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Preparation of Ir/IrO$_x$ pH electrode based on melt-oxidation and its response mechanism investigation①

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Abstract: A method of melt-oxidation at high temperature is adopted to prepare Ir/IrO$_x$ pH electrode, and different carbonates such as Li_2CO_3, K_2CO_3, Na_2CO_3 and their mixture were used in this process. It is shown that the electrode prepared in carbonate melt has good pH response characteristics, such as stability, sensitivity, response time, and anti-corrosion ability in the solution containing F^-, etc. The hysteresis mechanism was also investigated based on a storage model with a cyclic voltammetry experiment. It is found that the valence of Ir in the oxide film is + 4, and the iridium oxide on the surface of the film is co-ordinate with - OH and H_2O from the result of XPS spectra. The mole fraction ratio of Ir to O is 1∶2.1 in the bulk of the oxide, but $x(\mathrm{Ir}) : x(\mathrm{O})$ is 1∶6.78 on the surface of the oxide film by EDX technology. The hydration effect of the thermally prepared iridium oxide was investigated. Therefore, a H^+ response mechanism is suggested, being much different from the reported theory for thermally prepared iridium oxide electrode, which previously does not take the hydration of oxide into consideration.

Key words: pH; electrode; iridium; oxide; mechanism
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1 INTRODUCTION

Metal oxides were regarded as the alternatives to conventional glass electrode. Various metal oxides have been suggested as pH sensing electrode, such as MnO_2, PbO_2, Co_3O_4, TiO_2, PtO_2, RuO_2, RhO_2, OsO_2, IrO_2 [1-6].

Among the large number of the reported materials, iridium oxide is the one of the most possible candidates for such application[2], and it can be prepared by several methods, such as electrochemical oxidation[7], sputtering[8], thermal oxidization [9-13]. Although IrO$_x$ is one of the best metal oxide for pH sensing by far, many performances remain to be improved[14].

It is reported that the iridium powder can be oxidized in carbonate [15], and Yao et al[14] has devoted to this method and made an improvement in the response performance. Based on this, we made a detailed investigation on the response performance in this paper. The used carbonate, oxidized temperature and duration for electrode preparation were all taken into consideration. In addition, the application in the solution containing F^- has been studied. Emphasis was placed on the H^+ response characteristics, such as the decisive factor on the response time, hydration effect to the potential drift, the correlation of the surface morphology with the hysteresis effect, as well as the effect of electrode surface to response sensitivity.

2 EXPERIMENTAL

2.1 Preparation of IrO$_x$ electrode

Li_2CO_3, Na_2CO_3, K_2CO_3 and their mixture melt bath was used as the medium to oxidize iridium wires (0.48 mm in diameter)[14]. After a pretreatment for degreasing and dust cleaning, Ir metal wires were held in a crucible covered with carbonate power and put into an oven. The oxidization of the Ir wires was performed at above 700 ℃ for several hours in a furnace under air atmosphere, and the oxidizing temperature and time could be adjusted according to different requirements. After being cooled down to room temperature, the attached carbonate on the electrode was removed after dissolution in acid. At last a cleaning procedure was conducted in distill water.

To prepare the pH electrode, a small section at one end of the oxidized wire was scraped off in order to expose the base metal and 10 cm Cu wire was spot-welded to form an ohmic contact. This junction as well as Cu wire was sealed with heat-shrink silicone adhesive or epoxy resin, so that only the iridium oxide surface was exposed to the solution. Additionally, in order to avoid the potential drift, an accelerated aging process was tried.

2.2 pH response measurement

Open-circuit potential of the IrO$_x$ electrode was measured as a function of pH value of the test solution

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against of a single junction saturated calomel reference electrode by using a potentiostat (the input resistance $> 10^{12}$ Ω). Before measurement, IrO_x electrode was stored in distilled water. All the potentiometric measurements were performed in an air-saturated buffer solution at room temperature. The buffer solution consists of 0.01 mol/L $CH_3COOH/HBO_3/H_3PO_4$ & 0.1 mol/L KCl[14, 16]. The pH of the buffer solution was varied by dropwise addition of 0.1 mol/L KOH or 0.1 mol/L HCl. For the buffer solution of fixed pH value, such as pH 4.01, pH6.86, pH9.23 buffer solution could be got in market. A previously calibrated glass electrode and a digital pH meter were used to monitor the pH of the solution.

