Zirconium hydrogen phosphate as an additive in electrocatalytic layers for the oxygen evolution reaction in PEM water electrolysis

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Abstract

For reasons of electrode integrity and durability it is desirable to add zirconium hydrogen phosphate to electrocatalytic layers in PEM water electrolysis. Common synthesis methods are frequently associated with an accompanying addition of phosphoric acid. The presence of free phosphoric acid is known to be detrimental for catalytic activity of the common oxygen evolution catalysts. In this work composite electrocatalytic layers of iridium oxide, Nafion® and zirconium hydrogen phosphate were fabricated on glassy carbon disk electrodes. Zirconium hydrogen phosphate was prepared by mixing zirconium oxychloride and phosphoric acid. The effect of the electrocatalyst constituents were electrochemically investigated with respect to the oxygen evolution reaction in 0.5 M sulfuric acid electrolyte at room temperature. Slow linear sweep voltammograms showed that the electrocatalyst performance depends only to a small

extent on the way the composite electrodes were manufactured. However, the coexistence of zirconium hydrogen phosphate particles in the electrode structure offsets the destructive effect of any phosphoric acid remaining in the electrode more or less completely. Inherent catalyst activity is unaffected by the addition of zirconium hydrogen phosphate, but apparently worsen the current per mass emphasizing the necessity of optimizing the catalytic layers with respect to performance and mechanical properties.

Keywords

Oxygen evolution; PEM water electrolysis; Electrocatalytic layer; Zirconium phosphate; Iridium oxide; Phosphoric acid

1. Introduction

Proton exchange membrane water electrolyser (PEM WE) systems were developed during the 1960's for space applications [1]. Such systems are now being reconsidered as promising energy storage alternatives and represent an environmentally friendly method to produce high purity hydrogen in terrestrial applications. It offers a non-polluting alternative for hydrogen production if powered with electricity from renewable energy sources [2, 3].

PEM WE has some considerable advantages such as very high gas purity, fast dynamic response times, design flexibility, and operation at high current densities [4, 5]. However, oxygen evolution kinetics is particularly slow in the acidic environment introduced by the proton conductive membrane and accounts for a large fraction of the overall efficiency loss experienced

in a PEM WE [6]. Thus increasing the reaction kinetics is essential to reduce the overall energy consumption. As a consequence of this, more recent research in both PEM fuel cell and PEM water electrolysis has moved into the intermediate temperature range, i.e. above the boiling point of water and up to about 200 °C. Increasing the operating temperature of a water electrolysis system allows for faster reactions, higher production rates, less loading of expensive electrocatalysts and may lead to satisfactorily development of alternative and cheap electrocatalysts. Furthermore, an increased temperature also reduces the electricity demand for the water splitting process as the reversible voltage decreases [7, 8].

Typical PEM water electrolysis, or PEM fuel cell, systems employ conventional membranes like perfluorosulfonic acid ionomers (e.g. Nafion®) and components which are optimized for operation up to 80 °C [9, 10]. These membranes have a satisfactorily mechanical strength, high chemical stability and proton conductivity at low temperatures [11, 12]. However, they are found to be unsuitable in itself for use in the higher temperature regime due to chemical and mechanical degradation of the polymer structure [9, 12, 13]. Several strategies to overcome problems associated with conductivity and mechanical integrity through cross-linking, physical reinforcement or developing alternative membranes or solid acids are being pursued [7, 9, 10, 14-23].

Costamagna et al. [16] used the inorganic compound zirconium hydrogen phosphate, $Zr(HPO_4)_2 \cdot nH_2O$ (ZrP), as an additive to Nafion®. ZrP is a layered compound and has a moderate proton conductivity of about 10^{-3} S cm^{-1} when humidified [21, 24, 25]. It is a Brønsted acid with the ability to donate protons, and will therefore in principle also increase the mobility

of protons on its surface. However, Yang et al. found that ZrP had little impact on proton conductivity through a Nafion/ZrP composite membrane [26]. Moreover, ZrP is a hygroscopic insoluble salt with hydrophilic character that is suggested by Alberti and Casciola to interact with the sulfonic acid groups in Nafion and partially replace the loosely bonded water within the hydrophilic domains [25]. This is further suggested to somehow also protect the triple contact in the electrocatalytic layer and better retain water under dehydrating conditions. Use of ZrP as an inorganic filler is shown to improve the performance and durability of Nafion in PEM fuel cells at elevated temperatures under dehydrating conditions [16, 25-28].

