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Identification of the byproducts of the oxygen evolution reaction on Rutile-type oxides under dynamic conditions

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ABSTRACT

This paper examines the detection and quantification of the potentially corrosive byproducts of the oxygen evolution reaction on iridium and iridium–ruthenium mixed oxides. A conventional but stationary ring-disc electrode was employed in a flow cell configuration for the detection of volatile reaction product other than oxygen, and the formation of at least two active species was detected. Potential-modulated UV–VIS reflectance spectroscopy helped to identify one of these volatile reaction byproducts as hydrogen peroxide, and the other is tentatively suggested to be ozone. It was found that these species are formed under potentiodynamic conditions due to the chemical recombination of the absorbed reaction intermediates. The influence of the electrode material composition on the production yield of these byproducts was studied, and we found that the generation of these corrosive reaction byproducts is suppressed the more active the catalyst is for the OER. The formation of by-products can therefore be addressed by a rational choice of the electrode materials based on the adsorption energy of the reaction intermediates as is done for the OER itself. Steady-state electrolysis minimizes hydrogen peroxide formation as byproduct of the oxygen evolution reaction.

1. Introduction

Pure hydrogen can be produced in an environment-friendly way with a low CO_2 footprint by using electricity from renewable energy sources (solar, wind, hydropower) for electrochemical water splitting [1]. However, a key characteristic of renewable energy sources is their intermittent nature, which frequently results in a fluctuating voltage being supplied to the water electrolyzer. Therefore, it becomes essential that these electrolyzers are able to accept such fluctuations in the supplied power. If water electrolysis is to be integrated as an energy storage system in the renewable energy production chain, it is crucial to understand the mode of operation of the electrolyzers under dynamic conditions and not only in the steady state [2,3].

Currently three technologies for water electrolyzers exist, classified according to the kind of electrolyte employed: alkaline, proton exchange membrane (PEM) and solid oxide electrolysis. Although alkaline water electrolysis is widely used in industry, PEM electrolyzers are an alternative that does not require any corrosive electrolyte, and PEM electrolyzers offer high efficiency, compactness, low degradation rates and easy maintenance.

Rutile-type oxides, such as RuO_2 and IrO_2, are known as excellent catalysts for the oxygen evolution reaction (OER), the anodic reaction of water electrolysis [4], in PEM electrolysis. The activity of iridium dioxide is lower than that of ruthenium dioxide; however, the former is far more stable. Mixing of IrO_2 and RuO_2 has been shown to be particularly efficient for the stabilization of the catalysts without compromising the activity of RuO_2 [5,6]. This can be explained by the tendency of ruthenium to segregate toward the bulk when placed in an IrO_2 matrix [7,8]. Therefore, depending on the synthesis conditions, the surface of the mixed oxide is enriched in iridium. With adequate iridium concentrations, ruthenium oxide kink sites, which are the most unstable toward corrosion, will be protected by iridium, thereby significantly increasing the stability of the mixed iridium–ruthenium oxide electrodes.

The OER,

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^0 = 1.229\ \text{V} \tag{1}$$

as well as its reverse, the oxygen reduction reaction (ORR), is still not completely understood, and many reaction mechanisms have

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been proposed [4,9–12]. The formation of the oxygen molecule at the electrocatalyst surface can proceed through either a mononuclear [13–16] or a binuclear [17,18] pathway.

The mononuclear mechanism was used for a computational analysis of the trends in catalytic activity for oxygen evolution by Rossmeisl et al. [14]. The mechanism assumes the formation of an O—O bond between a transition metal S—O* intermediate and a water molecule through the formation of the adsorbed hydroperoxy intermediate S—OOH:

$$H_2O \rightarrow HO^* + H^+ + e^- \quad (2)$$

$$HO^* \rightarrow O^* + H^+ + e^- \quad (3)$$

$$O^* + H_2O \rightarrow HOO^* + H^+ + e^- \quad (4)$$

$$HOO^* \rightarrow O_2 + H^+ + e^- \quad (5)$$

where * represents an active surface site, such as the coordinatively unsaturated site on top of fivefold-coordinated metal ions on the rutile (110) surface.

From the description of the mononuclear mechanism in Ref. [14] it follows that the electrocatalytic properties of the transition metal oxide can be improved by tuning the binding energy of O*, and a volcano plot describing the catalytic activity of metal oxides was derived. It was found that both IrO_2 and RuO_2 are good choices for the OER, but IrO_2 bonds O* more strongly and RuO_2 more weakly than an ideal catalyst for OER should do.

In the binuclear mechanism [19–21], the first step involves oxidation of water with the formation of S═O species. The subsequent chemical steps correspond to an internal surface redox step whereby two neighboring S—O* groups produce a μ-peroxo bridged intermediate S—O—O—S. This reaction is followed by the release of O_2.

Both reaction mechanisms thus include S—O* reaction intermediates which can recombine with water with the formation of absorbed hydroperoxy species, S—OOH.