A duration as long as 15 d was spent to keep track of the change of response characteristic, in order to investigate the open-circuit potential drift in the aging process. The data collection of the open-circuit potential, response time and the open-circuit potential drift of the IrO_x electrode were carried out with a computer, and the data were processed by a specific program. In the case of experiment in the solution containing hydrofluoric acid, a home-made plastic salt-bridge/ junction and beaker were used.

2.3 Microscope analysis

The chemical composition and valence of the oxide were determined by EDX and XPS; the morphology and thickness of the oxide film were investigated with SEM, and in order to observe the cross-section of the electrode for the measurement of film thickness, the metal wire was fixed in the bulk of epoxy resin.

2.4 Cyclic voltammetry experiment

In order to make a further understanding of the relationship between response characteristic and surface state, a cyclic voltammetry experiment was conducted between 0 and 1 V(vs. SCE).

3 RESULTS AND DISCUSSION

3.1 Response sensitivity and response time

The Ir/IrO_x electrode has a H^+ linear response in the pH range of 1 - 13. The increased film thickness will improve the response sensitivity. The response sensitivity increases from 51 mV/pH to 58 mV/pH, when the film thickness varied from 5 μm to 20 μm, and the species of melt-carbonate makes some effect on the response sensitivity. The electrode prepared in carbonates mixture has a sensitivity of 54.3 mV/pH, when the film thickness is 20 μm. All can be explained by the theory that the response characteristic is dependent of the film thickness, morphology and composition. The thicker film provides more active surface, which will increase the response sensitivity and shorten the response time.

It is also found that the dipping in 10% (volume fraction) HF solution for 5 h made less effect on the response performance, such as response time and sensitivity.

For the convenient pH determination, the quick response of the pH electrode is needed. According to the regulation of IUPAC, it is believed that a steady state is arrived, when the open-circuit potential drifts are less than 1 mV/min. A computer installed with a specific software was used to record the open-circuit potential response. The electrodes with a film-thickness above 15 μm can get to steady state in 1 min at the buffer solution of pH 1 - 13.

Fig. 1 shows the record of the open-circuit potential of IrO_x electrode in pH4.01 solution. The open-circuit potential will quickly get stable with film thickness increasing, and the pH value of the solution also makes some effect on the response time. The response time in low pH solution (pH< 4) is less than 0.5 min, while in basic solution the response time will be near to 1 min, in addition, the stirring will accelerate the response. Maybe the pH response is partially decided by the diffusion of H^+ concentration in the solution .

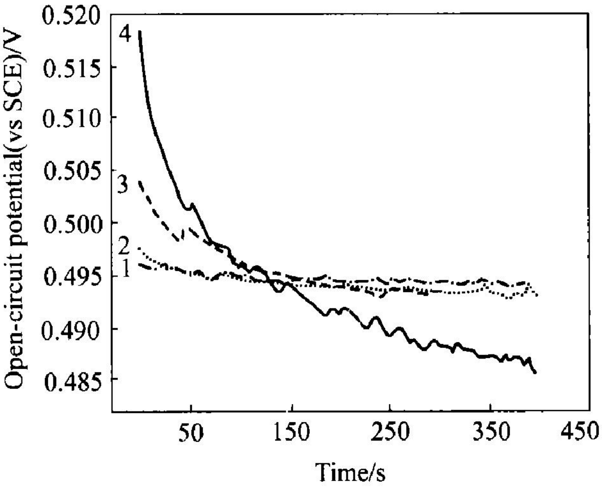


Fig. 1 Potential response of electrode with different thickness in pH4.01 buffer at 25 ℃
1—20 μm; 2—15 μm; 3—10 μm; 4—5 μm

It is also found that the solution temperature, the kind of the carbonate applied for oxidization, and electrode surface morphology are all the decisive factors to affect the response time.