Although developing alternative membranes or utilising membrane additives can solve problems associated with conductivity and mechanical integrity at elevated temperatures, it may create another. If the membrane or membrane additives adsorb on or otherwise block the catalyst surface, this may reduce catalyst overall efficiency. Noble Ru and Ir metal oxides are considered to be the best oxygen evolution catalysts in the acidic media. While ruthenium oxide is known as the most active single metal oxide [9, 29] it is not stable enough for prolonged operation and is often omitted or stabilized with another active oxide such as iridium oxide [30,31]. Phosphates in general are known to adsorb strongly on ruthenium oxide [32] and on iridium oxide films [33], and has a significant and unfavourable impact on catalyst activity [33]. Radioactive tracer measurements concluded that dihydrogen phosphate ions adsorb the strongest while perchlorate ions adsorb the weakest on ruthenium and iridium oxide surfaces [34]. In this respect, phosphoric acid doped membranes may not be compatible with the requirements of a low overpotential at the oxygen evolving electrode, in particular if present in the catalytic layer. Due to the weak

interaction between Nafion moieties and catalysts such as iridium oxide [35], it seems highly desirable to retain membranes similar to Nafion in high-temperature PEM WE.

Most of the available literature on high temperature PEM fuel cells and water electrolysis deal with either the membrane or catalyst development separately. Understanding the influence of additives and the importance of physical structure and composition of the electrocatalytic layer itself is essential to develop more efficient PEM water electrolysis systems. Specifically, in this work we aim to show that ZrP additives in IrO2-Nafion electrode structures almost completely alleviates the adverse effects of phosphoric acid in the electrolyte on electrocatalytic performance.

2. Experimental

2.1 IrO$_2$ electrocatalyst preparation

Iridium oxide electrocatalyst was prepared from dihydrogen hexachloroiridate(IV) hydrate ($H_2IrCl_6 \cdot$ n H_2O, W.C. Heraeus Chemical GMbH, 43 % metal basis) by hydrolysis, as described in Marshall et al. [36] and recently by Skulimowska et al. [37]. 0.45 mmol dihydrogen hexachloroiridate(IV) hydrate was dissolved in 26.8 mL deionized water and subsequently alkalinized by addition of 17.9 mL 0.5 mol dm^{-3} analytical grade sodium hydroxide (Merck). The mixture was then heated to 80 °C and continuously stirred for 1 h. Afterwards, the mixture was slowly cooled to room temperature and pH adjusted to 8 by dropwise addition of 1 mol dm^{-3} nitric acid (69% Baker) before heated to 80 °C again and stirred for another 30 min. The precipitate was thoroughly rinsed with deionized water and separated by centrifuging. This procedure was repeated three times and the final precipitate was dried overnight at 90 °C and

ground. The resulting black iridium powder was heated in a furnace for 1 hour at 500 °C in air to obtain crystalline iridium oxide, cooled to room temperature and ground. The quality of the synthesized oxide structure was verified with a powder diffractometer, model D8 Focus XRD.

2.2 Electrocatalytic layer preparation

Addition of zirconium hydrogen phosphate (ZrP) to the electrocatalytic layers were prepared either i) through mixing a solution of zirconium oxychloride and phosphoric acid (Eq. 1) [22] with subsequent mixing with a dilute Nafion solution, or ii) dispersing powdered preformed particles in water followed by mixing with a dilute Nafion solution.

i) 1 mg of iridium oxide powder was mixed in 1 mL deionized water in an ultrasonic bath for at least 30 minutes. 20 µL of the slurry, corresponding to 20 µg iridium oxide, was placed on to a pretreated glassy carbon disk surface and dried under nitrogen gas purge. The electrocatalyst was then covered with either 20 µL of a diluted Nafion solution (5 wt%, Sigma-Aldrich, which was further diluted with water to a Nafion:water ratio of 1:100) or 20 µL of a composite Nafion solution comprising of Nafion with a combination of zirconium oxychloride (30% $ZrOCl_2$ in HCl, Sigma-Aldrich), phosphoric acid (65% Merck) and in situ formed ZrP (Eq. 1). 1 mL solutions with various concentrations of $ZrOCl_2$ and H_3PO_4 were prepared (Table 1), and formation of ZrP was allowed during a 15 min mixing in an ultrasonic bath. Afterwards, the solution was mixed with 1 mL of the diluted Nafion solution for another 15 min in the ultrasonic bath. 20 µL of the final mixture was added on top of the electrocatalyst and dried under nitrogen gas purge.

