*Int. J. Electrochem. Sci.*, 4 (**2009**) 1 - 8

**International Journal of**
**ELECTROCHEMICAL**
**SCIENCE**
www.electrochemsci.org

# An Electrochemical Cell Configuration Incorporating an Ion Conducting Membrane Separator between Reference and Working Electrode

*K.J.J. Mayrhofer*[*], *Sean J. Ashton, J. Kreuzer and M. Arenz*

Institut für Physikalische Chemie, Technische Universität München, Garching D-85748
[*]E-mail: karl.mayrhofer@mytum.de

*Received:* 8 August 2008 / *Accepted:* 18 November 2008 / *Published:* 20 December 2008

---

Ionic impurities can significantly interfere with certain electrochemical measurements and should therefore be completely avoided. However, standard reference electrodes such as the widely used Saturated Calomel Electrode (SCE) and the Ag/AgCl electrode contain saturated chloride solutions. Typically, this chloride solution is only separated from the electrochemical cell electrolyte by a porous glass frit, which still allows chlorides to diffuse through and contaminate the electrochemical system. In order to avoid this undesired effect, a new electrochemical cell setup is presented here. The modification incorporates an ion conducting membrane that serves to further separate chloride containing reference electrodes from the electrochemical cell, and thereby actively prevents the diffusion of chlorides to the surface of the working electrode. The benefits of this modification, in particular for long-term electrochemical measurements in which the electrodes are positioned closely, is demonstrated by means of the investigation of the oxygen reduction reaction (ORR) on polycrystalline Pt in both a single- and three-compartment electrochemical cell.

---

**Keywords:** electrocatalysis, reference electrodes, chloride contamination, long-term measurements, Tschurl modification

## 1. INTRODUCTION

Techniques involving electrochemical cells have a long standing tradition in the study of the thermodynamic and kinetic behavior of half cell reactions, and are currently widely used in electrocatalysis, corrosion and sensor research [1, 2]. Depending on the application, various cell designs and experimental assemblies are employed [3]. For electrochemical investigations setups with three electrodes are preferred over those involving two electrodes due to the reduction in uncompensated resistance [4, 5]. Moreover, the electrodes can either be situated in one single electrochemical cell compartment, or in several, separate electrode compartments connected via electrolytic bridges. The latter configuration has the advantage that interaction between reactions at each of the electrodes is avoided, which is crucial for studies that are prone to impurities [6].

In a three-electrode, three-compartment cell the counter electrode is shielded to prevent excessive diffusion of gaseous products into the working electrode compartment. If no undesirable products are produced at the counter electrode, a simple microporous frit is sufficient for this purpose. The effective separation of the reference electrode, on the other hand, can be decisive for the quality and accuracy of electrochemical measurements; in particular for reference electrodes, which contain ions that can influence certain reactions at the working electrode. The most convenient and therefore most widely used reference electrodes, namely the Saturated Calomel Electrode (SCE) or the Ag/AgCl electrode, are embedded into saturated KCl solution in order to maintain their highly constant reference potential [7]. These electrodes are normally contacted to the electrolyte via a porous frit that serves as a salt bridge. The large chloride concentration gradient across the porous frit, however, leads to the diffusion of chloride ions into the electrochemical cell electrolyte, which can severely impact adsorption and reaction kinetics at the surface of the working electrode [8, 9]. These gradual changes in chloride concentration are in general hard to detect and can often be overlooked during the course of an electrochemical measurement. Consequently, experimental data can easily be misinterpreted, and electrocatalytic activities can be erroneous.

In order to avoid contamination from chlorides, we have modified the setup of our three-compartment cell by introducing an ion conducting membrane (Nafion®) in order to prevent the chlorides in the reference electrode from diffusing to the working electrode. Nafion® consists of a polytetrafluoroethylene skeletal structure with sulfate groups located at the end of protruding side chains. The latter structure introduces partial hydrophilic character to the otherwise hydrophobic polymer backbone. Consequently solvation shells form around the sulfate groups inside the membrane and water molecules can be absorbed. Accordingly, channels allowing the diffusion of water and small positive ions such as $H^+$ or $Na^+$ are established inside the membrane. Negative ions are however, repelled by the negative charge of the sulfate groups and ideally cannot enter these channels and diffuse through the membrane [10]. In this study we present the application of the new setup for the measurement of oxygen reduction on platinum, a reaction that is particularly sensitive to chloride impurities [8, 11].

