A Comparative Study of Fabricating IrOx Electrodes by High Temperature Carbonate Oxidation and Cyclic Thermal Oxidation and Quenching Process

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Abstract: IrOx electrodes were fabricated by cyclic thermal heating and water quenching (CHQ) process and high temperature carbonate oxidation (HCO), respectively. By examining the E-pH relationship, response rate, potential drift behavior of the fabricated electrodes, the electrodes prepared by CHQ process seemed to show better comprehensive performance. Characterization tests such as scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and electrochemical impedance spectroscopy (EIS) were used to characterize the fabricated IrOx electrodes and find out the reason for the better performance of the electrodes prepared by CHQ process. Morphology tests indicate that the CHQ electrode shows a multi-layer structure with more ion channels, which could provide larger surface area for the H+ response process. Furthermore, combining the XPS, Raman and EIS tests etc., more effective response composition, better crystal quality, and smaller response reaction resistance of surface IrOx film could account for the better performance of the CHQ-fabricated IrOx electrode. The film formation process, H+ response mechanism, as well as the response behavior difference between the two kinds of the electrodes are further elaborated.

Keywords: IrOx electrode; cyclic thermal heating and water quenching (CHQ) process; high temperature carbonate oxidation (HCO); H+ response mechanism

1. Introduction

Among the metal/metal oxides that could be used as H+ detection material/pH electrode, including Pt/PtO2, W/WO3, RuO2, OsO2, IrOx, Ta2O5, SnO2, TiO2, Sb2O3, or a mixture of two kinds of oxides [1–4], iridium oxide is one of the most promising for the better performance of the CHQ-fabricated IrOx electrode. The film formation process, H+ response mechanism, as well as the response behavior difference between the two kinds of the electrodes are further elaborated.
super Nernst sensitivity. The electrochemical CV fabricated ones showed poor reproducibility for both the pH sensitivity and the electrode potential, whereas the electrodes prepared by electrodeposition illustrated poor IrO\textsubscript{x} film to substrate adhesion, the preparation and preservation of the plating solution was also difficult [5,6].

The IrO\textsubscript{x} electrodes fabricated by K. G. Krerder through RF sputtering showed near Nernst response behavior (−59 mV/pH) and good film to substrate adhesion, however the electrode potentials of the fabricated electrodes were quite scattered and greatly depended on the sputtering parameters [17].

The pH sensitive films prepared by high temperature oxidation methods including high temperature carbonate oxidation, and thermal oxidation etc. displayed significant advantage over the other fabricated methods on comprehensive costs, which also illustrated near Nernst response sensitivity, and good film to substrate adhesion, etc.

Sheng Yao et al. [9], and Yiwen Pan et al. [12] all prepared the IrO\textsubscript{x} pH electrodes by method of high temperature carbonate oxidation. Even though large potential deviations existed among the fabricated electrodes, the sensitivities were quite close. Researchers who fabricated the IrO\textsubscript{x} electrodes by thermal oxidation found that electrodes illustrated wide E-pH linear range, relatively fast response rate, and near Nernst response sensitivity [13–16]. Furthermore, electrodes prepared by this method also showed scattered potential distributions, as well as potential drift aroused by hydration effect.

By summarizing the research on IrO\textsubscript{x}-based pH sensors, it is evident that the main efforts are concerned with improving the fabrication method and the examination of electrode performance. The response mechanism of the H\textsuperscript{+} response process is rarely referred.

Based on the transformations among different oxidation states of iridium oxide, the following reactions were proposed.

\[
\begin{align*}
\text{Ir}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- &\leftrightarrow 2\text{Ir} + 3\text{H}_2\text{O} \quad (1) \\
\text{IrO}_2 + 4\text{H}^+ + 4\text{e}^- &\leftrightarrow \text{Ir} + 2\text{H}_2\text{O} \quad (2) \\
2\text{IrO}_2 + 2\text{H}^+ + 2\text{e}^- &\leftrightarrow \text{Ir}_2\text{O}_3 + \text{H}_2\text{O} \quad (3)
\end{align*}
\]

Research carried out by Chen et al. [11] and Huang et al. [13] demonstrated that the surface film was made up of IrO\textsubscript{3}, IrO\textsubscript{2}, Ir\textsubscript{2}O\textsubscript{3} and hydroxide of corresponding valence of iridium, therefore, the H\textsuperscript{+} response reaction could be regarded as reaction 3. However, hydration reaction (reaction 4) is inevitable when the IrO\textsubscript{x} electrodes are immersed in the solution, which should be taken into account when analyzing the H\textsuperscript{+} response mechanism [21].

\[
\text{IrO}_2 + 4\text{H}_2\text{O} \leftrightarrow \text{IrO}_2\cdot 4\text{H}_2\text{O} \quad (4)
\]

Fog et al. [22] and Yao et al. [23,24] believe that “oxygen intercalation” mechanism can be used to describe the H\textsuperscript{+} sensing mechanism of the IrO\textsubscript{x} electrodes prepared by high temperature carbonate oxidation. It is essentially a conversion between compounds with different valence states of Ir.