3.2 Potential drift and hydration

The open-circuit potential drift in aging process is a common phenomenon in many sputtering or electrochemically prepared IrO_x electrodes reported in Ref. [17], which is usually as large as 100 mV/ d. In order to investigate the stability of the electrode, the open-circuit potential change of two electrodes (NO. 1, NO. 2) in buffer solution were recorded in a term of 15 d. NO. 2 electrode was treated beforehand with a method of accelerated aging process, and NO. 1 was not. It is found that NO. 2 drifts less than 1 mV/ d in the whole duration, however NO. 1 has a potential drift of nearly 10 mV/ d.

In the last stage of the hydration from 13 d to 15 d, No. 1 and No. 2 nearly have the same speed for potential change. Fig. 2 and Fig. 3 indicate the change of the intercept of E —pH linear relationship (E^0) and sensitivity (slope) of the E —pH relationship for the pH electrode over time. It is found that the electrode sensitivity keeps the same (the change about ± 0. 5 mV/ pH) in the course of aging, while the E_0 decreases quickly for the electrode without an accelerated process beforehand.

Therefore, it can be concluded that the melt-oxidized electrode has a good stability after an aging treatment. The quick potential drift of NO. 1 electrode can be explained by the fact that the oxidized films is a dried-film, and its hydration needs a long time immersion, but the hydration will speed up with a specific process.

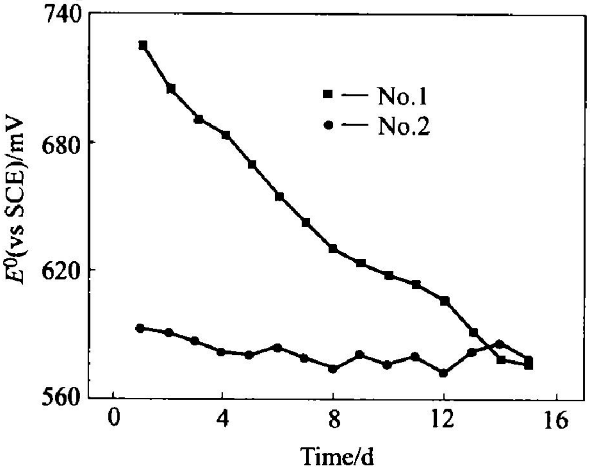


Fig. 2 Change of E^0 with pH electrode over time

3. 3 Hysteresis and electrode surface

Hysteresis is a common phenomenon for glass pH electrode or metal oxide pH electrode. Here several experiments are conducted to investigate the mechanism of the hysteresis effect. The hysteresis could be neglected when the measurement is carried out in turns form pH1 → pH13 or pH13 → pH1, with a response change from $E = 722.9 - 57.20$ pH to $E = 720.58 - 57.02$ pH; but the hysteresis would not be a negligible factor for accurate determination, when the electrode is put to application in the case of random measurement. The hysteresis effect arrived to 4 mV and 7 mV respectively, when pH value of the determination changes from pH9 → 3 → 9 and pH3 → 9 → 3.