$$ZrOCl_2 + 2H_3PO_4 \rightarrow Zr(HPO_4)_2 + H_2O + 2HCl \qquad (1)$$

The ZrOCl$_2$ to H$_3$PO$_4$ ratios used were 0:0, 1:5, 1:0, 1:2 and 0:1, and the associated amounts of each constituent added to the prepared electrocatalytic layers are given in Table 1. The electrocatalytic layer with only iridium oxide and Nafion was prepared for comparison reasons.

< Table 1 >

ii) Three structurally different electrocatalytic layers were made with the synthesized iridium oxide, Nafion and commercial ZrP (Sigma-Aldrich), and are illustrated in Figure 1. (a) As before, a layer of iridium oxide and Nafion was placed on a pretreated glassy carbon disk electrode and dried. Subsequently, 5 mmol ZrP powder was dispersed in 1 mL deionized water and mixed with 1 mL of the diluted Nafion solution for 15 min in an ultrasonic bath and applied to the top of the deposited oxide layer. (b) Several aliquots (2x2) of ZrP in Nafion and iridium oxide in Nafion were deposited alternatingly onto the glassy carbon disk electrode and dried under a nitrogen gas purge before application of each layer. (c) ZrP, Nafion and Iridium oxide powder were all mixed for 15 min in an ultrasonic bath and applied to the disk electrode. An effort was made to keep the overall amount of catalyst components constant.

<Figure 1>

2.3 Electrochemical characterization

A glassy carbon disk electrode (0.5 cm diameter, Pine instruments) was used as the working electrode substrate, and was mechanically polished (5.0 microns alumina followed by 0.05

microns deagglomerated alumina), carefully washed and degreased with deionized water and isopropanol prior to any catalyst film deposition. A Pt plate (5 cm^2 geometric area) was used as the counter electrode and a hydrogen electrode in the same electrolyte functioned as the reference electrode (RHE). Electrochemical measurements were performed in a glass cell of conventional design, where the potential between the working and reference electrodes was controlled with a Gamry Instruments Series G 300 potentiostat. All measurements were carried out at room temperature (23 °C) in 0.5 mol dm^{-3} sulfuric acid (Merck, p.a.) supporting electrolyte, which was deaerated prior and during experiments with continuous Ar purging (5.0, Yara). Glassware were cleaned in hot diluted (10%) hydrogen peroxide solution (Sigma-Aldrich, 35%) added 1% sulfuric acid (Sigma-Aldrich, 96%) for minimum 2 hours and then thoroughly rinsed in deionized water and dried before use.

Each preparation followed the same testing procedure and was repeated and checked for reproducibility. Activation of the electrocatalytic film was done through cycling the working electrode 50 times between 0.05 V and 1.4 V at 200 mV s^{-1} prior to each experiment. Cyclic voltammograms of various sweep rates were subsequently performed between the same potential limits with current density reported with respect to the geometric area. Finally, linear sweep voltammograms were performed from 1.1 V up to 1.7 V at a sweep rate of 5 mV min^{-1}. The linear sweep current-potential data were post treated by compensating for the ohmic resistance estimated by using a Levenberg-Marquardt algorithm and normalized with respect to the outer charge, as described in Owe et al. [38]. However, the lack of a well-defined linear relation between charge vs. inverse square root of sweep rate in some of the measurements made the extrapolation to zero uncertain. As a compromise, we assumed therefore the outer charge to

equal the area under the curve during the positive-going sweep between 0.4 and 1.4 V at 200 mV s^{-1}.

3. Results and Discussion

3.1 Additives to the electrocatalytic layer

Electrochemical comparisons between a catalyst layer containing IrO_2 with a Nafion cap and a series of catalyst layers with selected amounts of $ZrOCl_2$ with phosphoric acid in the Nafion cap (Table 1) are given by cyclic voltammetry (Figure 2) and slow linear sweep voltammetry (Figure 3). All recorded cyclic voltammograms display similar features, including the iridium oxide oxidation/reduction peaks at 0.8-0.9 and 1.25-1.35 V both in the positive-going and negative-going sweep direction, reflecting the redox transitions of Ir^{3+}/Ir^{4+} and Ir^{4+}/Ir^{6+}, respectively [39]. Although the amount of electrocatalytic oxide remained constant for the various electrodes, a mismatch was found between the current responses in the respective voltammograms (Figure 2).

