHE is integrated from the difference of the first and the second anodic potential sweep, allowing for the contribution of the platinum oxide formation.

Results

Figure 2 shows an ethanol stripping experiment started from the adsorption potential of 0.3 V vs. RHE in anodic direction.

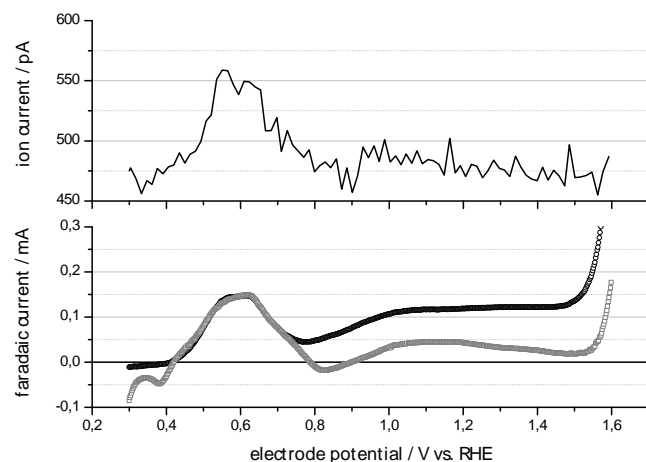


Figure 2: Oxidation of adsorbed ethanol at platinum in 0.1 M KOH: Mass spectrometric ion current m/z 44, first anodic potential sweep (black line), Faradaic current, first anodic potential sweep (black circles), difference between in the Faradaic current of the first and second anodic potential sweep (grey squares). Adsorption potential 0.3 V vs. RHE, adsorption time 5 minutes, scan rate 10 mV / s.

As seen from figure 2, the carbon dioxide formation is restricted to two separate potential regions: one below 0.9 V vs. RHE and the other above 0.9 V vs. RHE. As shown in figure 3, the total oxidation charge for the two potential regions in the anodic stripping experiments passes through a maximum dependent on the adsorption potential.

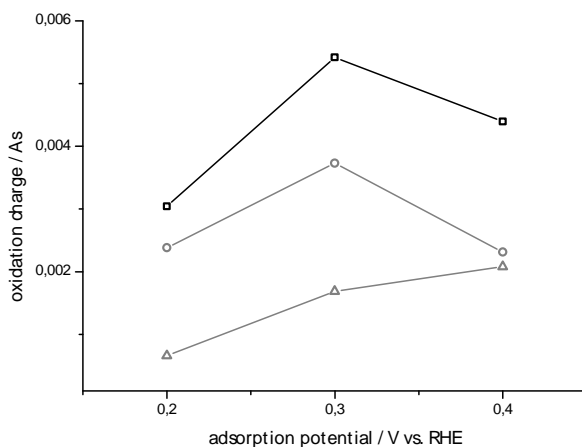


Figure 3: Oxidation charge vs. adsorption potential for anodic stripping of pre-adsorbed ethanol at platinum in 0.1 M KOH: Total oxidation charge (black squares), oxidation charge for the potential region below 0.9 V vs. RHE (grey circles) and oxidation charge for the potential region above 0.9 V vs. RHE (grey triangles). Scan rate 10 mV / s.

The same accounts for the oxidation charge for the first potential region below 0.9 V vs. RHE, while the oxidation charge in the second potential region above 0.9 V vs. RHE increases with rising adsorption potential.

The fact that the oxidation charge in the potential region below 0.9 V vs. RHE passes through a maximum might be due to reduction processes already taking place at a potential of 0.2 V vs. RHE or oxidation processes taking place at a potential of 0.4 V vs. RHE.

When the potential sweep is started in cathodic direction after the ethanol adsorption, the formation of methane is observed below 0.2 V vs. RHE. As exemplarily shown in figure 4 for an adsorption potential of 0.3 V vs. RHE, carbon dioxide is only formed in the potential region below 0.9 V vs. RHE. The current observed above 0.9 V vs. RHE in the first potential sweep in figure 4 is entirely caused by the platinum oxide formation.