Although much research has been carried out aimed at improving the performance of the IrO\textsubscript{x} electrodes including the E-pH response range, response rate, long-term stability, etc., more attention should be concentrated on the formation process of the IrO\textsubscript{x} sensitive film, as well as clarifying the essence of the H\textsuperscript{+} response process. In current work, the authors fabricated the IrO\textsubscript{x} electrodes by high temperature carbonate oxidation (HCO) process and cyclic heat treatment and quenching (CHQ) process. The parameters indicating the response performance of the fabricated electrodes were tested in different pH buffers. The morphology, composition, the crystal quality, as well as the response behavior were further characterized. Finally, IrO\textsubscript{x} film formation and H\textsuperscript{+} response mechanism, and the response differences between the electrodes fabricated by HCO and CHQ were discussed.
2. Experimental

2.1. Electrodes Fabrication

2.1.1. Fabrication of IrO$_x$ Electrodes by Cyclic Heat Treatment and Quenching Process (CHQ)

Iridium wires of 99.9% purity with the dimensions of 0.5 mm in diameter and 10 mm in length were ultrasonically cleaned in concentrated hydrochloric acid for 15 min and then soaked in 5 M sodium hydroxide solution for 24 h after washing with deionized water. The wet iridium wires were placed in an alumina crucible and then exposed to ambient air in a medium-temperature muffle furnace. The heat treatment was processed for 0.5 h in air at 800 °C, the oxidized iridium wires were then quenched in deionized water at room temperature. The above heat treatment and quenching process was repeated for 3 times to obtain a thicker and more porous IrO$_x$ film. The iridium wires after oxidation process were soaked in deionized water over 2 days for hydration. As a result, a dark blue sticky iridium oxide film forms on the surface of the iridium substrate.

2.1.2. Fabrication of IrO$_x$ Electrodes by High Temperature Carbonate Oxidation (HCO)

Similarly, iridium wires with the same dimensions and purity were cleaned first, and then placed in an alumina crucible covered by lithium carbonate. After that process, the whole crucible was constantly heated for 5 h in air at 870 °C in a medium-temperature muffle furnace in ambient air, which was followed by a furnace cooling process. Afterwards, the iridium wires were soaked in diluted hydrochloric acid overnight. A constant temperature drying process was then processed for 12 h at 120 °C.

Three parallel samples were prepared under each oxidation condition, the fabricated samples were cured in deionized water when not in use.

2.2. Electrochemical Tests

Buffer solutions of pH ranged from 3 to 11 were prepared by mixing 0.01 M H$_3$PO$_4$, 0.01 M H$_3$BO$_3$, 0.01 M CH$_3$COOH, and 0.1 M KCl, which were calibrated by a commercial glass pH electrode; 0.1 M NaOH and 0.1 M HCl solution were used to adjust the pH of the solutions.

The open-circuit potentials (OCPs) of the HCO- and CHQ-fabricated IrO$_x$ electrodes in different pH buffers were recorded by a potentiostat from Shanghai Chenhua (CHI760D), a saturated calomel electrode (SCE) was used as reference electrode (RE).

EIS tests with applied AC voltage signal of an amplitude of ±10 mV and a scanning frequency range from $10^{-2}$ to $10^5$ kHz were carried out through a three-electrode system utilizing the SCE as the RE, a platinum electrode as the counter electrode (CE) and the fabricated IrO$_x$ electrodes as the working electrodes (WEs) in acid (pH = 3) and alkaline (pH = 11) pH solutions through an electrochemical workstation (Gamry Reference 600, Gamry instruments, Warminster, PA, USA). The fitting of the obtained impedance data was carried out through ZsimpWin software (version 3.50, Princeton Applied Research).

All the electrochemical tests were carried out at room temperature of 24 ± 2 °C.

2.3. Characterizations of the Fabricated IrO$_x$ Electrodes

Surface morphologies of the HCO and CHQ-fabricated IrO$_x$ electrodes were characterized by a scanning electron microscope (SEM, Zeiss Supra 55, Carl Zeiss, Jena, Germany). X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD) tests of the HCO and CHQ-fabricated IrO$_x$ electrodes were performed by employing Al Kα irradiation as the photo source. High-resolution XPS spectra of Ir 4f and O 1s were collected after the acquisition of the wide XPS spectra of the HCO and CHQ-fabricated IrO$_x$ electrodes. The C 1s standard electron peak at 284.8 eV was used to calibrate Binding energies (B.E.) of the obtained spectra. To further figure out the chemical state of the obtained Ir 4f and O 1s data, the deconvolution the photoelectron peaks was processed by Xpspeak41 software, which was fitted graphically within the constraints of Gaussian/Lorentzian peak shapes.
Raman spectra of the fabricated electrodes were recorded using argon ion laser with \( k = 532 \) nm as exciting source through Alpha300RA at room temperature. The spectra were fitting by Origin@ (version 9.2) according to Gaussian/Lorentzian peak shapes.

3. Results

3.1. E-pH Relationships

Cyclic thermal oxidation and high temperature carbonate oxidation methods were used to fabricate the IrO\(_x\) electrodes. Of these processes, cyclic thermal oxidation was an improvement on the traditional high temperature thermal oxidation method. Potential time curves of the IrO\(_x\) electrodes fabricated by the two methods were recorded in different pH buffer solutions of pH ranging from 3 to 11. According to the stable potential at each pH, the E-pH relationships and their error bar plots of the HCO and CHQ electrodes were obtained and are showed in Figure 1a–c.

As shown in Figure 1, the fitting E-pH sensitivities of IrO\(_x\) electrodes fabricated by the above methods are around \(-55--57\) and \(-44--49\) mV/pH, which is quite close to the Nernstian response theoretical value of \(-59.16\) mV/pH; the linear fitting correlation coefficients \( R^2 \) are all larger than 0.97. It is worth mentioning that the pH range of current fabricated methods are satisfactory and superior to previously reported ones showing...
a smaller pH range \cite{12,22,25}. Reason for this phenomenon may be ascribed to suitable surface film compositions generated by appropriate heat treatment conditions.