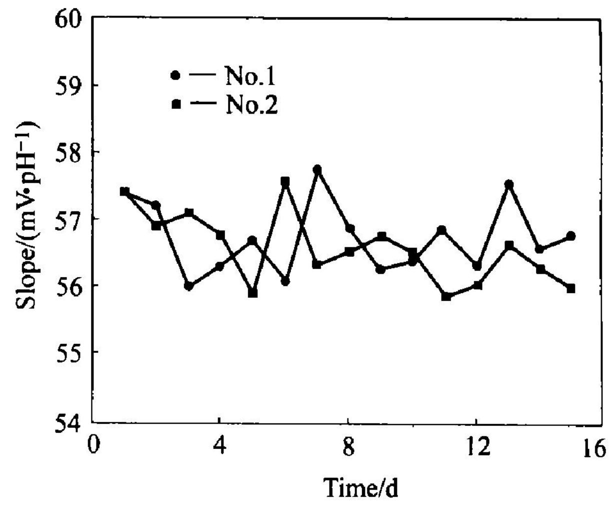


Fig. 3 Change of slope with pH electrode over time

So far, there is little explanation to the hysteresis phenomenon. H^+ response speed is related to the electrode active surface, and the iridium oxide surface could be defined as outer and inner surface[18, 19]. The inner surface is composed of pores, cracks and grain boundary. An attempt is made to understand the hysteresis in this article, which attributes the phenomenon to the slow diffusion of the H^+ between inner and outer surface and the slow adjustment of the hydration situation of the electrode surface. All the open-potential determination in different pH solutions are quickly carried out in less than 1 min, so that the electrode surface fails to adjust instantaneously with the corresponding solution.

In order to make a further understanding to the relationship between response characteristic and surface situation, a cyclic voltammetry experiment is conducted. The charge storage (Q_T) of the cyclic voltammetry (0 ~ 1 V, vs. SCE) can be calculated according to the mathematical model as follows[20, 21]:

$$Q_T = Q_i + Q_o \tag{1a}$$

$$Q_v = Q_o + K_1 v^{-1/2} \tag{1b}$$

$$1/Q_v = 1/Q_T + K_2 v^{1/2} \tag{1c}$$

where v is scanning speed, Q_i, Q_o are the charges related to the inner (less accessible) and outer (more accessible) surface respectively, Q_v is the integral storage at the scanning speed of " v " . Fig. 4 and Fig. 5 plot the charge storage against scanning time, and No. 1 ~ No. 5 are the electrode arranged in the turns of film thickness reduction. Through the above equation, the proportion of the storage between inner and outer surface, as well as the proportion of surface composition could be obtained. As shown in Table 1, the inner surface increases with the film thickness. According to observed experiment results that the H^+

response speed and hysteresis effect increases with the oxide thickness. The oxidized time should be controlled, in order to make a balance between response speed and hysteresis effect.

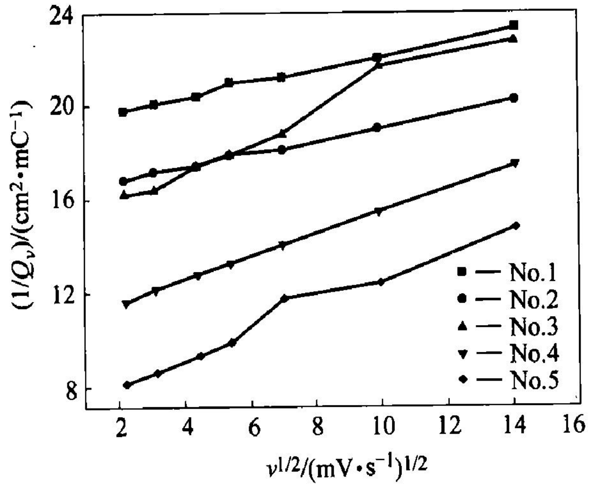


Fig. 4 Relationship between $1/Q_v$ and $v^{1/2}$

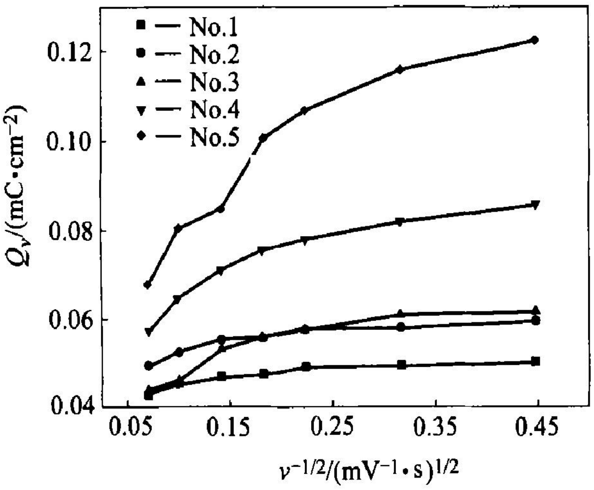


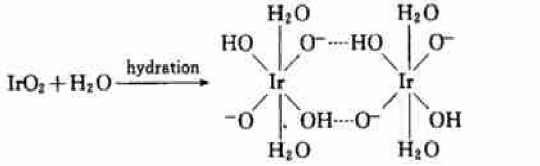
Fig. 5 Relationship between Q_v and $v^{-1/2}$

