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The Determination of Electrochemical Active Surface Area and Specific Capacity Revisited for the System MnO_x as an Oxygen Evolution Catalyst

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Abstract: In the last decades several different catalysts for the electrochemical water splitting reaction have been designed and tested. In so-called benchmark papers they are compared with respect to their efficiency and activity. In order to relate the different catalyst to each other the definition of well-defined procedures is required. Two different methods are mainly used: Either the normalization with respect to the geometric surface area or to the catalyst loading. Most often only one of these values is available for a sample and the other one cannot be estimated easily. One approach in electrocatalysis is to determine the Helmholtz double layer capacitance (DLC) and deduce the electrochemical active surface area (ECSA). The DLC can be obtained from two different methods, either using differential capacitance measurement (DCM) or impedance spectroscopy (EIS). The second value needed for the calculation of the ECSA is the specific capacitance, which is the capacitance for a perfectly flat surface of given catalyst material. Here, we present the determination of the different capacitance values using manganese oxide as the exemplary model for the oxygen evolution reaction (OER). We determine the capacitance by DCM and EIS to calculate the ECSA using literature values for the specific capacitance. The obtained values are comparable from the two methods, but are much larger than the surface areas obtained by atomic force microscopy. Therefore, we consider the possibility of using the measured AFM area together with the Helmholtz capacitance to determine the specific capacitances for this

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material class. The comparison of these results with literature values illustrates the actual limits of the ECSA method, which will be discussed in this paper.

Keywords: double layer capacitance; ECSA; electrochemical active surface area; manganese oxide; Helmholtz capacitance; MnO; MnO₂.

1 Introduction

Renewable energy systems like solar and wind power show strong fluctuations in their availability over time. In order to achieve an energy supply with a high amount of renewable energy it is necessary to develop energy storage systems to overcome these fluctuations [1]. Electrochemical water splitting is one of the promising ways to obtain clean and sustainable chemical fuels [2, 3]. These fuels can be stored and used on demand. For the water splitting reaction highly active catalysts are needed, which are stable, low cost and abundant [4]. In the last decade different transition metals, their oxides and alloys have been extensively studied, with respect for their catalytic properties for the oxygen evolution reaction (OER) [5–7]. In benchmark articles the results have been summarized and compared, but the comparison of different experimental data is still difficult due to a lack of standardization of the measurement procedure and reference system [8, 9]. Electrochemical parameters like electric current or electrode reaction rates have to be normalized to obtain comparable values [10]. For powder catalysts the loading is often used to quantify these values, but for flat film catalysts these values are not easily accessible. Therefore, for flat films the projected surface area is commonly taken as reference. The question, which shall be addressed here, is how to determine the specific active surface area to quantify the activities of different catalyst materials.

One often used approach is to determine the surface area with an electrochemical measurement of the double layer capacitance (DLC). Therefore, a differential capacitance measurement (DCM) with different scan rates in a narrow potential range is used. If this measurement is in a range with no Faradaic reaction the resulting differential capacitance equals the double layer capacitance (C_{DL}) [11]. With this capacitance it is possible to calculate the electrochemical active surface area (ECSA) by the following equation 1:

$$ECSA = \frac{C_{DL}}{C_S} \quad (1)$$

For the determination of the ECSA the specific capacitance (C_S) is needed. This value describes the capacitance of an ideal flat surface of the catalyst. In the paper of Barton and Infield [1] one can find procedures to get a standardized

value for the specific capacitance in alkaline or acid solution [8]. But even McCrory et al. reported in his benchmarking publications that the C_s values for different catalysts vary between 0.022 and 0.130 mF/cm² in alkaline solutions [8]. This shows, that for different materials the specific capacitance exhibits already huge differences. Nevertheless, there are many publications which use the average value of 40 μ F/cm² reported by McCrory as value for the specific capacitance in alkaline solutions without taking the used material and measurement conditions into account [12–14]. But, also other values for the specific capacitance, such as 80 μ F/cm² or 20 μ F/cm² are reported [15, 16]. The specific capacitance is not only different for different electrodes, but it can also vary with the oxidation state. Trasatti et al. reported that the existence of an oxidation layer on top of the catalyst has a huge influence on the capacitance value [11].