To be specific, the linear fitting coefficients of the electrodes fabricated by CHQ method are larger than 0.99; those fabricated by HCO are larger than 0.97, and the degree of potential deviation from linear relationship is larger. There is a potential difference existing among the fabricated electrodes although the electrodes are fabricated in the same batch. The error plots of the potential measured in different pH buffer solutions (Figure 1c) demonstrate that those fabricated by CHQ method have a smaller potential difference than those fabricated by HCO method (Figure 1b). As previously investigated, the electrode potential is determined by the $\text{Ir}^{4+}/\text{Ir}^{3+}$ ratio in the surface oxide film \cite{13,21}. Therefore, the electrode potential difference phenomenon is attributed to different heat treatment conditions of each electrode, generating a difference in $\text{Ir}^{4+}/\text{Ir}^{3+}$ ratio in the surface film of each fabricated $\text{IrO}_x$ electrode.

### 3.2. Response Rate

The response rate of an electrode is quite an important parameter. The potential-time curves in pH buffers of 3–11 were recorded, in order to calculate the response rate of the fabricated electrodes. The response time that is needed for an electrode to reach potential stabilization is calculated according to the rules of International Union of Pure and Applied Chemistry (IUPAC), which stipulates that the electrode could be considered as achieving a steady state when the changing rate of the potential is less than 1 mV/min. Therefore, the time period required for the stabilization of the electrode potential of the HCO and CHQ-fabricated electrodes is defined as response time.

The calculated response time and corresponding error bar distribution results of the fabricated HCO and CHQ electrodes is illustrated in Figure 2. As shown in Figure 2, both electrodes fabricated by HCO and CHQ could respond quickly in the pH buffers of 3–11, especially in weakly acidic, nearly neutral, and weakly alkaline solutions. However, all the $\text{IrO}_x$ electrodes fabricated by HCO illustrate longer response time than the CHQ-fabricated ones. To be specific, the average response time of $\text{IrO}_x$ electrodes fabricated by CHQ method are within 30 s in weakly acidic, nearly neutral, and weakly alkaline solutions, whereas this time becomes larger when responding in pH = 3 and pH = 11 solutions. This behavior is quite similar to that of the commercial glass electrode. It is noteworthy that the CHQ-fabricated electrodes could response within seconds in some conditions. Similarly, the response time of the HCO-fabricated electrodes is almost three times larger than that of the CHQ ones.

![Figure 2](image_url)

**Figure 2.** Error bar plots of the response time in pH buffers of 3–11 for electrodes fabricated by HCO (■) and CHQ (●).
3.3. Relative Long-Term Stability

Relative long-term stability is another important parameter for evaluating the performance of pH electrode. Electrode potential monitoring before/after five days in different pH buffers of the HCO- and CHQ-fabricated electrodes were recorded. The obtained E-pH relationships of the two kinds of fabricated electrodes are displayed in Figure 3. The relative long-term performance indicators including E-pH intercept, potential drift, E-pH sensitivity, E-pH sensitivity change, and coefficients for linear fitting of the IrO\textsubscript{x} electrodes before/after five days of immersion are illustrated for a clearer comparison (seen in Table 1).

![Figure 3](image)

Figure 3. Relative long-term stability within 5 days (■ before five days, ● after five days) of electrodes fabricated by HCO (a) and CHQ (b) in different pH buffers.

| Heat Treatment Conditions | E\textsubscript{intercept} (mV) | Potential Drift in pH 3–11 (mV) | E-pH Sensitivity (mV/pH) | E-pH Sensitivity Change (mV/pH) | Linear Fitting Coefficient |
|---------------------------|--------------------------------|---------------------------------|--------------------------|-------------------------------|---------------------------|
| Before 5 Days             | 432.1                          | 0–90.3                          | −38.08                   | −20.50                        | 0.9951                    |
| After 5 Days              | 578.3                          |                                 | −59.58                   |                               | 0.9989                    |
| Before 5 Days             | 630.1                          | 6.62–13.82                      | −59.60                   | −60.50                        | 0.90                      |
| After 5 Days              | 626.18                         |                                 | −60.50                   |                               | 0.9998                    |

The results of relative long-term monitoring shown in Figure 3 and summarized in Table 1 indicate that the E-pH relationship (E-pH sensitivity, intercept) of the HCO IrO\textsubscript{x} electrode changes markedly, whereas the linear relationship, and the linear fitting coefficient remain. To be specific, the potential drift in pH 3–11 solutions and E-pH change are 0–90.3 mV and −20.5 mV/pH, respectively, the fitting linear relationship changes from E = 432.1–38.08 pH to E = 578.3–59.58 pH. The E-pH relationship illustrated in Figure 3b does not show much change, changing from E = 630.10–59.60pH to E = 626.18–60.50pH, among which, the potential drift in pH 3–11 solutions and E-pH change are 6.62–13.82 mV and −0.90 mV/pH, respectively. The lineairties for both cases are quite satisfied, however potential drift phenomenon of the HCO IrO\textsubscript{x} electrode indicates frequent calibration is required during its usage. It should be noted that even commercial glass pH electrode needs to be calibrated before each use to ensure accurate measurement.