## 2. EXPERIMENTAL PART

The electrochemical measurements were conducted in either a Teflon [12, 13] or a standard glass three-compartment electrochemical cell, using a rotating-disc electrode (RDE) setup, potentiostat (*Princeton Applied Research*) and rotation controller (*Radiometer Analytical*). A saturated calomel reference electrode (SCE, *Schott*), Pt mesh counter electrode and a polycrystalline bulk Platinum sample (5 mm diameter, 0.196 $cm^2$ geometrical surface area) working electrode were used in each measurement of this study. The electrolytes were prepared using Millipore® water and suprapure

$HClO_4$ (*Merck*). The polycrystalline sample was cleaned with concentrated perchloric acid for approximately 5 minutes and then rinsed thoroughly with Milipore® water prior to each experiment. For the oxygen reduction reaction (ORR), cyclovoltammograms in argon and the hydrogen evolution/oxidation reaction (HER/HOR), the electrolyte was purged and saturated with the respective gases (*Air Liquide*). The exact potential of the SCE versus the reversible hydrogen electrode (RHE) was measured shortly after each ORR measurement. All measurements were conducted at room temperature.

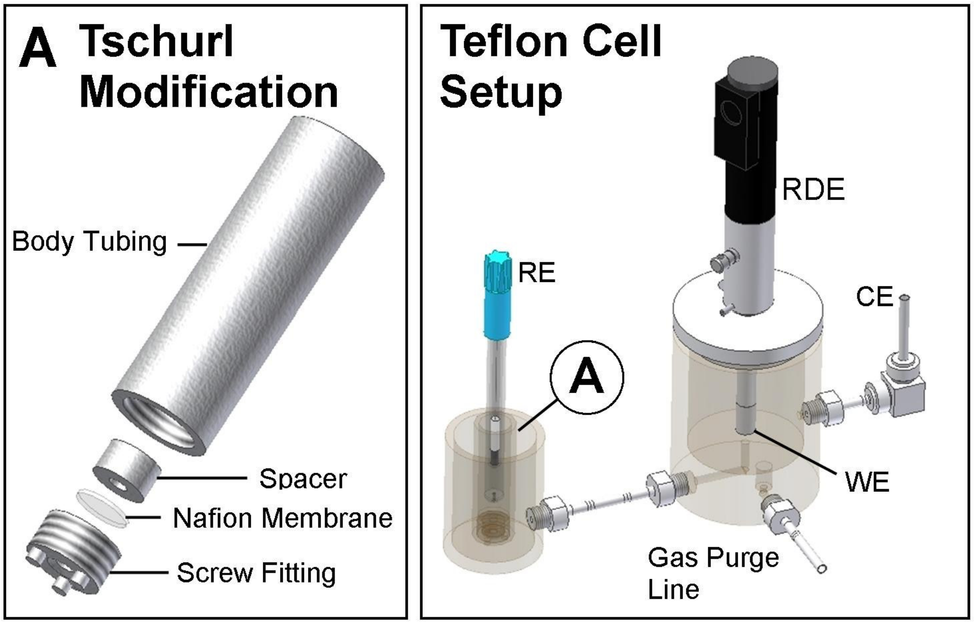

**Figure 1.** Teflon Cell setup and magnification of the modified reference electrode side compartment (A) applied in this study. WE = working electrode; RE = reference electrode; CE = counter electrode.