Table 1 Charge storage of different electrode ($\mathrm{mC \cdot cm^{-2}}$)

Electrode	Q_o	Q_T	Q_i/Q_T
No. 1	0.039	0.052	0.250
No. 2	0.044	0.062	0.291
No. 3	0.034	0.068	0.500
No. 4	0.044	0.099	0.556
No. 5	0.054	0.140	0.614

3.4 Study on iridium oxide film

SEM, EDX, XPS are used to investigate the morphology and composition of the iridium oxide layers. Iridium oxide will grow up very well in Li_2CO_3 or in the mixture of Li_2CO_3 with other carbonate, while dissolving in the pure K_2CO_3 or Na_2CO_3 melt solution. The film thickness is dependent on the time and temperature for oxidation. The degree of oxidation makes much effect on the morphology of the electrode surface as shown in Fig. 6. The oxide grains grow up, and the surface becomes more uneven with increment of the oxidizing time. The EDX results show that the mole fraction ratio of Ir to O in the bulk of the oxide film is 1:2.1, and is 1:6.78 in the surface, being much greater than that in the bulk. The phenomenon is observed that the surface is composed of lots of $-OH$ and H_2O by XPS spectra. As seen in Fig. 7, the binding energy of O 1s is 531.9 eV. The signal of O 1s can be attributed to the lattice oxide ions O^{2-}, to OH^- groups and to strongly bound water H_2O. The binding energy of O 1s of these oxygen species is (530 ±0.5) eV, (531.5 ±0.5) eV, (533 ±1) eV, respectively[22]. The hydration of the iridium oxide could be described as Eqn. (2)[23]. As seen in Fig. 8, the binding energy(BE) of Ir $4f_{7/2}$ is 62.4 eV, coinciding well with the data reported in Ref. [22], which is usually BE(Ir $4f_{7/2}$) = (62.2 ±0.2) eV for IrO_2. Therefore, it can be concluded that the Ir element in oxide film is mainly Ir^{4+}. The hydration of IrO_2 can be expressed as follows:



$$IrO_2 + H_2O \xrightarrow{\text{hydration}} \begin{array}{ccc} & H_2O & \\ HO & | & O^-\cdots HO \\ & Ir & \\ {}^-O & | & OH\cdots O^- \\ & H_2O & \end{array} \begin{array}{ccc} & H_2O & \\ & | & O^- \\ & Ir & \\ & | & OH \\ & H_2O & \end{array} \qquad (2)$$

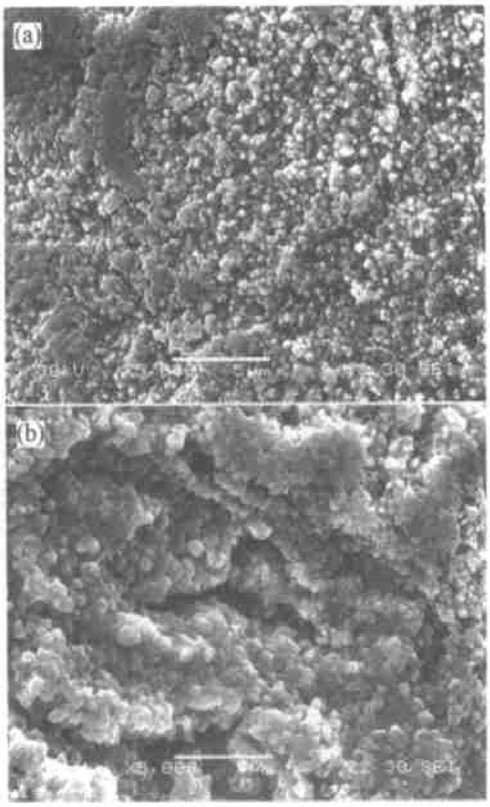


Fig. 6 Surface morphologies of electrode prepared in Li_2CO_3 melt solution at 800 ℃
(a) —3 h; (b) —5 h