3.4. Surface Morphology

The macro-/micro-structures of the IrO\textsubscript{x} electrodes fabricated by CHQ and HCO were inspected, the surface appearances of which are shown in Figure 4. As shown in Figure 4a,b, macro-structures of the surface film of all the fabricated IrO\textsubscript{x} electrodes show

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Table 1. Long-term performance parameters variation of the HCO and CHQ-fabricated IrO\textsubscript{x} electrodes within 5 days.
significant difference in surface appearance, i.e., a uniform surface is obtained for the electrode fabricated by CHQ, whereas quite obvious surface inhomogeneity appeared for the electrode fabricated by HCO. This phenomenon is attributed to melt at high temperature. Micro-structures of the fabricated IrO\textsubscript{x} electrodes (Figure 4a',b') show that the surface film is made up of particles with size ranging from several nanometers to micrometer order. The particle size range of the CHQ-fabricated electrode is much more uniform than that of the HCO one. It is believed that the particles continue growing with higher temperature and heating time, resulting in an irregular structure and nonuniform size in particle volume. Uniform particles on the surface film correspond to more ion channels and larger reaction area of the electrodes, which results in a faster response rate during H\textsuperscript{+} response process.

Figure 4. Macro (a,b) and micro (a',b') morphologies of electrodes fabricated by HCO and CHQ, respectively.

3.5. XPS Results

The elemental chemical state and surface film composition of the IrO\textsubscript{x} electrodes fabricated by HCO and CHQ methods were collected and illustrated in Figure 5. Wide spectra of the IrO\textsubscript{x} film surface were collected first, then, the two top intense lines, Ir 4f and O 1s spectra, were identified. The collected Ir 4f and O 1s spectra and corresponding deconvolutions are shown in Figure 5a,a' (HCO) and Figure 5b,b' (CHQ), respectively. The experimental results and the deconvoluted results are displayed as bold black lines, and dash and dot lines, respectively. Detailed analysis was carried out based on the deconvoluted data. Binding energies (B. E.) of Ir 4f and O 1s obtained from our experiments and from the literatures are summarized and listed in Table 2. Comparing the experimental data with the ones in the table, the valence state and elements existing form were determined.
Figure 4. Macro (a,b) and micro (a’,b’) morphologies of electrodes fabricated by HCO and CHQ, where (a,b) are the Ir 4f spectra and (a’,b’) are the O 1s spectra. The experimental results and the fitted results are displayed as bold black lines, and broken lines, respectively.

Figure 5. XPS results of IrOx electrodes fabricated by HCO (a,a’) and CHQ (b,b’), where (a,b) are the Ir 4f spectra and (a’,b’) are the O 1s spectra. The experimental results and the fitted results are displayed as bold black lines, and broken lines, respectively.

The Ir 4f spectrum acquired from the IrOx electrode fabricated by HCO method can be deconvoluted into two peaks, one located at 62.71 eV (4f(7/2)) and 65.66 eV (4f(5/2)) corresponding to Ir⁴⁺, and the other one located at 64.00 eV (4f(7/2)) and 66.95 eV (4f(5/2)), the binding energy of which is close to the binding energy of Ir⁶⁺. The peak at 62.71 eV (4f(7/2)) and 65.66 eV (4f(5/2)) is generated due to high temperature carbonate oxidation. The structures at 64.00 (4f(7/2)) and 66.95 eV (4f(5/2)) are defective and resulting from

### Table 2. B.E.s of Ir and O obtained from our XPS results and in the literature.

|                  | B.E. of Ir (4f 7/2, 4f 5/2)/eV | B.E. of O (1s)/eV | Oxide | Hydroxide or Bound Water | H₂O or O₂ |
|------------------|--------------------------------|-------------------|-------|--------------------------|-----------|
| **Ir³⁺**         | 61.6, 64.55                     | [26,27]           | 528.1–531 [28] | 530.6–532 [28] | 532.5–533.5 [28] |
| **Ir⁴⁺**         | 62.7, 65.65                     | [26,27]           | 531.0 | 531.9                    | 533.0     |
| **Ir⁶⁺**         | 64.3, 67.25                     | [26,27]           |       |                          |           |
| **Oxide**        |                                 |                   | 530.6–532 [28] | 532.5–533.5 [28] |
| **Hydroxide or Bound Water** | 531.0 | 531.9 | 533.0 |
| **H₂O or O₂**    |                                 |                   | 532.5–533.5 [28] |
| **Relative content** | 0.7611 | 0.2389 | 0.1572 | 0.7137 | 0.1291 |

**CHQ**

|                  | B.E. of Ir (4f 7/2, 4f 5/2)/eV | B.E. of O (1s)/eV | Oxide | Hydroxide or Bound Water | H₂O or O₂ |
|------------------|--------------------------------|-------------------|-------|--------------------------|-----------|
| **Ir³⁺**         | 61.75, 64.70                    | [26,27]           | 530.6–532 [28] | 532.5–533.5 [28] |
| **Ir⁴⁺**         | 62.40, 65.35                    | [26,27]           | 532.0 | 533.0                    | 533.0     |
| **Ir⁶⁺**         | 64.20, 67.15                    | [26,27]           |       |                          |           |
| **Oxide**        |                                 |                   | 532.5–533.5 [28] |
| **Hydroxide or Bound Water** | 532.0 | 533.0 |
| **H₂O or O₂**    |                                 |                   | 533.0 |
| **Relative content** | 0.3245 | 0.4440 | 0.2315 | 0.2069 | 0.6624 |

The relative content of different valences within a spectrum was calculated according to the binding energy of which is close to the binding energy of Ir⁶⁺.