Figure 1 shows a schematic of the Teflon cell and the modified reference electrode side compartment. The working electrode (WE) is located at the tip of the rotating disc electrode assembly (RDE), and is submerged in the electrolyte of the main compartment. The counter electrode (CE) is connected to the main compartment by a small hole in the side wall. The incoming gases meanwhile are purged through a porous Teflon plug into the electrolyte of the main compartment. The reference electrode (RE) is simply free-standing inside the 'Tschurl Modification' (A) in the RE compartment. The Haber-Luggin capillary, which connects the RE compartment with the main compartment and ends close to the surface of the working electrode, is necessary for precise potential control and the avoidance of any uncompensated resistance in the measurements. The 'Tschurl Modification' itself (A) consists of a Teflon body-tubing and screw fitting with a hole in the base. The ion conducting membrane (*Nafion*®) is pressed tightly, with the aid of a Teflon spacer, to the bottom of the screw fitting in order to prevent the leakage of electrolyte and efficiently separate the electrolyte in the 'Tschurl Modification' from the electrolyte in the reference electrode compartment. The three feet at the base ensure that diffusion to the membrane is not physically blocked at any time.

## 3. RESULTS AND DISCUSSION

In order to evaluate the impact of chlorides on the ORR on polycrystalline Pt, KCl was added to the oxygen purged electrolyte in concentrations ranging from $10^{-7}$ mol $L^{-1}$ to $2x10^{-5}$ mol $L^{-1}$. The polarization curves closely resemble previously published curves of the ORR [6, 14], upon which the effect of chlorides on several Pt systems has been described previously [6, 8, 11]. For the quantitative analysis of the ORR activity in this study, the cyclovoltammograms (CVs) are corrected for the non-faradaic background by subtracting the CVs recorded in Ar-purged electrolyte. No correction for the uncompensated resistance is applied. Since the kinetic region of the ORR may shift by up to 200 mV towards more negative potentials in the course of an experiment due to the impact of chlorides, a comparison of kinetic currents at a certain, fixed potential is unfeasible [ 14]. Therefore the apparent activity for the ORR is specified by the potential at half of the diffusion limited current (ORR half-wave potential) of the anodic potential scan at 1600 rpm throughout this study. The dependence of the ORR half-wave potentials on the chloride concentration is depicted in Figure 2.

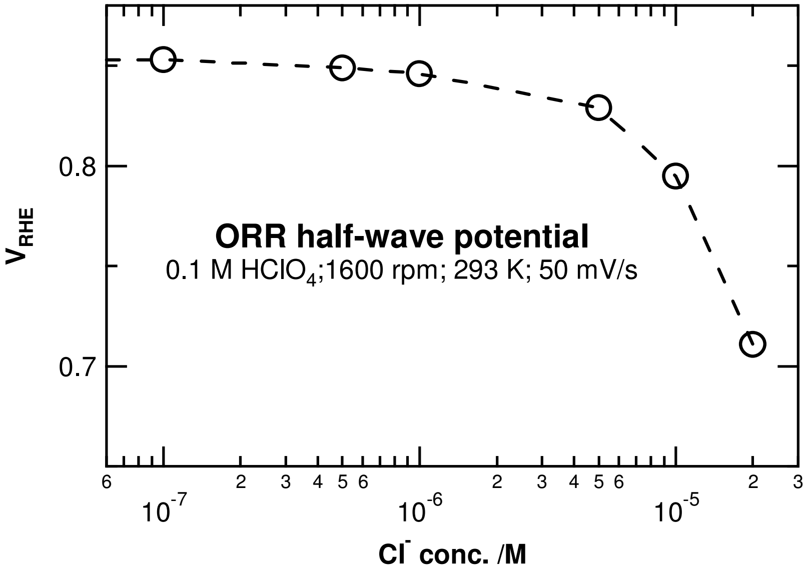

**Figure 2.** Impact of Chlorides on the ORR on polycrystalline Pt in 0.1 mol $L^{-1}$ $HClO_4$ electrolyte (Teflon cell).

At a chloride concentration of $10^{-7}$ mol $L^{-1}$ the ORR activity on polycrystalline Pt deviates only by 1 mV from the half-wave potential in a chloride-free electrolyte (855 mV), which is within the experimental error of the measurement. Above a concentration of $5x10^{-7}$ mol $L^{-1}$, however, the decrease in the activity (6 mV shift in the ORR half-wave potential) becomes more significant. This would already be equivalent to a loss in kinetic current density of approximately 15%. With increasing chloride concentration the ORR curves shift further negative, at $2x10^{-5}$ mol $L^{-1}$ (highest concentration used in this study) the half-wave potential is as low as 711 mV, a decrease of 144 mV. This clearly demonstrates that in order to determine the precise electrocatalytic activities of ORR catalysts, even minor contamination by chlorides must be avoided.