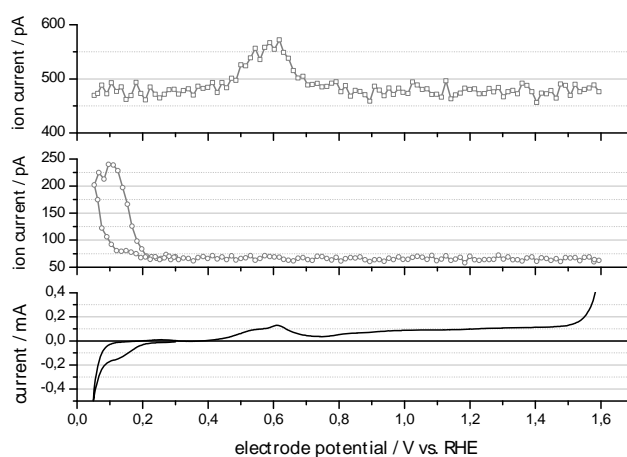


Figure 4: Cathodically started stripping of ethanol adsorbates in 0.1 M KOH at platinum: mass spectrometric signal for carbon dioxide (m/z 44, grey squares), mass spectrometric signal for methane (m/z 15, grey circles) and Faradaic current of the first potential sweep (black line). Adsorption potential 0.3 V vs. RHE, adsorption time 5 minutes, scan rate 10 mV / s.

Taking into account the figures 2 and 4, the adsorbates which are oxidized above a potential of 0.9 V vs. RHE seem to predominantly be the same ones which can be reduced in case of a cathodic starting direction of the potential sweep from the adsorption potential.

A comparison of the oxidation charges in the potential region below 0.9 V vs. RHE from anodically and cathodically started potential sweeps shows that the dependency of the oxidation charge on the adsorption potential is qualitatively the same (figure 5). However, the oxidation charges from cathodically started potential sweeps, attained after methane formation, are somewhat smaller than those from anodically started potential sweeps.

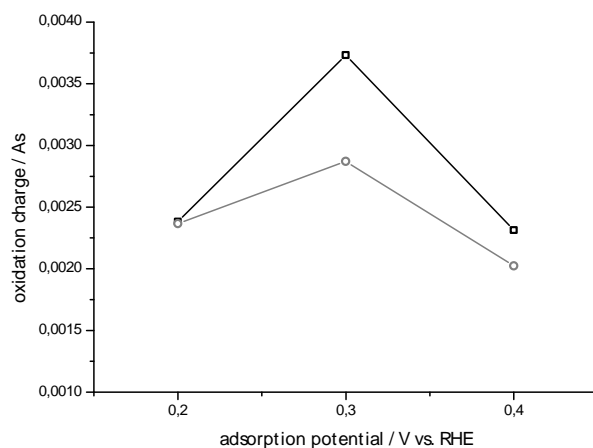


Figure 5: Oxidation charge vs. adsorption potential in the potential region below 0.9 V vs. RHE for stripping of pre-adsorbed ethanol in 0.1 M KOH at platinum: Potential sweep started in anodic direction from the adsorption potential (black squares) and potential sweep started in cathodic direction from the adsorption potential (grey circles). Scan rate 10 mV / s.

From the mass spectrometric charge for the mass to charge signal m/z 44 and the Faradaic charge, the number of electrons transferred per molecule of carbon dioxide evolved can be calculated. Figure 6 demonstrates that a constant number of two electrons is found for the anodically started stripping experiments in the potential region below 0.9 V vs. RHE.

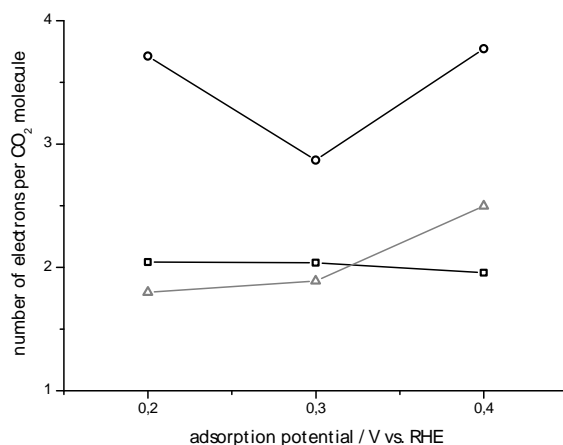


Figure 6: Number of electrons per carbon dioxide molecule vs. adsorption potential for stripping of pre-adsorbed ethanol at platinum in 0.1 M KOH: stripping started in anodic direction, potential region below 0.9 V vs. RHE (black squares), stripping started in anodic direction, potential region above 0.9 V vs. RHE (black circles) stripping started in cathodic direction, potential region below 0.9 V vs. RHE (grey triangles). Scan rate 10 mV / s.