The relative content of different valences within a spectrum was calculated according to the binding energy of which is close to the binding energy of Ir⁶⁺.
heat treatment at high temperature, which does not take part in the H⁺ response process. The ratio of iridium with different valences within a spectrum was calculated according to the deconvoluted peak areas. The content of Ir⁴⁺ is 0.7611, while that of Ir⁶⁺ is 0.2389. Differing from the Ir 4f spectrum of HCO method, the Ir 4f spectrum obtained from CHQ method shows three structures, i.e., the structure at 61.75 eV (4f(7/2)) and 64.70 eV (4f(5/2)), 62.40 eV (4f(7/2)) and 65.35 eV (4f(5/2)), and 64.20 eV (4f(7/2)) and 67.15 eV (4f(5/2)), corresponding to Ir³⁺, Ir⁴⁺, and Ir⁶⁺, respectively. Relative content for different valence of Ir is 0.3245, 0.4440, and 0.2315, respectively.

The O 1s spectra of the IrOₓ electrodes fabricated by HCO and CHQ methods are illustrated in Figure 5a,b. The O 1s deconvoluted peaks of the HCO electrode locate at 531.0, 531.9, and 533.0 eV, which could be assigned to lattice oxide, hydroxide or bound water, and adsorbed H₂O or O₂, respectively. The peak located at 531.0 eV is caused by high temperature carbonating oxidation; while the peak at 531.9 eV is ascribed to hydration process during the IrOₓ electrode’s soaking in solutions; the peak at 533.0 eV is considered to be aroused by adsorbed H₂O or O₂. Similar deconvoluted peaks are also observed for the IrOₓ electrodes fabricated by CHQ method, detailed peak positions and relative content are shown in Table 2.

The electrode surfaces for both fabricated conditions are made up of different valences of Ir oxides and hydroxides. Among the components that generated on the electrodes’ surface, Ir³⁺ and Ir⁴⁺ are the effective ones contributing to the H⁺ response process of the IrOₓ electrode, whereas Ir⁶⁺ is considered as a defective structure by Kim et al. [27], which does not participate in the H⁺ response process. Obviously, higher heat treatment temperature makes the oxidation state of Ir fabricated by HCO method higher than that of the Ir fabricated by CHQ method, which results in higher concentration of defect structures.

3.6. Raman Results

Raman tests were performed to investigate the surface crystal qualities of the surface IrOₓ films fabricated by HCO and CHQ, the collected results and their deconvolution peaks are illustrated in Figure 6. The experimental results and the deconvoluted results are shown as bold black lines and colored lines, respectively.

![Figure 6](image-url) Raman spectra of the IrOₓ electrodes fabricated by HCO (a) and CHQ (b). The measured results and the fitted results are shown as bold black lines and broken lines, respectively.

Raman spectrum of the IrOₓ electrode fabricated by HCO shown in Figure 6a displays two major peaks at 547.4 and 700.4 cm⁻¹, whereas spectrum of the electrode fabricated by CHQ (Figure 6b) after deconvolution shows three peaks located at 552.9, 712.5 and 735.9 cm⁻¹, respectively. The Raman peaks of CHQ treatment electrode are quite close to the first order single crystal Raman modes of IrO₂ namely E₂g, B₁g, and A₁g modes, located.
at 561, 728, and 752 cm\(^{-1}\), respectively,\([29–31]\), demonstrating the good quality of the surface \(\text{IrO}_x\) film of the electrode fabricated by CHQ. It is believed that two peaks indicating \(A_{1g}\) and \(B_{2g}\) modes of the HCO electrode overlap with each other merging into one peak. Comparing with the Raman bands of single crystal, both of the fabricated electrodes exhibit Raman red-shift. The Raman features of the CHQ electrode illustrate a blue-shift in contrast to that of the HCO electrode, indicating an enhancement of compressive stress or the relief of tensile stress in the crystal \([31]\). The line-shape and position of Raman features vary for the different films fabricated by different methods, these differences are due to the existence of stress between the generated films and the Ir substrates \([30]\).

Additionally, fitting parameter of Raman spectrum, full width at half-maximum (FWHM), can be used to estimate the crystal size. By referring to spatial correlation theory \([32,33]\), the spatial correlation length is related to the crystal packing and the structural damage. If each microcrystalline grain on the substrate is considered as a perfect crystallite, the larger and more uniform grain exhibits a longer coherence length and then illustrate a narrower FWHM in the Raman spectrum. Thus, the larger FWHM is, the smaller the grain size is \([34]\). As shown in Table 3, FWHM value of the \(\text{IrO}_x\) electrode fabricated by CHQ is smaller than that of HCO electrode, indicating an enlargement of \(\text{IrO}_x\) grain size and more uniform surface. This phenomenon can account for the fast response rate of electrodes fabricated by CHQ during the response process.

