



Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Measurement of competition between oxygen evolution and chlorine evolution using rotating ring-disk electrode voltammetry

J.G. Vos, M.T.M. Koper*

Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

ARTICLE INFO

Keywords:

Chlorine evolution
Oxygen evolution
Electrocatalysis
Selectivity
Iridium oxide
Rotating ring-disk electrode

ABSTRACT

Selectivity between chlorine evolution and oxygen evolution in aqueous media is a phenomenon of central importance in the chlor-alkali process, water treatment, and saline water splitting, which is an emerging technology for sustainable energy conversion. An apparent scaling between oxygen vs. chlorine evolution has been established, making it challenging to carry the two reactions out individually with 100% faradaic efficiency. To aid selectivity determination, we developed a new method to quickly measure chlorine evolution rates using a conventional RRDE setup. We showed that a Pt ring fixed at 0.95 V vs. RHE in pH 0.88 can selectively reduce the Cl_2 formed on the disk and this allows precise and flexible data acquisition. Using this method, we demonstrate that oxygen evolution and chlorine evolution on a glassy carbon supported IrO_x catalyst proceed independently, and that the selectivity towards chlorine evolution (ϵ_{CER}) rapidly approaches 100% as $[\text{Cl}^-]$ increases from 0 to 100 mM. Our results suggest that on IrO_x , oxygen evolution is not suppressed or influenced by the presence of Cl^- or by the chlorine evolution reaction taking place simultaneously on the surface.

1. Introduction

The electrochemical oxidation of chloride ions is a reaction of great importance to the chemical industry. The electrolysis of brine for the joint generation of Cl_2 and concentrated NaOH, known as the chlor-alkali process, is the most straightforward example [1–3]. This process underpins approximately 50% of the global chemical industry [4], and consumed approximately 334 PJ of electrical energy in the U.S. in 2006 [5]. Another chloride-affected process, which is expected to play a major role in the future energy infrastructure [6–9], is the (photo) electrochemical splitting of water. The latter relies on the endergonic conversion of H_2O into H_2 and O_2 , and is typically studied in electrolytes which are $[\text{Cl}^-]$ -free. From an industrial perspective however, it would be a great advantage to perform selective electrolysis of saline water, not just for water splitting but also for metal plating, for which OER is usually the desired counter reaction [10,11]. Without a selective anode, there is a risk of forming large amounts of toxic and corrosive Cl_2 gas as byproduct. Lastly, the oxidation of chloride into strongly oxidizing ‘active chlorine’ may be used to eliminate pollutants in electrochemical wastewater treatment [12,13], but its formation has to be tightly controlled or is sometimes unwanted [14,15].

In brine solutions, the selectivity between the oxygen evolution reaction (OER) and chlorine evolution reaction (CER) is of central importance. In the chlor-alkali process, the OER is a parasitic side reaction

that degrades process efficiency and electrode stability [2], whereas it is the desired reaction in saline water electrolysis for hydrogen production. Virtually all known OER catalysts also catalyze formation of chlorine [16–18], indicating that the OER and CER are intimately coupled. This interdependence makes it challenging to carry them out individually with 100% faradaic efficiency.

Both OER and CER have been the subject of intense study over the past five decades, with significant improvements in catalyst performance for both reactions [1]. Today, TiO_2 -supported mixtures of RuO_2 , IrO_2 and varying metal dopants (Dimensionally Stable Anodes) represent the state of the art materials for industrial water splitting and the chlor-alkali process. Previous work on the CER in aqueous media has generally been done in acidic solutions with very high Cl^- concentrations, often in the range of 3–5 M [19–25]. CER activity and Tafel slopes in such studies were derived from raw electrode current densities, with the assumption that all observed current could be ascribed to CER and that OER plays only a negligible role. Although this assumption is reasonable for high Cl^- concentrations, a complete picture of the competition between OER and CER behavior in chloride-containing media cannot be drawn in this way. If we want to develop anodes selective for OER from (acidic) brine solutions, we will need to understand this competition in more detail, and a reliable and easy method for the determination of the selectivity between OER and CER would be of great interest.

* Corresponding author.