### *3.1 Reference electrode – side compartment*

In order to relate these findings to practical measurements, the influence of the Saturated Calomel Electrode (SCE) on the ORR measurement was investigated using a number of experimental configurations. The results obtained from long-term measurements in a standard glass cell and a Teflon cell with and without the use of our modified reference electrode side compartment are presented in Figure 3.

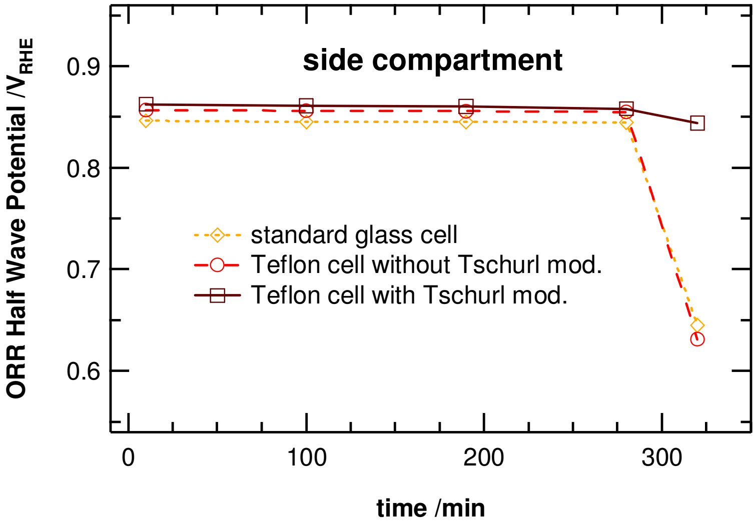

**Figure 3.** Long-term stability of the measurement of the ORR on polycrystalline Pt in 0.1 mol $L^{-1}$ $HClO_4$ electrolyte in a standard glass and a Teflon electrochemical cell setup. The SCE was placed in the side compartment in all cases. After 290 minutes, convection of electrolyte from the side compartment to the main compartment was enforced in both the glass cell (orange), and the Teflon cell with (brown) and without (red) the modified reference electrode side compartment.

The SCE was placed in the RE compartment of the three electrode setup described in Figure 1. The activity for the ORR did not change over 290 min, within the experimental error of 2 mV. This indicates that measurements can be conducted over a period of 5 hours and the system remains free of contaminations. A slightly reduced activity is observed for each measurement in the glass cell; however, this is attributed to a slightly different cell geometry and the resulting difference in the uncompensated resistance in comparison to the Teflon cell. In the standard glass cell diffusion of chlorides from the reference electrode side compartment to the main compartment is additionally inhibited by a stop-cock, and a very thin Luggin capillary. In the Teflon cell the distance from the reference compartment to the main compartment also seems to be sufficient, so that in this time period chlorides do not diffuse to the working electrode surface. This limited effect of chlorides can be attributed to the deliberate design of the three-compartment cells. Therefore, in this cell geometry the modified reference electrode side compartment does not enhance the stability of ORR measurements to any significant degree.

If, however, convection of the electrolyte from the side compartment to the main compartment occurs, as it is often the case in the course of an electrocatalytic measurement, then the apparent activity for the ORR reduces drastically. This can be seen in Figure 3, where after the initial 5 hours of measurement we forced convection between the different compartments. Evidently, chlorides had continuously diffused through the porous frit of the reference electrode and accumulated in the reference side compartment of the glass and the Teflon cell. When the chloride containing electrolyte in the side compartment is mixed with the electrolyte in the main compartment, these chlorides can diffuse to the surface of the working electrode. At potentials above 0.5 $V_{RHE}$ they adsorb strongly onto the Pt surface and as a consequence block active sites for the ORR. The effect is almost identical in the glass cell and the Teflon cell without modified reference electrode side compartment, suggesting that in both cases an equal amount of chlorides had diffused from the reference electrode into the cell electrolyte. According to the decrease in activity observed in Figure 2, the concentration is estimated to be greater than $2x10^{-5}$ mol $L^{-1}$. If the reference electrode is placed inside the modified reference electrode side compartment, however, the diffusion of chlorides into the electrolyte can be reduced significantly. After forced convection the activity drops only by 14 mV, which infers a final chloride concentration of approximately $2x10^{-6}$ mol $L^{-1}$ that can be ascribed to the minor co-ion diffusion through the Nafion membrane [15].