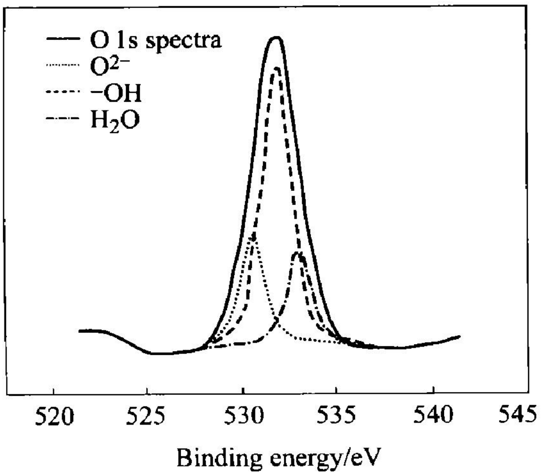


Fig. 7 O 1s XPS spectra of iridium oxide prepared in Li_2CO_3 melt solution at 800 ℃

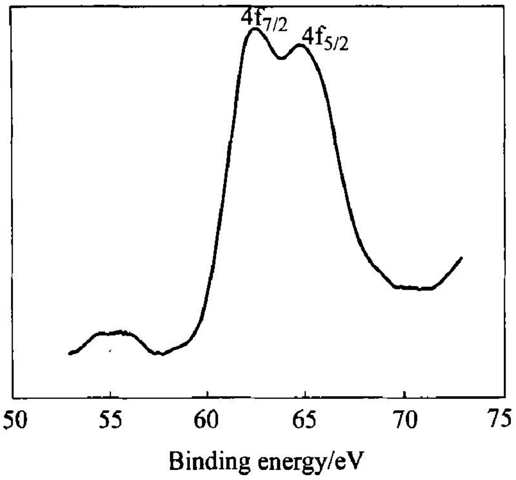


Fig. 8 Ir 4f XPS spectra of iridium oxide prepared in Li_2CO_3 melt solution at 800 ℃

4 RESPONSE MECHANISM OF Ir/ IrO_x pH ELECTRODE

There are mainly two equilibria to describe the H^+ response of the IrO_2 electrode[13]:

$$IrO_2 + 4H^+ + 4e = Ir + 2H_2O \qquad (3)$$

$$2IrO_2 + 2H^+ + 2e = Ir_2O_3 + 2H_2O \qquad (4)$$

The theoretical standard electrode potential of the two reactions are all identical as 681 mV (vs. SCE). It is hard to decide which is the potential determining equilibrium. Different authors hold different opinions, and Ir^{3+} is so susceptible to oxidize in air that it can't be observe by XPS easily[22], unless completely being performed in vacuum condition. On purely theoretical grounds the equilibrium with the highest exchange current density would be expected to be the dominant one, but for equilibria with comparable degrees of reversibility, mixed control of the rest potential could be expected. However, on more empirical grounds the fact that the thick oxide layer formed on iridium by thermal oxidation is hard to be penetrated by ion suggests that the involvement of the underlying metal would be more unlikely. Therefore Eqn(3) is not likely to be significant contributors to the rest potential and we concentrate solely on Eqn (4). A cyclic voltammetry test is carried out to measure the charge storage between 0 and 1 V (vs. SCE), and it is found that the charge storage is as small as 0.058 ~ 0.086 mC/ cm^2 (corresponding to sweep rate of 5 ~ 200 mV/s), much less than the electric quantity needed for the oxidation/reduction involved with bulk oxide. Only the reaction on the oxide surface (comprises of inner and outer surface) is taken into consideration in this article, and this supposition is in good agreement with the theory for thermally prepared RuO_2 electrode[18]. A reaction is presented as Eqn. (5)[24], in which it is also believed that only the surface is involved in the reaction and the surface is co-ordinated with – OH.