In this work it is shown, that even for the same element in different oxidation states the capacitance for flat surfaces can vary by 100%. The capacitance is determined with two different methods which were compared to each other. One method is the DCM and the other one is electrochemical impedance spectroscopy (EIS). As catalyst model system manganese oxide (MnO_x) was examined and measured in alkaline solution for the OER. Manganese oxide MnO_x was chosen due to different aspects MnO_x is considered as electrocatalytic material because of its central role in the photo system II [17–19], and it is one of the 10 most abundant element in the earth's crust [20]. Furthermore, it is a transition metal with many different oxidation states and therefore is a promising candidate to investigate the effect of oxidation state changes on the DLC.

2 Experimental

2.1 Sample preparation

An ITO coated glass sheet (Alineason Inc. 1×1 cm) was cleaned in an ultrasonic bath for 10 min in both acetone and isopropanol (Carl Roth, purity $\geq 99.8\%$). Afterward a 50 nm gold layer was deposited on top of the sample with a direct current sputtering process. The catalyst was deposited in an ultra-high vacuum (UHV) chamber with a base pressure of 8×10^{-8} mbar. After the introduction of the sample into the UHV system, an additional cleaning step with radiofrequency (RF) sputtering was accomplished (5 W, 20 sccm Ar (99.999% pure), 0.03 mbar, 1 min) to remove carbon contaminations on the surface. The manganese oxide layers were deposited by a reactive magnetron sputtering processes of a metallic manganese target in a reactive gas mixture of argon (99.999% pure) and oxygen (99.995% pure). To obtain different manganese oxide phases, the argon and

oxygen gas flow were changed, whereas the power (20 W) and base pressure (0.03 mbar) remained constant. The total gas flow was 20 sccm. The amount of oxygen in the gas flow was 0.5% for MnO and 2% for MnO₂.

2.2 Sample characterization

The deposition chamber is part of the vacuum system DAISY FUN (Darmstadt integrated system for fundamental research) [21] that allows an in-line transfer of the sample to the photoelectron spectroscopy measurement chamber (all in a base pressure of 1×10^{-9} mbar or below). The X-ray photoelectron spectroscopy (XPS) analysis chamber has a base pressure of 5×10^{-10} mbar. XP spectra were measured with a SPECS Phoibos 150 hemispherical analyzer and a SPECS Focus 500 X-ray source (Al K_α 1486, 74 eV). The system is calibrated using freshly sputtered gold, silver and copper reference foils, which results in an accuracy of ± 50 meV.

For the electrochemical characterization the sample was removed from the vacuum system and placed into a PECC-2 cell from Zahner. The measurements were carried out with a GAMRY Interface 1000E potentiostat in a three-electrode setup with a Hg/HgO reference electrode. As electrolyte 0.1 M KOH (Carl Roth, $\pm 0.2\%$) was used for all electrochemical measurements.

The measurement protocol consists of three parts. In part one (EC1) the DLC was determined with two different methods – namely, fast potential sweep curves and electrochemical impedance spectroscopy (EIS). The fast potential sweep curves were performed at three potentials: 1.10 V, 1.25 V and 1.40 V vs. RHE in a range of 0.10 V around these potentials with sweep rates between 10 and 50 mV/s. From these measurements the differential capacitance can be calculated. The second method uses impedance spectroscopy at the same potentials (1.10 V, 1.25 V and 1.40 V vs. RHE) in a frequency range of 0.1 Hz–100 kHz to calculate the capacitance. The second part of the measurement protocol (EC2) contains the following measurement steps:

1. Electrochemical Impedance Spectroscopy (EIS) at OCP to determine electrolyte resistance
2. Cyclic Voltammetry (CV) 1.0–1.9 V vs. RHE, 50 mV/s, 2 Cycles
3. Conditioning 1.0–1.5 V vs. RHE, 100 mV/s, 50 Cycles
4. Cyclic Voltammetry 1.0–1.9 V vs. RHE, 50 mV/s, 5 Cycles
5. Cyclic Voltammetry 1.0–1.9 V vs. RHE, 10 mV/s, 2 Cycles

With the EIS measurement in step one the electrolyte resistance is determined in order to be able to perform an IR correction of the CV curves. Step two and four are used to measure the efficiency of the catalyst before and after the conditioning step. After collecting the activity of the catalysts (EC2) the DLC is calculated

a second time ($EC3 = EC1$) from the fast differential capacitance measurements and the EIS. The EC1 and EC3 part are measured at identical parameters and are used to check if there are any capacitance changes due to the conditioning and CV measurement in the EC2 part. To determine compositional changes on the catalyst surface after the electrochemical measurement, the sample was directly transferred back to the vacuum system and XPS was measured again.