Hydroperoxy species have been detected as intermediates in the electrochemical evolution of oxygen on gold using surface-enhanced Raman spectroscopy (SERS) [22] and in the photocatalytic oxidation of water on IrO_2 nanoclusters [23]. Hydroperoxy species can desorb from the transition metal active sites to the solution, which may result in a number of reactions. For example, the hydroperoxyl radical, HOO* is known to be unstable and to decompose readily to oxygen and hydrogen peroxide in protic media [24,25].

The formation of hydrogen peroxide is also thermodynamically possible directly through electrochemical reactions at high anodic potentials:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E^0 = 1.776V \quad (6)$$

or after direct recombination of oxygen and hydrogen due to hydrogen crossover through the membrane to the anode:

$$H_2 + O_2 \rightarrow H_2O_2 \quad (7)$$

Ando and Tanaka [26] have proposed a new system in which the products of water electrolysis are hydrogen and hydrogen peroxide, produced simultaneously in order to benefit from the higher economic value of hydrogen peroxide as compared to oxygen. However, hydrogen peroxide is a very powerful oxidizing species in acidic solutions, and it can potentially provoke the dissolution of the transition metal oxides used as electrocatalysts. Moreover, the formation of hydrogen peroxide and radicals during water electrolysis promotes the chemical degradation of the Nafion membrane, a key component of the PEM electrolyzers, leading to a significant decrease of the electrolyzer's durability [27]. Thus, the formation of hydrogen peroxide during water electrolysis is important from the perspective of electrolyzer degradation, and it becomes important to delineate favorable operating conditions and to identify a catalyst that suppresses the formation of this species.

Formation of ozone and hydrogen peroxide during the OER has been reported at synthetic boron-doped diamond thin film anodes, which operate under significant anodic overpotentials in acidic media [28].

Commercial water electrolyzers typically operate at a voltage of 1.7–2 V, and thus several of the reaction byproducts listed above may result on the anode, both under steady state and dynamic conditions, an ignorance or neglect of their impact may thus significantly decrease the electrolyzer lifetime.

The purpose of this paper is to quantify the formation of some potentially corrosive byproducts of the OER under dynamic high current conditions at the anodic catalysts for PEM water electrolysis. Since PEM technology employs composite electrodes in which the electrocatalyst is in intimate contact with the membrane material we perform our measurements for thin-layer electrodes to avoid issues of by-product diffusion and reaction within porous layers. Below we provide electrochemical and spectroscopic evidence that hydrogen peroxide and other volatile species are actually formed as a by-product of the OER in acidic media. Finally, we address the consequences of the electrocatalyst composition on the hydrogen peroxide yields during the OER.

2. Experimental

2.1. Electrode preparation

Iridium oxide powders were used as electrode materials on the disk of the ring-disc electrode in the flow-cell measurements. The powders were prepared by the hydrolysis method as described in [29], except that the catalyst was not covered by any Nafion film which renders the working electrode free of any polymer. The precursors, $H_2IrCl_6{\cdot}4H_2O$ (OMG AG&Co. KG, 99.2%) and $RuCl_3{\cdot}xH_2O$ (Sigma–Aldrich, ReagentPlus) (for the mixed iridium–ruthenium oxide) were dissolved in aqueous 0.2 M NaOH solution (J. T. Baker, Baker Analyzed). The resulting solution was stirred at 80 °C for one hour, before cooling and adjusting the pH to 8 with nitric acid (Merck, p.a.). After 30 additional minutes of stirring and heating at 80 °C, the precipitate was separated and washed by centrifuging at 5000 rpm. The precipitate was then heat-treated at 550 °C in air for 30 min. For the preparation of the thin film electrodes employed for the flow-cell experiment, the oxide catalysts prepared by the method described above were dissolved in water ($1\ mg\ mL^{-1}$) in an ultrasonic bath, and 20 μL of the resulting dispersion was pipetted onto the central gold disc (6 mm in diameter) of a PINE E6 series ring-disc electrode assembly (platinum ring).

Anodic iridium oxide film (AIROF) electrodes formed anodically on an iridium disc were prepared as described in Ref. [30], and were used for UV-potential-modulated reflectance spectroscopy (UV-PMRS) and for electrolysis of the solutions used for transmission UV–vis spectroscopy. Briefly, iridium metal electrodes were mechanically polished to a mirror finish with 5.0, 0.3 and 0.05 μm alumina, rinsed with Milli-Q water and washed four successive times in an ultrasonic bath. They were then immersed in 0.5 M H_2SO_4 and cycled 200 times between 0 and 1.5 V at $100\ mV\ s^{-1}$ in order to grow the AIROF layers. An iridium metal sheet with an electrode area of $1.5\ cm^2$ embedded in epoxy was used for the electrolysis experiments, and an iridium disc with a diameter of 1 cm cut from 1 mm thick iridium sheet and inserted in a polypropylene holder with a Viton O-ring was used for the UV-PMRS experiments.