$$IrO_x(OH)_y + \delta H^+ + \delta e \rightarrow IrO_{x-\delta}(OH)_{y-\delta} \qquad (5)$$

It is known that the surface is full of – OH and strongly binding H_2O, so the hydration can be described as[11]:

$$IrO_2 + 4H_2O \rightarrow IrO_2 \cdot 4H_2O \qquad (6)$$

$$IrO_2 \cdot 4H_2O \rightarrow [IrO_2(OH)_2 \cdot 2H_2O]^{2-} + 2H^+ \qquad (7)$$

Here a new equilibrium is presented to describe the H^+ response in this melt-oxidized prepared electrode, on the experience of the H^+ response model for electrically grown oxide film[23]:

$$2\{[IrO_2(OH)_2 \cdot 2H_2O]^{2-} \cdot 2H_f^+\} + 2e + 2H_s^+ \rightarrow [Ir_2O_3(OH)_3 \cdot 3H_2O]^{3-} \cdot 3H_f^+ + 3H_2O \qquad (8)$$

In this case, H_f^+ is the protons being already presented as counter ions on the surface, which produced in the process of hydration, and they are equivalent to electrostatically bounded counter ions of exchange resin. H_s^+ is the protons transferred from solutions which will participate the reaction.

$$E = E^0 - \frac{2.303RT}{2F} \lg \frac{\{[Ir_2O_3(OH)_2]\}}{\{[IrO_2 \cdot (OH)_2]\}} \cdot \frac{\{[3H_2O]^{3-} \cdot 3H_f^+\} \cdot [H_2O]^3}{\{[2H_2O]^{2-} \cdot 2H_f^+\}^2 \cdot [H_s^+]^2}$$

$$E = E^0 - \frac{2.303RT}{2F} \lg \frac{\{[Ir_2O_3(OH)_2]\}}{\{[IrO_2 \cdot (OH)_2]\}} \cdot \frac{\{[3H_2O]^{3-} \cdot 3H_f^+\} \cdot [H_2O]^3}{\{[2H_2O]^{2-} \cdot 2H_f^+\}^2} + \frac{2.303RT}{2F} \lg [H_s^+]^2$$

$$E^{0'} = E^0 - \frac{2.303RT}{2F} \lg \frac{\{[Ir_2O_3(OH)_2]\}}{\{[IrO_2 \cdot (OH)_2]\}} \frac{\{[3H_2O]^{3-} \cdot 3H_f^+\} \cdot [H_2O]^3}{\{[2H_2O]^{2-} \cdot 2H_f^+\}^2}$$

$$E = E^{0'} - 0.059\text{pH}$$

That is why $E^{0'}$ is 0.722 ~ 0.576 V (vs. SCE) in the course of hydration, which is a little different from 0.681 V of Eqn.(4).

The Li element in the composition of the surface oxide is not taken into consideration in the above discussion. For metal oxide produced in a Li_2CO_3 melt, however lithiation may occur and a Li-containing product is formed[13, 25]:

$$IrO_2 + Li_2O \rightarrow Li_2IrO_3 \tag{9}$$

The surface of the iridium oxide film is full of -OH and H_2O, so the hydration of the iridium oxide can be written as:

$$Li_2IrO_3 + xH_2O \rightarrow [Li_2IrO_{4-0.5\alpha}(OH)_{\alpha}nH_2O]^{2-}\,2H_f^+ \tag{10}$$

The mole fraction ratio of Ir to O on surface of the oxide is 1∶6.78, determined by EDX, so it is believed that $\alpha = 2$, $n = 2$ in this case, and it is also supposed that the oxide surface in the solution is written as $[Li_2IrO_3(OH)_2 2H_2O]^{2-}\,2H_f^+$.

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