Table 3. Raman shift and deconvoluted peaks messages of electrodes fabricated by HCO and CHQ.

| Sample          | HCO     | CHQ     |
|-----------------|---------|---------|
| Raman shift/cm\(^{-1}\) | 547.4   | 700.4   |
| FWHM/cm\(^{-1}\)     | 88.75   | 90.18   |
| Peak area ratio    | 62.05   | 37.95   |

3.7. EIS Results

EIS tests were carried out to study the \(\text{IrO}_x\) film because of its non-destructive measurement ability, which could also help to understand the reason for the different response rates and the dynamic behavior of \(\text{IrO}_x\) electrodes fabricated by different methods. EIS tests performed in pH = 3 and pH = 11 buffers of the HCO- and CHQ-fabricated electrodes were conducted. The experimental and fitted results obtained from pH = 3 are plotted as Nyquist and Bode plots, shown in Figure 7. Porous \(\text{IrO}_x\) film generated on the Ir substrate as a result of the heat treatment process, the \(\text{H}^+\) response process occurs at the film/solution interface. For this \(\text{IrO}_x\) electrode/solution system, the surface electrode film is inhomogeneous and conductive, the behavior of which deviates from the capacitance, therefore, \(Q\) and \(n\) were used to replace capacitance. The equivalent circuit model is proposed based on the above actual physical structure of the electrode and \(\text{H}^+\) response process. Similar results could be acquired from the pH = 11 buffer (in Supplementary Materials, Figure S2). For the sake of saving space, corresponding results will not be demonstrated here.

It can be seen that there are two arcs in Nyquist and Bode plots, among which, the arcs at the high frequency band correspond to the properties of the HCO/CHQ-fabricated \(\text{IrO}_x\) films, while the arcs at the low frequency side reflects the \(\text{H}^+\) transportation, i.e., response process, namely, the electrode/solution response process of the fabricated electrodes \([35,36]\). In Nyquist plots, the presence of diffusion tails in the low frequency side indicates the occurrence of mass transport process.
Figure 7. Electrochemical impedance spectra of the IrOx electrodes in pH = 3 (a-c) buffer. (a) Nyquist plots, (b) Bode modulus plots, (c) Bode angle plots. The original data are shown as spots and fitted data are shown as lines.

Based on the EIS data and the understanding of the practical electrochemical response process, the equivalent circuit (EC) model $R(QR)(Q(RW))$ illustrated in Figure 8a was selected to fit the impedance data, among which, $R_s$ is the solution resistance, $R_f$ is the film resistance, $R_{ct}$ is the reaction resistance of the $H^+$ response process, and $W$ is the Warburg resistance. The surface electrode film fabricated by HCO and CHQ is inhomogeneous and conductive, the behavior of which deviates from the pure capacitance; therefore, $Q$ and $n$ are used instead of capacitance. $Q$ is used to offset the dispersion of the current electrode/solution system, representing the frequency dispersion of time constants aroused by the local inhomogeneity, porosity, and roughness of the fabricated electrode film. The different craft for fabricating the two kinds of electrodes act to oxide film with different properties, leading to differences in the values of $Q$. A model in Figure 8b indicating a porous structured IrOx film was also proposed. $H^+$ will transport from the outer layer to the inner layer of the oxide film during the response reaction, meanwhile, the electrochemical reaction takes place at the solution/film interface.

Figure 8. Equivalent circuit model $(R(QR)(Q(RW)))$ (a) and schematic (b) of fabricated surface film when the electrodes are soaked in pH buffers.
As shown in Figure 7, the proposed EC illustrated in Figure 8a could fit the impedance data well. The fitted results illustrated in Table 4 indicate that the film resistances of the electrodes fabricated by the two methods do not have larger differences. However, the reaction resistances of the IrO\textsubscript{x} films fabricated by CHQ electrodes are much lower than that of the electrodes fabricated by HCO, which means much more channels of the CHQ electrodes are provided, indicating a faster response rate during the H\textsuperscript{+} response process. These response-reaction results can also correspond to the results of the response rate part.

### Table 4. EIS fitting parameters for equivalent circuit model R(QR)(Q(RW)) of HCO- and CHQ-fabricated electrodes obtained in pH = 3 and pH = 11 buffer solutions, respectively.

| Condition   | R, S\text{Ω} \cdot \text{cm}^{2} | Q, \mu\text{F} \cdot \text{cm}^{-2} | n, | R, S\text{Ω} \cdot \text{cm}^{2} | Q, \mu\text{F} \cdot \text{cm}^{-2} | n, | R, S\text{Ω} \cdot \text{cm}^{2} |
|-------------|----------------------------------|----------------------------------|----|----------------------------------|----------------------------------|----|----------------------------------|
| pH3-(CHQ)   | 8.806 \times 10^{-3}             | 0.752                            |    | 1.160 \times 10^{-3}             | 0.684                            |    | 453.2                            |
| pH11-(CHQ)  | 2.702                            | 0.728                            | 1.554 | 8.973 \times 10^{-4}             | 0.759                            | 1.512 \times 10^{-3}             |
| pH3-(HCO)   | 3.04                             | 0.719                            | 8.514 \times 10^{5}             | 0.759                            | 1.536 \times 10^{-3}             |
| pH11-(HCO)  | 10.7                             | 0.702                            | 3.33 \times 10^{5}             | 0.939                            | 396.5                            | 2.043 \times 10^{-3}             |

3.8. IrO\textsubscript{x} Film Formation and H\textsuperscript{+} Response Behavior Discussion

#### 3.8.1. IrO\textsubscript{x} Film Formation

It is not easy to oxidize Ir metal to a stable oxide by conventional electrochemical or chemical methods. Oxidizing the Ir metal through high temperature oxidation is an effective way. For electrodes fabricated by HCO, the formation of sensitive surface oxide film on Ir substrate involves the formation of a peroxide ion (O\textsubscript{2}\textsuperscript{2-}) in alkaline environment during the high temperature oxidation process [37]. In this oxidation process, O\textsubscript{2} in the air will react with the solute and form O\textsubscript{2}\textsuperscript{2-}, which is a strong oxidant, especially at high temperature.