Additional to the electrochemical characterization measurements, an atomic force microscope (MFP3D Asylum Research, Oxford Instruments) was used to determine the roughness of the surface and therefore the geometric surface area. These measurements were performed using the peak force tapping mode on fresh prepared samples.

3 Results and discussion

3.1 Phase characterization

The composition of the manganese oxide films was determined by XPS after sample preparation and after electrochemical analysis. The resulting XP spectra are shown in Figure 1. The phase composition of the catalytic layers was determined from the Mn 2p spectra since the distance between the Mn 2p_{1/2} and its satellite is characteristic for different manganese oxidation states. The values of this distance are depicted in Figure 1. In literature, the peak-satellite distance for MnO is

Fig. 1: XPS spectra of MnO_x layers on ITO/Au substrates before and after electrochemistry measurement. In red the MnO phase before and after (') electrochemistry and in blue MnO₂ phases before and after (') electrochemistry.

6.0 eV and for MnO_2 it is 11.8 eV. For the bottom red curve the distance fits well with literature values for MnO whereas for the upper blue one the larger distance values reveal a MnO_2 phase [22–24]. It is common to compare the results of the Mn 2p spectra with the Mn 3s multiplet splitting. However, for this sample this comparison is hindered by the strong emission of the gold layer underneath. The Au 4f possesses stronger emissions than the Mn 3s peak in this spectral region.

In the oxygen spectra two main results can be detected: One is that the lattice oxide peak shifts from 530.1 eV for MnO to 529.1 eV for the MnO_2 species, which indicates the change in the oxidation state. Another one is that the MnO spectra contain an additional peak with a binding energy of 531.9 eV ($\text{O } 1s^*$), which could result from oxygen defect states like a vacancy or interstitial. All these positions fit well with values reported in the literature [25, 26]. The catalytic MnO and MnO_2 layers are free from carbon or other contaminating elements. Their survey spectra are presented in the supporting information (SI) figure S 1.

The spectra labeled with MnO' and MnO_2' are measured after electrochemical testing. In the detail spectrum of Mn 2p, an increase in distance between the Mn $2p_{1/2}$ and its satellite is visible due to a change in the oxidation state. In the O 1s spectra a new component appears at a binding energy of 530.3 eV, which can be attributed to the formation of hydroxide on the surface [25, 27]. The oxygen defect state in the MnO^* spectra decreases after the electrochemical measurement. The survey spectra show small amounts of carbon after EC2, figure S 1. The MnO_2 spectra show only minor changes. In all cases, the XP spectra before and after the electrochemical treatment show the formation of a manganese hydroxide phase at about 530.5 eV at the catalyst surface.

3.2 Electrochemical measurement

The electrochemical test procedure contains three different parts as described in the experimental section. The results of the second part EC2 will be discussed in this chapter. The CV scans (steps 2 and 4), plotted in Figure 2, are recorded in EC2 before and after the conditioning step (step 3). The MnO_2 phase shows a better onset potential as the MnO phase. For both of them the activity slightly decreases after the conditioning step, but the MnO_2 phase still shows a higher activity as the MnO phase.

The inset plot of Figure 2 shows the magnified potential range between 1.0 and 1.5 V vs. RHE. The potentials for the capacitance determination of the EC1 and EC3 are indicated with dashed lines at 1.10, 1.25 and 1.40 V vs. RHE. From the magnification a hysteresis in this area becomes visible, which reveals a change in oxidation state from Mn^{3+} to Mn^{4+} at a potential of approximately 1.10 V vs. RHE [28]. For higher potentials no reaction is visible. Gorlin et al. reported, that this

Fig. 2: Second sweep of the cyclic voltammogram of the MnO and MnO₂ phases on ITO/Au substrate before (pre, step 2) and after (post, step 4) conditioning. The scans were measured with a scan rate of 50 mV/s in a potential range of 1.0–1.9 V vs. RHE in 0.1 M KOH. The inset plot shows the magnified area between 1.0 and 1.5 V vs. RHE.

change in oxidation state involves only the top-most surface layers. The current density is normalized to the geometric area of the catalyst.