### *3.2 Reference electrode – main compartment*

In simple, commercially available electrochemical cells the reference electrode is often placed inside the main compartment, and not in a separate side compartment. The influence of the 'Tschurl Modification' in such a setup was therefore additionally studied.

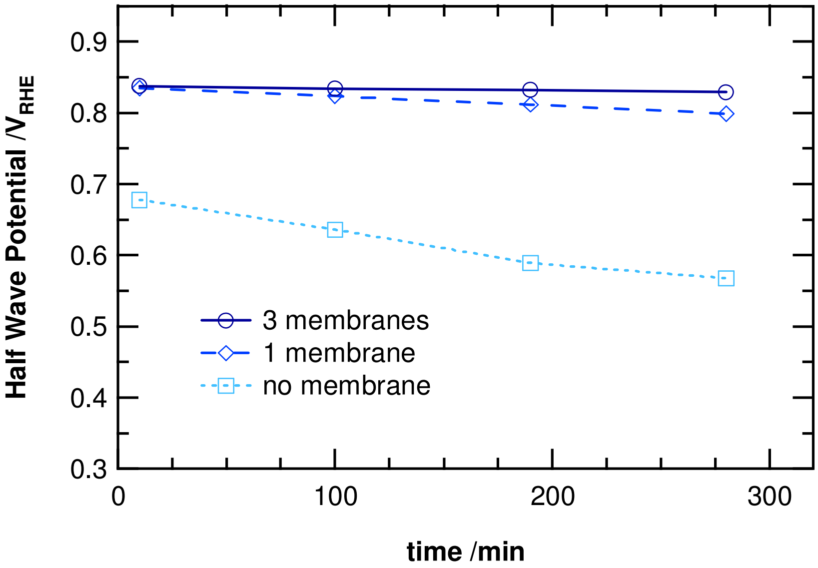

**Figure 4.** Long-term stability of the measurement of the ORR on polycrystalline Pt in 0.1 mol $L^{-1}$ $HClO_4$ electrolyte in a Teflon Cell with the Calomel reference electrode placed in the main compartment.

Figure 4 clearly demonstrates the serious effect of chloride contamination of the electrolyte on the ORR activity, when no modified reference electrode side compartment is used. During the first ORR measurement, after only approximately 10 minutes the half-wave potential had already shifted negatively by about 150 mV, despite thoroughly rinsing of the reference electrode with Millipore water beforehand. Note that part of this lower initial activity observed in Figure 3 compared to Figure 2, is due to the difference in uncompensated resistance. Over the course of the experiment chlorides continuously diffuse through the porous frit, a process observed in the corresponding decrease in ORR activity. If, however, the reference electrode is placed into the 'Tschurl Modification' with only one Nafion membrane, no chloride contamination is initially evident and the deterioration in the ORR activity over time is significantly reduced. A superior chloride diffusion inhibiting effect can be achieved by employing 3 membranes in the reference electrode compartment. In this case the ORR activity remains almost unaltered after 290 minutes, with a negative shift of the half-wave potential of only 10 mV. However, it is clear that the Nafion membranes do not completely prevent the diffusion of chlorides into the cell electrolyte. There is the possibility that other types of ion conducting membranes with different polymer chain length, equivalent weight and thickness can be used in order to optimize the reference electrode compartment [10].