<Figure 2>

IrO_2 catalyst with a thin Nafion cap gave the highest current density in the cyclic voltammetry experiment (Figure 2). The current density is in this case related to the geometric area, thus indicating that this electrocatalytic layer provides the largest active surface area. On the other hand, application of a thin Nafion cap to the IrO_2 catalyst with only phosphoric acid added to it provided the lowest current density by far. This implies that the related phosphate anions partially block active sites towards proton exchange with the solution and thus reduce the active surface area. Intuitively, it is further expected that electrocatalytic layers containing ZrP prepared

with excess phosphoric acid (according to Eq. 1) would give a reduced active surface area compared to the pure IrO_2/Nafion catalyst layer. This was indeed found to be the case, and can be seen from the voltammogram in Figure 2 for the sample prepared with 1:5 zirconium oxychloride to phosphoric acid ratio. The detrimental effect of phosphate adsorption on AIROF electrodes was recently described in a work by Owe et al. [33], employing phosphoric acid as supporting electrolyte and comparing voltammograms and massograms with those recorded in sulfuric and perchloric acid. Furthermore, voltammograms of electrodes with excess phosphoric acid were surprisingly reproducible and did not show any noticeable changes over the course of the experiment, suggesting negligible loss of phosphoric acid from the composite layer with time.

The electrocatalyst layers with the composite Nafion cap including 1:5, 1:2 and 1:0 ratios of zirconium oxychloride to phosphoric acid all gave similar voltammograms (Figure 2), and in between the voltammograms of catalyst with Nafion alone and catalyst with Nafion including added phosphoric acid. The sweep rate of 200 mV s^{-1} is rather high and the current (hence charge) is associated with the surface rather than the bulk, which will be different for the various composite film electrodes.

Charge normalized and IR corrected slow linear sweep voltammograms of the same electrodes as in Figure 2 were recorded to study the catalytic effect of the additives (Figure 3). An indication of the total surface area available for proton exchange was estimated from the voltammetric charges in Figure 2, which can be assumed to be the area available also for the oxygen evolution reaction. A Tafel slope of 40 mV dec^{-1} was found for all electrodes consistent with the second

step of the electrochemical oxide path being rate determining [40]. As expected, strong phosphate anion adsorption is detrimental for catalyst performance, generating a current of only 10 mA C^{-1} at 1.55 V for the catalyst with a Nafion cap including only phosphoric acid (Figure 3).

<Figure 3>

The electrode prepared with a 1:2 stoichiometric ratio of zirconium oxychloride and phosphoric acid (Eq. 1), ideally completely converted to ZrP, is slightly better than the the following three electrodes. It generated a charge normalized current of about 500 mA C^{-1} at 1.55 V. This suggests, despite the similar fast cyclic voltammetry responses for all catalysts with a composite Nafion cap (Figure 2), that ZrP as an additive to the electrocatalytic layer in fact may slightly improve the activity of the IrO_2 electrocatalyst in some circumstances. Addition of ZrP is not expected to improve the proton conductivity within the layer itself [25, 26] nor contribute catalytically to the oxygen evolution. We thus tentatively ascribe the slightly better performance to structural changes within the composite electrocatalytic layer [28]. Furthermore, addition of ZrP to the Nafion in the electrocatalytic layer may improve stability and assist in maintaining the mechanical integrity of the layer in a similar way as suggested for fuel cell electrodes operating at elevated temperatures [25].