3.3 Measurement of the DLC

As mentioned in the experimental section before two different methods are used to measure the capacitance. Both of them are performed in 0.1 M KOH with a Hg/HgO reference electrode. The resulting CV curves of the fast potential sweep curve measurement are plotted in figure S 2. It shows the scans for the two different manganese oxides phases measured at the potentials of 1.10 V, 1.25 V and 1.40 V vs. RHE in a range of 0.10 V around these potentials with scan rates between 10 and 50 mV/s. In the potential range between 1.25 V and 1.40 V vs. RHE no Faradaic reaction takes place (see Figure 2). For the calculation of the differential capacitance two basic equations are used:

$$C_{DL} = \frac{dQ}{d\varphi}, \quad (2)$$

$$i = \frac{dQ(\varphi)}{dt}, \quad (3)$$

with C_{DL} as double layer capacitance, Q as charge and f as potential. From equations (2) and (3) the following equation (4) is derived [8, 10]:

$$i = C_{DL} \frac{d\phi}{dt} \tag{4}$$

The differential capacitance was determined for all samples at potentials of 1.10 V, 1.25 V and 1.40 V vs. RHE. The obtained values for the current densities as a function of the scan rate are displayed in Figure 3. All curves show a linear behavior over the measured scan rate range. The resulting average capacitance values are tabulated in Table 1. The graphs labeled without dash are recorded before measuring EC2, while the graphs labeled with a dash are measured afterward. A capacitance change after EC2 is visible in the graph. The MnO capacitances have increased or stayed constant, while the capacitance of the MnO₂ phase has decreased.

First, the DLC of the EC1 measurement will be discussed. The capacitance of the MnO phase is between 150 μ F and 250 μ F, while the capacitances of the MnO₂

Fig. 3: Anodic and cathodic charging current densities measured at the potentials 1.10 V, 1.25 V and 1.40 V vs. RHE plotted as a function of scan rate. The slope of the linear fit gives the DLC. The left column shows the measured capacitances of the EC1 while the right column (MnO' and MnO₂') shows the capacitance of EC3.

Tab. 1: Calculated average differential capacitances for different manganese oxide phases at different potentials obtained by DCM, determined before (EC1) and after (EC3) the activity measurement.

	ΔC_d (μF)		ΔC_d (μF)		ΔC_d (μF)	
	1.10 V vs. RHE		1.25 V vs. RHE		1.40 V vs. RHE	
	EC1	EC3	EC1	EC3	EC1	EC3
ITO/Au/MnO	235	404	203	245	168	145
ITO/Au/MnO ₂	545	458	386	302	257	207

phase are between 250 μF and 550 μF . The potential dependence of the DLC is higher for the Mn^{4+} phase than for the Mn^{2+} phase. The most accurate value for the capacitance should be reached at a potential with no or the lowest faradaic contribution. In the case of manganese oxide, the potential with no faradaic contribution is 1.40 V vs. RHE (see Figure 2). This should lead to the most accurate DLC value and therefore only the capacitance value for the 1.40 V vs. RHE will be discussed in the following part. At this potential the Mn^{4+} phases have an average capacitance value of 257 μF . The value for the Mn^{2+} phase is lower with an average of 168 μF . Due to the phase change during the EC2 procedure also the capacitance values change. After the EC2 treatment the capacitance at 1.40 V vs. RHE of the MnO and MnO₂ phase decreases slightly. This effect arises from the phase change of the catalysts during the conditioning and CV curve measurement. Both the MnO phase and the MnO₂ phases change partially to a hydroxide on the surface, which is visible in the XP spectra in Figure 1. It can be assumed, that with longer electrochemical treatment the phases would adapt to the same final phase composition with a comparable capacitance value. After the electrochemical treatments the formed layer consist out of a Mn^{4+} phase and a MnOOH/Mn(OH)₂ phase. The amount of Mn^{4+} in the MnO sample is slightly smaller, which explain the lower Mn2p_{1/2} satellite distance. After longeterm measurement both samples are fully changed to Mn^{4+} . At a potential of 1.40 V vs. RHE after EC2 the capacitance value for the Mn^{4+} phase is 207 μF , for Mn^{2+} the average is 145 μF . In both cases, before and after EC2, the average value for the DLC of the MnO phase is lower than the one of MnO₂. The average value was determined from the cathodic and anodic part of the current density measurement in Figure 3. To check the reproducibility of the differential capacitance measurements for the MnO₂ sample at the potentials of 1.25 V and 1.40 V vs. RHE, these measurements were repeated three times for different samples showing a standard deviation of ± 25 μF . All other samples where measured two times with a deviation of less then ± 25 μF . From these values it can be seen that the trend for the DCM measurements is similar for the