Roughly the same accounts for cathodically started stripping experiments. Although the electron number for an adsorption potential of 0.4 V vs. RHE deviates. In the potential region above 0.9 V vs. RHE, the number of electrons transferred per molecule carbon dioxide formed is significantly higher than two.

Discussion

In the present study the adsorbates from the ethanol adsorption in alkaline medium is investigated by stripping voltammetry in combination with differential electrochemical mass spectrometry. A quantification of the results is done by the calibration of the mass spectrometer for carbon dioxide.

It is shown that in alkaline medium ethanol adsorbates can only be desorbed in form of carbon dioxide and methane. Other reaction products, especially C₂-products are not detected. This leads to the assumption that the ethanol adsorption occurs dissociatively. As pre-adsorbed carbon monoxide cannot be reduced to methane at platinum in alkaline medium, methane formation from ethanol adsorbates is ascribed to an adsorbed CH_x or CO_xH_y species.

The adsorbates from the ethanol adsorption can be oxidized in two potential regions, one below 0.9 V vs. RHE and the other above 0.9 V vs. RHE. While the oxidation charge in the potential region above 0.9 V vs. RHE increases monotonically with rising adsorption potential, the oxidation charge in the potential region below 0.9 V vs. RHE passes through a maximum at an adsorption potential of approximately 0.3 V vs. RHE. Keeping in mind that carbon monoxide oxidation starts as low as 0.24 V vs. RHE and reduction of ethanol adsorbates takes place below 0.2 V vs. RHE, this could be explained by reduction or oxidation processes already taking place at 0.2 V vs. RHE or 0.4 V vs. RHE, respectively.

The calculated number of electrons per molecule of carbon dioxide evolved in the potential region below 0.9 V vs. RHE is found to be two, independent of the adsorption potential. This leads to the assumption that an adsorbed species in the form of CO_{ads} is present. The higher calculated number of electrons per molecule of carbon dioxide in the potential region above 0.9 V vs. RHE points to the coexistence of more than one adsorbate species. The deviation of the number of electrons per molecule of carbon dioxide from the value of two in the potential region below 0.9 V vs. RHE for stripping experiments started in cathodic direction indicates an alteration of the adsorbate in the form of CO_{ads}, initially being present, or again, the coexistence of two adsorbate species. The finding that no carbon dioxide formation is observed in the potential region above 0.9 V vs. RHE for stripping experiments started in cathodic direction shows that the adsorbates which are oxidized in the potential region above 0.9 V vs. RHE are the ones which can be reduced to methane.

Conclusion

Taking into account the presented results, the following preliminary reaction scheme for the dissociative adsorption of ethanol can be formulated (figure 7).

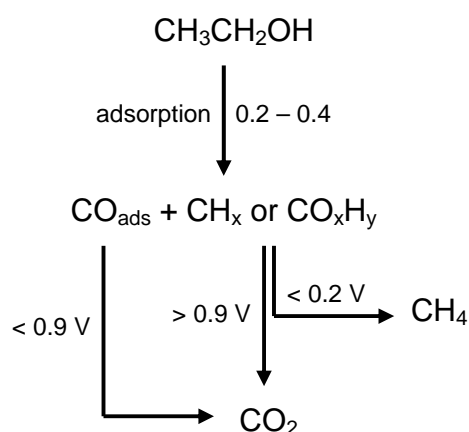


Figure 7: Reaction scheme for adsorption and stripping of ethanol at platinum in 0.1 M KOH.

The reaction scheme is to be seen as a working hypothesis, as it contains only structural information gathered with DEMS. As only volatile products can be detected with DEMS, the existence of other soluble species cannot completely be excluded. While the existence of a CO_{ads} -like species is most likely, the adsorbate structure of the adsorbate which is oxidized above 0.9 V vs. RHE is still speculative. To address this question, in-situ spectroscopic investigations shall be conducted.

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