The two electrodes containing either zirconium oxychloride or in situ formed ZrP with excess phosphoric acid seem to give similar normalized activity as the pure IrO_2/Nafion electrode with currents of about 250 mA C^{-1} at 1.55 V (Figure 3). First of all, a more or less identical charge normalized current in conjunction with a significantly lowered cyclic voltammetry response

(Figure 2) implies that addition of zirconium oxychloride does not contribute to hydrogen exchange with the solution nor oxygen evolution. In this case, it functions merely as spectator species diluting, or blocking, the iridium oxide surface sites that otherwise would be available for proton exchange. The same reasoning does not work for the catalyst with Nafion including ZrP and excess phosphoric acid, as catalyst with Nafion and phosphoric acid alone is significantly worse and catalyst with Nafion and ZrP alone (ideally) improves the charge normalized activity. Since the loss of phosphoric acid with time was found to be negligible, the effect must be due to the presence of ZrP itself in the Nafion cap. A probable explanation may be that excess phosphoric acid molecules are sequestered by the ZrP particles present in the catalytic layer [41], and therefore unavailable to block the active IrO_2 surface sites. A major point in this work is thus that the addition of ZrP makes the IrO_2/Nafion composite electrodes more resistant towards phosphoric acid. In this case, ZrP may play a crucial role in maintaining catalytic activity for phosphoric acid based membranes or additives, typically for high-temperature PEM operation. It is also worth pointing out that the optimum $ZrOCl_2$ to H_3PO_4 ratio may be lower than expected from simple stoichiometry (Eq. 1), as in situ formation of ZrP and interaction with Nafion may attain a complex polymeric structure [25].

3.2 Structuring the electrocatalytic layer

Figure 4 shows cyclic voltammograms of selected composite electrodes (illustrated in Figure 1) together with a conventional electrocatalyst comprising of IrO_2 and Nafion at a sweep rate of 200 mV s^{-1}. The iridium redox transitions in both positive and negative going sweep directions are visible for all electrode compositions and are the same as in Figure 2. The current densities are corrected with respect to the geometric area and as expected, the IrO_2 catalyst with the Nafion

cap again provided the highest voltammetric response. Lower responses were observed for all samples with addition of ZrP to the catalytic layer, due to the high sweep rate used making the active area associated to the surface rather than the bulk. Furthermore, it is worth pointing out that the voltammetric responses for the three samples containing ZrP in Figure 4 differed somewhat from each other. This suggests that the selected composite electrocatalysts obtained different electrochemically active surface areas.

<Figure 4>

Among the electrodes containing ZrP, the electrode where IrO_2 is added a cap with Nafion and ZrP in one step (Figure 1a) gives the highest voltammetric response, followed by the layer-by-layer structured electrode (Figure 1b), and finally the sample where all components are mixed together before applying it onto the glassy carbon substrate (Figure 1c). Apparently, the voltammetric response decreases the more interwoven the iridium oxide catalyst particles are with the ZrP and Nafion.

Charge normalized and IR-corrected slow linear sweep voltammograms for the same electrodes as in Figure 4 are given in Figure 5. Immediately, the results appear to indicate but very small differences with respect to the rate of the oxygen evolution reaction. Interestingly, the geometrically corrected cyclic voltammograms in Figure 4 suggest that the presence of ZrP in the catalytic layer decreases the apparent active surface area of the catalyst, while the charge-normalized polarization curves imply that the addition of ZrP does not negatively affect the intrinsic electrocatalytic activity of the iridium oxide catalyst. However, due to the differences in

charge observed in the cyclic voltammograms, the current per mass is lower for the iridium oxide and Nafion catalyst layers containing ZrP. The performance of the membrane-oxide composite may therefore expect to depend on the way the electrocatalytic layers are assembled.

<Figure 5>

The current series of experiments were performed in sulfuric acid, and the proton supply of all open parts (i. e. not blocked) of the oxide is secured through the aqueous electrolyte. This will not be the case in an electrolyser unit into which demineralized water will be supplied. This implies that there will be a balance between providing an efficient proton transport in the catalytic layers and the desire to keep the surface open to the OER. The pure Nafion electrolyte appears to provide a surface much more open to the OER than the other electrolyte compositions investigated in the current work. Thus, the requirement of a more mechanically robust membrane material in the catalytic layer may make the design of catalytic layers much more critical in high-temperature PEM WE than for units operated at low temperatures.

4. Conclusions

The effects of the presence of zirconium hydrogen phosphate in composite electrodes of iridium oxide and Nafion were examined. The catalytic activity is little affected by the presence of the hydrogen phosphate. Moreover, the presence of the zirconium hydrogen phosphate appears to completely compensate for any adverse effects stemming from the phosphoric acid frequently employed in the zirconium hydrogen phosphate synthesis. The resulting catalytic performance is therefore not significantly sensitive to different ratios of zirconium oxychloride to phosphoric acid employed during synthesis. On this basis, zirconium hydrogen phosphate is therefore suggested to be able to sequester excess amounts of phosphoric acid in the electrocatalytic layer, making it highly desirable in combination with membranes that depend upon phosphoric acid to facilitate proton conductivity.