three potentials, but the values for the two different MnO_x phases show strong deviations.

The second method to determine the DLC is by using EIS at the same potentials as defined before. The electrical impedances were measured in EC1 and EC3 in the frequency range from 0.1 Hz up to 100 kHz at the potentials of 1.10 V, 1.25 V and 1.40 V vs. RHE. For EC1 the resulting Nyquist plots are displayed in Figure 4. EC3 are basically similar.

To evaluate the data an equivalent circuit shown in the inset of Figure 4 was used to fit the data points. It contains the electrolyte resistance R_s and a charge transfer resistance R_p in parallel to a constant phase element (CPE). The CPE provides a good description of the behavior of solid-liquid interfaces [29]. To evaluate all values of the equivalent circuit the simplex algorithm was used [30]. The fitting with the equivalent circuit leads to a set of parameters, namely R_p , R_s , Y_0 and α . The value of α is between 0 and 1 in which the limit of 0 equals a normal resistance and the limit of 1 equals a normal capacitor. With these values it is possible to calculate the capacitance of the double layer employing the following equation 5. The results of the calculation are given in Table 2.

$$C = \frac{(Y_0 * R_p)^{\frac{1}{\alpha}}}{R_p} \quad (5)$$

A comparison of the capacitances calculated by the two methods (DCM and EIS) shows, that the capacitance values determined by EIS are generally larger as the ones obtained by DCM. But, the trend for the different MnO_x phases is the

Fig. 4: Nyquist plots of different manganese oxide phases measured in EC1 at potentials of 1.10 V, 1.25 V and 1.40 V vs. RHE. Again, in red the MnO phase and in blue the MnO_2 phases. The used equivalent circuit is shown as an inset.

Tab. 2: Calculated capacitances from the impedance spectroscopy measurements of the different MnO_x phases at the three different potentials, determined before (EC1) and after (EC3) the activity measurement.

	C (μF)		C (μF)		C (μF)	
	1.10 V vs. RHE		1.25 V vs. RHE		1.40 V vs. RHE	
	EC1	EC3	EC1	EC3	EC1	EC3
ITO/Au/MnO	260	497	214	313	160	157
ITO/Au/MnO ₂	672	664	520	446	352	296

same for both methods. MnO shows lower capacitance values while MnO₂ phases possesses larger ones.

The potential dependence of the capacitances at the three potentials can be explained by two phenomena. First, the rearrangement of the water dipoles in an electric field. At the potential of zero charge the water dipoles are evenly distributed [31]. After the application of a voltage the dipoles rearrange, which results in a change of the electric field. This leads to a dielectric saturation which decreases the capacitance value. The second effect is material dependent and is called pseudo capacitance. It describes that between solid and liquid charge exchange processes occur, which are similar to processes in batteries. These processes could be adsorption and desorption of excess charge carriers which screen the electrode surface and increase the DLC [31]. All these effects illustrate the complexity and difficulties in the determination of the Helmholtz DLC.