E-mail address: m.koper@chem.leidenuniv.nl (M.T.M. Koper).<http://dx.doi.org/10.1016/j.jelechem.2017.10.058>Received 28 July 2017; Received in revised form 23 October 2017; Accepted 25 October 2017
1572-6657/ © 2017 Elsevier B.V. All rights reserved.

An analytical method to measure Cl_2 and O_2 evolution separately, irrespective of chloride concentration, is Differential Electrochemical Mass Spectrometry (DEMS) [26–30], which directly probes O_2 vs. Cl_2 formation near the electrode surface and can provide highly accurate and quantitative results online [31–33]. However, DEMS suffers from some inflexibility due to specific cell and electrode requirements, and relatively slow response times. Alternatively, a common method of selectivity determination is long-term bulk electrolysis, followed by titration of the working solution using diethyl-phenylenediamine salts (DPD) or iodometry, to determine the amount of Cl_2 formed [33–36]. Such methods, although accurate, are not suitable for generation of extended data sets and do not offer the on-line selectivity determination that DEMS does.

In this paper, we develop and study the suitability of a rotating ring-disk electrode (RRDE) setup for measuring OER vs. CER selectivity in acidic chloride-containing media. The RRDE method has been well established for faradaic efficiency (FE) measurements in benchmarking OER catalysts [37–39], and for the detection of the formation of H_2O_2 during the oxygen reduction reaction (ORR) on model PEM fuel cell cathodes [40–42]. To the best of our knowledge, an RRDE approach for OER vs. CER selectivity measurements has not been previously reported. We used a Pt ring for Cl_2 detection during catalyst operation, as Pt was previously established as an effective CRR catalyst [43]. Other materials (such as Ru or Ir) may also be possible for Cl_2 detection [44], but we have not pursued this in detail. As proof of concept, we explore the CER vs. OER behavior of IrO_x nanoparticles, as this material constitutes a stable and active acidic OER and CER catalyst.

2. Experimental

KHSO_4 (EMSURE), KCl (EMSURE), and HClO_4 (60%, EMSURE) were purchased from Merck. Na_2IrCl_6 (99.9%, trace metals basis) and NaOH (30% solution, TraceSelect) were purchased from Sigma-Aldrich. All chemicals were used as received. The water used for cleaning glassware and preparing solutions was filtered and deionized using a Merck Millipore Milli-Q system (resistivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$, $\text{TOC} < 5 \text{ p.p.b.}$). Experiments were done in a home-made two-compartment borosilicate glass cell of 100 mL volume. IrO_x deposition experiments were done in a borosilicate glass vial of approximately 5 mL. Before the first-time use, all glassware was thoroughly made free from organic contaminants by boiling in a 3:1 mixture of concentrated H_2SO_4 and HNO_3 . When not in use, all glassware was stored in a 1 g/L solution of KMnO_4 in 0.5 M H_2SO_4 . Before each experiment, glassware was thoroughly rinsed with water, and then submerged in a dilute solution of H_2SO_4 and H_2O_2 to remove all traces of KMnO_4 and MnO_2 . The glassware was then rinsed three times with water, followed by triple boiling in Millipore water.

All experiments were carried out at room temperature ($\sim 20^\circ\text{C}$). Hydrodynamic measurements were performed using an MSR rotator coupled to E6 ChangeDisk RRDE tips in a PEEK shroud (Pine Research Instrumentation). As counter electrode, a Pt mesh separated from the main solution by a glass frit was used. The reference electrode was a HydroFlex® reversible hydrogen electrode (Gaskatel). All potentials in this paper are reported using the RHE scale. Using a Luggin capillary, the RHE reference was aligned to the center of the RRDE tip to minimize electrical cross-talk [45,46]. The liquid phase collection factor of the ring-disk system, N_r , was determined to be 0.245 in at least four separate experiments, where the GC disk was exchanged in between. The value was found using a conventional collection factor experiment on a freshly prepared blank GC electrode with Pt ring, studying the reduction/oxidation of 10 mM $\text{K}_3\text{Fe}[\text{CN}]_6$ in 0.1 M KNO_3 .

0.5 M KHSO_4 solutions were used for all CER activity experiments. pH values were 0.88 ± 0.05 , as measured with a Lab 855 meter equipped with a glass electrode (SI Analytics). pH values were verified by measuring the potential of a calibrated Ag/AgCl reference electrode

in the solutions. All working solutions were saturated with either O_2 or Ar (Linde, purity 6.0) before experiments. Mild gas bubbling through the solution was allowed during forced convection experiments, in all other cases gas was used to blanket the solution.