\[
\text{O}_2 + 2\text{CO}_2 \leftrightarrow 2\text{O}_2\textsuperscript{2-} + 2\text{CO}_2 \quad (5)
\]

\[
\text{Ir} + 2\text{O}_2\textsuperscript{2-} \leftrightarrow \text{IrO}_2 + 2\text{O}_2 \quad (6)
\]

\[
\text{O}_2\textsuperscript{-} + \text{CO}_2 \leftrightarrow \text{CO}_3\textsuperscript{2-} \quad (7)
\]

Hence, it is the oxidation of the metal by O\textsubscript{2}\textsuperscript{2-}, combining reactions of 5, 6, and 7, the overall reaction will be reaction (8) shown as follows:

\[
\text{Ir} + \text{O}_2 \leftrightarrow \text{IrO}_2 \quad (8)
\]

The reaction (8) illustrates that Ir is directly oxidized by O\textsubscript{2} from the air during high temperature heating process, although the oxidation mechanism is electrochemical in nature. Therefore, the carbonate melt acts as a solvent, and converts dissolved O\textsubscript{2} to a stronger oxidizing species, i.e., O\textsubscript{2}\textsuperscript{2-}.

It is believed that the high temperature oxidation process (reaction 8) occurs directly to the Ir electrode generating an oxide film on Ir surface for the electrodes fabricated by CHQ. In the experiment, we found that under an air atmosphere, the Ir wire could be easily oxidized by pre-treatment of the wires in strong alkaline solutions and a thick black oxide layer was observed on the wire surface with half an hour’s heat treatment. During the cyclic of high temperature oxidation and quenching process, the IrO\textsubscript{x} film will continuously grow thicker, and form a double layer structure, i.e., the porous outer layer and dense inner layer structure (Figure S1).

From the perspective of energy conservation, emission reduction, and economic conservation, it is recommended to prepare the IrO\textsubscript{x} electrode by CHQ for the reasons of energy and cost conservation.

#### 3.8.2. H\textsuperscript{+} Response Mechanism of the Fabricated IrO\textsubscript{x} Electrodes

The H\textsuperscript{+} response mechanisms of the fabricated IrO\textsubscript{x} electrodes are still not confirmed, the differences between the H\textsuperscript{+} response mechanisms of electrodes fabricated by HCO and CHQ are indistinct, which is discussed and compared in the following paragraphs.
Ir usually presents valences of +1, +2, +3, +4, and +6 in its oxides. The response models approved mainly bases on the redox equilibrium between the two oxidation states of the iridium oxide leading to the ability for pH response.

The “Oxygen intercalation” mechanism is proposed by Fog et al. [22], which is the best to describe the H⁺ sensing mechanism of the HCO electrodes. Operating on this theory, when the higher and lower valence iridium oxide couple achieves equilibrium in the solution, the following reaction occurs:

\[
\text{Li}_x\text{IrO}_y + 2\delta\text{H}^+ + 2\delta\text{e}^- \leftrightarrow \text{Li}_x\text{IrO}_y - \delta + \delta\text{H}_2\text{O} \quad (9)
\]

where Li₂IrOₓ and Li₂IrOₓ - δ are oxygen enrich phase with higher oxidation state and oxygen deficient phase with a lower oxidation state, respectively. The equilibrium potential can be inferred according to the Nernst equation and be shown as follows:

\[
E = E_0 + \frac{2.303RT}{2\delta F} \log \left[ \frac{[\text{Li}_x\text{IrO}_y] \cdot [\text{H}]^{2\delta}}{[\text{Li}_x\text{IrO}_y - \delta]} \right] = E_0 + \frac{2.303RT}{2\delta F} \log \left[ \frac{[\text{Li}_x\text{IrO}_y]}{[\text{Li}_x\text{IrO}_y - \delta]} \right] + \frac{2.303RT}{F} \log [\text{H}^+] \quad (10)
\]

\[
E = E_0' - \frac{2.303RT}{F} \text{pH} = E_0' - 59.16\text{pH} \quad (11)
\]

Therefore, the equilibrium electrode potential is pH/H⁺ dependent, the value of which is close to Nernstian slope of −59.16 mV/pH at 25 °C. While the \( E_0' \) in Equation (11) is decided by the ratio of Li₂IrOₓ and Li₂IrOₓ - δ, the higher the ratio is, the larger the \( E_0' \). According to Equations (10) and (11), this electrode potential \( E_0' \) is related to the oxidation state of the fabricated electrode, which is difficult to control. Therefore, the electrode potentials of the electrodes of different batches fabricated by the same craft differ from each other, and even the electrode potentials of the electrode made from the same batch differ. Additionally, the authors found that a hydration effect occurs when soaking the thermal oxidized electrodes into solutions, which may also occur to the HCO electrodes, and affect the electrode potential.