The determination of the Helmholtz DLC is most often used to calculate the ECSA. With the normalization of the measured activity and efficiency to an area it is possible to compare the catalysts to each other. For the calculation of the ECSA equation 1 is used. Therefore, the measured capacitance value is divided by a specific capacitance value C_S from literature. For C_S different values in a range of 20 μF/cm²–80 μF/cm² are reported, most often a value of 40 μF/cm² is used [8, 15, 16]. Using this value the ECSA for the DCM of the EC1 values are calculated. It results for the MnO phase in an area of 4.2 cm² while for the MnO₂ phase an area of 6.4 cm² is calculated.

Another option to obtain the surface area of the catalyst is to employ an atomic force microscope (AFM) measurement [32, 33]. Representative areas of the ITO/Au/MnO_x samples with a size of 4 μm² each were measured to determine the roughness of each sample. The 2D projections of these data are presented in Figure 5. The roughness and the surface area enlargement are determined and listed in Table 3. The difference between the geometrically flat surface and the real surface area of the catalyst layer differs by values of 37% or less. The values where calculated with the WSxM software [34]. Nevertheless the estimation of the

Fig. 5: AFM images of a pure ITO/Au surface and of the samples with MnO and MnO₂ on ITO/Au.

Tab. 3: Roughness and total surface area values for a pure ITO/Au sample and for MnO and MnO₂ on ITO/Au.

	ITO/Au	ITO/Au/MnO	ITO/Au/MnO ₂
Roughness R_a (nm)	3.27 ± 0.36	4.19 ± 0.31	9.27 ± 0.31
Surface area (cm ²)	1.012 ± 0.02	1.026 ± 0.02	1.250 ± 0.08

The total surface area is calculated with respect to the geometrically corrected surface area of 1 cm². The standard deviation was calculated from at least three different spots on two different samples.

surface area with AFM has also some issues. Due to tip size and surface structure the area of vertical nano-crevices are not considered. This leads to a smoothening of the surface and with that to an underestimation of the real surface area [35].

The comparison of the results of the DLC measurement and the AFM measurements show a high deviation. The area determination with the DLC method leads to 4–6 times higher value than the values measured with AFM. This deviation could be reduced with the choice of another C_s value, for example 80 $\mu\text{F}/\text{cm}^2$. The calculated ECSA for this value is 2.1 cm² for MnO and 3.2 cm² for MnO₂. All measured and calculated values for the surface area and ECSA are summarized in Table 4.

This illustrates the problem of the determination of the ECSA with the DLC. There is no standardization for the determination and application of the specific capacitance C_s . The C_s value should be an experimentally determined

Tab. 4: Overview of the measured and calculated surface areas for the two different MnOx phases. The ECSA was calculated once with a specific capacitance value of 40 μF and with 80 μF .

Surface area	AFM	ECSA ($C_s = 40 \mu\text{F}$)	ECSA ($C_s = 80 \mu\text{F}$)
MnO	$1.026 \pm 0.02 \text{ cm}^2$	$4.2 \pm 0.63 \text{ cm}^2$	$2.1 \pm 0.31 \text{ cm}^2$
MnO ₂	$1.205 \pm 0.02 \text{ cm}^2$	$6.4 \pm 0.63 \text{ cm}^2$	$3.2 \pm 0.31 \text{ cm}^2$

capacitance value of a flat catalyst surface and therefore, it has the same measurement problems as every other capacitance value. Many different factors influence the accuracy of this method. First of all, it depends on external factors such as the pH value and the used potential [36, 37]. This is also visible by the manganese oxide catalyst. At potentials of 1.25 V and 1.40 V vs. RHE the capacitance values for MnO_2 show a deviation of 50%. The definition of a benchmark potential is one of the main problems in determining a specific capacitance value for all transition metal oxides. For manganese oxide a redox reaction around 1.10 V vs. RHE takes place, requiring the determination of the capacitance value at higher potentials. Other metal oxides show chemical reactions in alkaline media at other potentials, e.g. nickel with its oxidation and reduction wave in a potential range around 1.10 V–1.45 V vs. Ag/AgCl [38]. Even for these two materials it is hard to find a benchmark potential without a faradaic reaction. Therefore, it seems to be impossible to have one value for the whole range of transition metal oxides. In addition, the material itself influences the capacitance value, for instance due to pseudo capacitances or other surface reactions. For the example of manganese oxide this effect is also visible. For MnO_2 the possibility of charge storage on the surface is known and could explain the differences in the capacitance values between MnO and MnO_2 [39].