Electrochemistry experiments were controlled with an IviumStat potentiostat (Ivium Technologies). For all experiments, the solution resistance was measured with electrochemical impedance spectroscopy, by observing the absolute impedance in the high frequency domain (100 KHz). Potentials were 85% corrected for these values during measurements. Before a CER activity experiment, the Pt ring was electropolished by cyclic voltammetry (CV) from -0.1 V to 1.7 V at 500 mVs^{-1} for 30 scans at a 1500 RPM rotation rate, after which the individual scans did not change. This step is vital to remove traces of alumina, as well as traces of IrO_x that tend to remain on the ring after being swept outward during IrO_x electroflocculation under rotation [47]. OER and CER experiments were done under hydrodynamic conditions at 1500 RPM by scanning the disk electrode in the range of 1.3–1.55 V at 10 mVs^{-1} . For quantitative analysis, the forward and backward sweeps were averaged to reduce contributions from double layer charging and IrO_x pseudocapacitance. The ring was kept at 0.95 V during CER Faradaic Efficiency measurements, as 0.95 V is in the diffusion-limited regime of Cl_2 reduction but still too positive to lead to oxygen reduction (see Results and discussion). In between experiments, the IrO_x film was kept at 1.3 V. Ring currents were corrected for background currents, and also collection delay, which was approximately 200 ms at 1500 RPM. Before proceeding with OER and CER activity measurements, the IrO_x film was treated by performing 20 scans between 1.3 and 1.55 V, in absence of Cl^- . This was done to ensure stable and reproducible catalyst behavior during experiments.

IrO_x nanoparticles electroflocculated on glassy carbon were used as active OER/CER catalyst. The GC support was prepared to a mirror finish by hand polishing with Al_2O_3 down to $0.05 \mu\text{m}$ particle size, followed by rinsing and 5 min sonication in acetone and water. IrO_x deposition was done from a suspension of IrO_x nanoparticles, obtained from alkaline hydrolysis of $\text{Na}_2\text{Ir}[\text{Cl}]_6$, as previously published [48–50]. The reader may consult the Supporting information for more details.

For iodometry experiments, amperometry was performed for 60s at 1500 RPM in 16 mL of 0.5 M KHSO_4 , in the presence of Cl^- , followed by titration of the bulk solution. Under identical conditions, amperometry was performed for 20 s and the Pt ring was used to measure selectivity towards CER. This selectivity was then applied to disk currents of the iodometry experiment to calculate the amount of Cl_2 that must have formed according to the RRDE method. In this way, both methods could be applied to a single experiment. The experiments were done in a glass vial without headspace, of approximately 16 mL volume. The vial was vertically elongated to minimize the contact area of the solution with air, and thus to prevent gaseous Cl_2 from escaping the acidic solution. All solutions were pretreated by briefly evolving chlorine and then purging the solution with Ar. Immediately after finishing an experiment, a large ($\sim 100\times$) excess of NaI was rapidly added to the solution to trap all Cl_2 as I_3^- and to minimize the equilibrium concentration of volatile I_2 . The vial was then closed air-tight and the solution was allowed to equilibrate for approximately 1 min. Iodometry was performed directly after. Reported values were the average of four titrations. For the sake of verification, RRDE experiments in the iodometry vial were compared to those in a standard glass RRDE cell of 100 mL volume. Although the absolute measured currents of the iodometry vial were slightly lower than the RRDE cell, the ratio $i_{\text{r}}/i_{\text{d}}$ (the ‘apparent chlorine collection factor’, N_{Cl_2}) was found to be exactly the same, indicating proper transport of Cl_2 from the disk to the ring in the iodometry vial. This justifies the comparison of our RRDE method and iodometry. We attribute the lower CER currents in the small volume iodometric cell to distortion of the hydrodynamic flow field, leading to lowered Cl^- mass transport.

Download English Version:

<https://daneshyari.com/en/article/6661763>

Download Persian Version:

<https://daneshyari.com/article/6661763>

[Daneshyari.com](https://daneshyari.com)