For the CHQ-fabricated electrodes, the following hydration reaction occurs once being immersed in the solution, which (Equation (4)) should be not neglected when discussing the H⁺ response mechanism. According to the XPS results, the transformation among \( \text{Ir}^{4+} \) and \( \text{Ir}^{3+} \) leads to the H⁺ response ability of \( \text{IrO}_3 \) electrode; \( \text{Ir}^{6+} \) is a defect structure verified by Kim et al. [27]. Therefore, the Equation (12) is proposed to give a clearer profile for the understanding of the H⁺ response mechanism. Obeying the criterion of Nernst equation, the equilibrium electrode potential can be speculated as Equations (13) and (14).

\[
2 \left[ \text{IrO}_2\text{(OH)}_2 \cdot 2\text{H}_2\text{O} \right]^{2-} \cdot 2\text{H}^+ + 2\text{e}^- + 2\text{H}^+ \leftrightarrow [\text{Ir}_2\text{O}_3(\text{OH})_3 \cdot 3\text{H}_2\text{O}]^{3-} \cdot 3\text{H}^+ + 3\text{H}_2\text{O} \quad (12)
\]

\[
E = E_0 + \frac{2.303RT}{2F} \log \left\{ \frac{[\text{IrO}_2\text{(OH)}_2 \cdot 2\text{H}_2\text{O}]^{2-} \cdot 2\text{H}^+}{[\text{Ir}_2\text{O}_3(\text{OH})_3 \cdot 3\text{H}_2\text{O}]^{3-} \cdot 3\text{H}^+} \right\}^2 + \frac{2.303RT}{F} \log \left[ \text{H}^+ \right] \quad (13)
\]

\[
E = E_0'' - \frac{2.303RT}{F} \text{pH} = E_0'' - 59.16\text{pH} \quad (14)
\]
3.8.3. Discussion about the Response Behavior Difference between the Electrodes Fabricated by HCO and CHQ

The electrodes fabricated by the HCO and CHQ all have the sensitivity close to Nernst response, although the HCO-fabricated electrodes need more time for achieving this response sensitivity. This state is further affected by the structure of the electrode. The response sensitivity is mainly influenced by the quantity of electron transfer during the H⁺ response process. The phenomenon of Nernst response can be interpreted by the response reactions for the HCO- and CHQ-fabricated electrodes listed in reactions 9 and 12.

The electrode potentials for all the fabricated electrodes are scattered, and drift with time’s prolongation, which is decided by the $\text{Ir}^{4+}/\text{Ir}^{3+}$ ratio as well as the hydration degree of the surface oxide film, among which, $\text{Ir}^{4+}/\text{Ir}^{3+}$ ratio is determined by the thermal oxidation process. Conversely, the hydration process is influenced by many factors including the composition, structure of the electrode, and the immersed time, etc. By examining the surface compositions of the fabricated electrodes through XPS, it is found that more effective compositions, namely $\text{Ir}^{3+}$ and $\text{Ir}^{4+}$, existing in the surface film of the CHQ-fabricated electrode, which is more preferable for the H⁺ response process. This is one of the reasons for its fast response.

The response time, another important parameter for the pH electrode, results of which displayed in the Figure 2, shows differences for the electrodes fabricated by HCO and CHQ. The response rate can also be reflected by the EIS results, although both of the two kinds of fabricated electrodes did not show significance differences in film resistance, the CHQ-fabricated electrode demonstrates a much smaller reaction resistance ($R_{\text{ct}}$). The CHQ-fabricated electrodes with a more uniform surface (Figure 4b) respond faster than the HCO-fabricated ones, meaning they have more channels and real surface area participating into the H⁺ response reaction process. Besides, the Raman spectrum of the CHQ-fabricated electrode is much closer to the first-order single crystal Raman modes of $\text{IrO}_2$ comparing with the HCO-fabricated electrode, indicating the good quality and response property of the surface $\text{IrO}_x$ film, which is considered to be another reason for its response property.

4. Conclusions

The $\text{IrO}_x$ electrodes were fabricated by the HCO and CHQ process. High temperature oxidation process occurs directly to the Ir electrode, generating an oxide film on Ir surface; the Ir wires could be easily oxidized by pre-treatment/treatment of the wires in strong alkaline solutions.

Both of the fabricated electrodes illustrate the near Nernst response behavior with the response sensitivity close to 59.16 mV/pH in the examined pH range. This is related to the number of electrons transferred during the H⁺ response process. The electrode potentials of the fabricated electrodes are scattered and drift with time, which is decided by the heat treatment conditions, i.e., $\text{Ir}^{4+}/\text{Ir}^{3+}$ ratio, as well as the hydration degree of the surface oxide film.

The CHQ-fabricated electrodes with uniform surface morphology and large real surface area show faster response rate, better relative long-term stability. Better crystal quality close to first order single crystal Raman modes and larger surface effective compositions composing of $\text{Ir}^{3+}$ and $\text{Ir}^{4+}$ can account for the fast response rate of the CHQ-fabricated $\text{IrO}_x$ electrodes.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/coatings11101202/s1, Figure S1: Cross section morphology of the fabricated $\text{IrO}_x$ electrode, Figure S2: Electrochemical impedance spectra of the $\text{IrO}_x$ electrodes in pH = 11.

Author Contributions: Conceptualization, F.H.; methodology, F.H.; software, F.H. and Q.W.; validation, F.H., Q.W. and W.W.; formal analysis, F.H. and Q.W.; investigation, F.H. and J.W.; resources, F.H. and Y.J.; data curation, F.H., S.W. and Y.Z.; writing—original draft preparation, F.H.; writing—review and editing, F.H.; visualization, F.H. and P.B.; supervision, L.W. and Y.J.; project administration,
Funding: This research was funded by Innovation Group Project of Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), grant number No.311021013. We are also grateful to the support from Beijing Municipal of Science and Technology (ID: Z20110000452001), Fundamental Research Funds for Central Universities (Project ID: FRF-TP-19-011A2), and the 111 Project (grant No. B12012) for promoting international exchange.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Data sharing is not applicable for this article.

Conflicts of Interest: The authors declare no conflict of interest.

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