Chlorides can significantly interfere with electrochemical measurements; even at concentrations as low as $10^{-7}$ mol $L^{-1}$ already decisive deviations in activity occur for the ORR on Pt. Standard reference electrodes such as the SCE or the Ag/AgCl electrode, which include saturated solutions of chlorides, can consequently act as a possible source of systematic errors. In order to avoid this chloride contamination, a newly developed reference electrode compartment is presented. An ion conducting membrane separates the electrolyte surrounding the reference electrode from the working electrode compartment, and thereby inhibits the diffusion of chlorides toward the electrolyte in the main compartment. Additional investigation is, however, necessary in order to optimize the membrane to further inhibit chloride diffusion, in particular for enabling long-term experiments for reactions that are sensitive to chloride impurities.

## 4. CONCLUSIONS

Chlorides can significantly interfere with electrochemical measurements; even at concentrations as low as 10-7 mol L-1 already decisive deviations in activity occur for the ORR on Pt. Standard reference electrodes such as the SCE or the Ag/AgCl electrode, which include saturated solutions of chlorides, can consequently act as a possible source of systematic errors. In order to avoid this chloride contamination, a newly developed reference electrode compartment is presented. An ion conducting membrane separates the electrolyte surrounding the reference electrode from the working electrode compartment, and thereby inhibits the diffusion of chlorides toward the electrolyte in the main compartment. Additional investigation is, however, necessary in order to optimize the membrane to further inhibit chloride diffusion, in particular for enabling long-term experiments for reactions that are sensitive to chloride impurities.

ACKNOWLEDGEMENTS

This work was supported by the DFG through the Emmy-Noether project ARE852/1-1. Karl J.J. Mayrhofer thanks the Austrian FWF, which supports him with an Erwin-Schrödinger Scholarship. Furthermore we would like to thank the machine shop at the TU Munich for producing the Teflon cell and the Tschurl modification. We thank M. Tschurl for fruitful discussions.

## References

1. A. J. Bard, L. R. Faulkner, *Electrochemical Methods*. John Wiley & Sons, Inc.: 2000.
2. W. Vielstich, C. H. Hamann, *Elektrochemie*. 4 ed.; Wiley-VCH: 2005; p 672.
3. R. E. White, *Electrochemical Cell Design*. Springer: 1984; p 400.
4. J. C. Myland, K. B. Oldham, *Analalytical Chemistry,* 72 (17)(2000) 3972.
5. W. Oelssner, F. Berthold, U. Guth, *Materials and Corrosion-Werkstoffe Und Korrosion* 57 (6) (2006) 455.
6. N. M. Markovic, P. N. Ross, *Surface Science Reports* 45 (4-6) (2002) 117.
7. D. J. G. Ives, G. J. Janz, *Reference Electrodes, Theory and Practice.* Academic Press: 1961; p 651.
8. V. Stamenkovic, N. M. Markovic, P. N. Ross, *Journal of Electroanalytical Chemistry***,** 500 (1-2) (2001) 44.
9. Z. Xinsheng, S. Gongquan, J. Luhua, C. Weimin, T. Shuihua, Z. Bing, X. Qin, *Electrochemical and Solid-State Letters,* 8 (3) (2005) A149.
10. N. P. Berezina, N. A. Kononenko, O.A. Dyomina, N. P. Gnusin, *Advances in Colloid and Interface Science,* 139 (1-2) (2008) 3.
11. T. J. Schmidt, U. A. Paulus, H. A. Gasteiger, R. J. Behm, *Journal of Electroanalytical Chemistry,* 508 (1-2) (2001) 41.
12. K. J. J. Mayrhofer, G. K. H. Wiberg, M. Arenz, *Journal of The Electrochemical Society* 155, (1) (2008) P1.
13. K. J. J. Mayrhofer, A. S. Crampton, G. K. H. Wiberg, M. Arenz, *Journal of The Electrochemical Society,* 155 (6) (2008) P78.
14. K. J. J. Mayrhofer, D. Strmcnik, B. B. Blizanac, V. Stamenkovic, M. Arenz, N. M. Markovic, *Electrochimica Acta,* 53 (2008) 3181.
15. A. Herrera, H. L. Yeager, *Journal of The Electrochemical Society,* 134, (10) (1987) 2446.