The multitude of different C_S values shows, that the aim to find a standard value for multiple material classes or even for transition metal oxides is not possible. McCrory et al. summarized, that the calculation of the ECSA has an inaccuracy of nearly one order of magnitude [8]. But in the end, it is desirable to compare the results. The goal is now to overcome the standardization problem. For normalization of, for example the activity, a single C_S value is needed. For the chosen C_S value three parameters have to be kept constant during the measurement, the pH value, the potential and the material composition.

In this paper the DLC values for MnO and MnO_2 in 0.1 M KOH were determined. With the surface area information from AFM measurement being used for ECSA it is possible to calculate the specific capacitance value using equation (1). The resulting specific capacitance values are listed in Table 5. The specific capacitance values for MnO are quite equal for the two different measurement techniques. The MnO_2 phase shows higher specific capacitance values for the EIS than for the DCM. The different values could result out of differences in the measurement technique. With these values normalization of other MnO or MnO_2 catalyst is possible and with that a comparison between these.

Nevertheless, the determination of the DLC itself and the determination of the geometric surface area are quite difficult. The problems in the determination of the DLC are discussed before and can be overcome with a standardization of the measurement protocol. For the determination of the geometric surface area a

Tab. 5: Normalized capacitance values for the EC1 for DCM and EIS at a potential of 1.25 V vs. RHE and 1.40 V vs. RHE.

Specific capacitances	ΔC_s ($\mu\text{F}/\text{cm}^2$) differential capacitance		C_s ($\mu\text{F}/\text{cm}^2$) impedance spectroscopy	
	1.25 V vs. RHE	1.40 V vs. RHE	1.25 V vs. RHE	1.40 V vs. RHE
Potential				
ITO/Au/MnO	203	168	214	160
ITO/Au/MnO ₂	386	257	520	352

lot of techniques are used and all of them have their own issues. BET (Brunauer-Emmett-Teller) method for example use the adsorption of a gas on the surface to calculate the area, but this is only possible with high surface areas, mostly powders or porous structures. Due to the different size of the used adsorbents the accessibility of the surface is different and with that the geometric surface area [36]. AFM measurements have a quite similar problem. With this method it is only possible to measure quiet flat structures without pores because of the limits of resolution [32]. Trasatti et al. and Wei et al. discuss in their paper further surface area determination techniques for catalysts and their limits [32, 36]. However, the here reported values could improve the calculation of the ECSA due to its material dependence and potential specific determination. The best approach seems to be to combine the preparation of a mostly flat surface and systematic electrochemical active area determination to obtain a good reference value. Especially for highly porous surfaces the correct determination of ECSA values is of great importance to obtain a valid comparison of the catalytic activities between different materials, which could be influenced by specific activity, conductivity and active surface area.

4 Conclusion

In this paper the ECSA is calculated with DCM as well as with EIS. Moreover, the catalyst surface area is determined with AFM measurement. Whereas the values obtained by DCM and EIS show a similar trend, the resulting areas of the ECSA calculated from these measurements employing C_s values from the literature show a large deviation to the areas obtained by AFM. Comparable ECSA values could only be reached if potential and pH values are the same for the measured capacitance and the specific capacitance. To find a benchmark potential is not easy due to the difference in redox potentials of the different transition metal oxides. However, even then the catalyst itself could have a pseudo capacitance. At the end,

a comparison of different catalysts is only possible with normalization to material depending C_s values measured at the same potential and at the same pH value.

The specific capacitance of different manganese oxides was calculated from differential capacitance measurements and from impedance spectroscopy. The AFM measurements show that the catalysts have a flat surface. With this the specific capacitance for MnO ($168 \mu\text{F}/\text{cm}^2$) and MnO₂ ($257 \mu\text{F}/\text{cm}^2$) in 0.1 M KOH with a deviation of $\pm 25 \mu\text{F}/\text{cm}^2$ are calculated. We propose our approach in combining reference experiments with mostly flat electrodes in combination with the determination of active areas by electrochemical methods to reduce the uncertainty in catalyst benchmarking studies.

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