Also, the presence of zirconium hydrogen phosphate in the iridium oxide and Nafion catalyst layers tends to decrease the current per mass activity the more intertwined the constituents are. Thus, the performance seems to depend on how it is structured, where a homogeneous oxide-ZrP/Nafion composite has a lower performance than that of an oxide covered with the same ZrP/Nafion membrane per mass.

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Figure captions

Figure 1. Illustrations of the catalyst composites on a glassy carbon disk electrode employing IrO_2 catalyst particles (black spheres), ZrP (yellow spheres) and Nafion (cyan threads) in the mix: a) IrO_2 catalyst with Nafion and added a cap consisting of ZrP mixed with Nafion, b) IrO_2 with Nafion covered with Nafion mixed with ZrP deposited layer-by-layer, and c) IrO_2 catalyst mixed with both Nafion and ZrP.

Figure 2. Cyclic voltammograms of IrO_2 based electrodes in 0.5 mol dm^{-3} H_2SO_4 at room temperature with a sweep rate of 200 mV s^{-1}. The IrO_2 catalyst was first deposited on a glassy carbon disk and then covered with either Nafion (black line) or a composite film of Nafion mixed with selected ratios of $ZrOCl_2$ to phosphoric acid (1:5 blue line, 1:0 green line, 1:2 purple line, and 0:1 red line). All electrodes contained a total of 20 µg of iridium oxide (see Table 1) and the legend shows the voltammetric response in descending order.

Figure 3. IR-corrected and charge-normalized polarization curves of various electrode compositions (Table 1) in 0.5 mol dm^{-3} H_2SO_4 recorded at a sweep rate of 5 mV min^{-1}. Nafion thin-film IrO_2 deposited catalyst electrode (black line) and samples of the same IrO_2 catalyst covered with a Nafion cap mixed with selected ratios of $ZrOCl_2$ to phosphoric acid (1:2 purple line, 1:0 green line, 1:5, blue line and 0:1 red line). The legend shows the normalized current in descending order with respect to the current observed at 1.55 V (dashed horizontal line).

Figure 4. Cyclic voltammograms of IrO$_2$ based composite electrodes deposited on a glassy carbon disk electrode substrate in 0.5 mol dm^{-3} sulfuric acid at room temperature and a sweep rate of 200 mV s^{-1}. IrO$_2$ catalyst with Nafion (black line), IrO$_2$ catalyst with Nafion and added a cap of Nafion with ZrP (green line), sequentially deposited IrO$_2$ catalyst with Nafion and Nafion with ZrP in a layer-by-layer structure (blue line), and a composite catalyst layer with a mixture of IrO$_2$, Nafion and ZrP (purple line). The legend shows the voltammetric response in descending order.

Figure 5. IR-corrected and charge normalized linear sweep voltammograms on IrO$_2$ composite electrodes in 0.5 mol dm^{-3} H$_2$SO$_4$ at room temperature and a sweep rate of 5 mV min^{-1}. IrO$_2$ with Nafion (black line), IrO$_2$ with Nafion and a Nafion with ZrP cap added on top (green line), IrO$_2$ catalyst with Nafion and Nafion with ZrP added layer-by-layer (blue line), and a mixture of IrO$_2$ catalyst, Nafion and ZrP (purple line). The inset gives a magnification around 1.53-155 V, and the legend shows the normalized current in descending order with respect to the current observed at 1.55 V.

List of tables.

Table 1. Amount of the various constituents in the electrocatalytic layers.

Sample	IrO_2	Nafion-water (1:100)	$ZrOCl_2$	H_3PO_4
	µg	µL	µmol	µmol
IrO_2	20	20	-	-
IrO_2 + 1:5 $ZrOCl_2$:H_3PO_4	20	10	1.34	6.66
IrO_2 + $ZrOCl_2$	20	10	1.0	-
IrO_2 + 1:2 $ZrOCl_2$:H_3PO_4	20	10	1.67	3.34
IrO_2 + H_3PO_4	20	10	-	10