

Article

The Form of Electrodeposited Iridium Ions in a Molten Chloride Salt and the Effects of Different Iridium Concentrations

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Abstract: A molten salt system was prepared using an optimized method. We studied the complex structure of Ir³⁺ ions in the molten salt system and the influence their concentration had on the quality of the coatings prepared via electrodeposition. Using TG-DSC and in situ XRD experiments, we studied the high-temperature characteristics and properties of IrCl₃ alongside its thermal stability. Using in situ XRD and Raman spectroscopy, we analyzed the Ir ions' complex structure and the variation in the molten salt system at high temperatures. Finally, the changes in the Ir ion concentration in the molten salt system and the influence of the microstructure of the coatings' surfaces were investigated under different anode conditions. IrCl₃ easily decomposes above 400 °C, and temperature increases accelerate the rate of this decomposition. When the NaCl-KCl-CsCl system is in a high-temperature, molten state, IrCl₃ forms stable complex structures (IrCl₆)^{3−} and (IrCl₆)^{2−}, and the valence state of Ir will be transformed with the increase in temperature. Generating these complex structures is conducive to improving the Ir coating quality. During the electrodeposition process, too few Ir ions in the molten salt can lead to concentration polarization, affecting the quality of the coating. Application of the molten NaCl-KCl-CsCl system is conducive to the electrodeposition of Ir coatings in a suitable temperature range. At the same time, using Ir as the anode can enhance the quality of the coatings.

Keywords: molten salt; IrCl₃; in situ XRD; in situ Raman; electrodeposition; coating; complex structure



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1. Introduction

The metal iridium (Ir) has an extremely high melting point (2445 °C), strong corrosion resistance, high strength, and stable physical and chemical properties. In high-temperature, oxygenated environments, Ir has a strong antioxidant capacity because of its extremely low oxygen permeability and vapor pressure [1–4]; it is an ideal material for thermal protective coatings and can be used in aerospace, weaponry, and other fields [5–7].

The most commonly used technologies for Ir coating preparation are chemical vapor deposition (CVD) [8–12], double glow plasma (DGP) [13–16], magnetron sputtering (MS) [17–20], Atomic Layer Deposition (ALD) [21–24], and electrodeposition (ED) [25–27]. CVD is an outdated means of preparing Ir coatings; the precursors required are expensive and less commonly utilized, and controlling the deposition atmosphere conditions is complicated. DGP and magnetron sputtering are used to prepare Ir coating target materials; these methods are expensive, and the resulting coating is thin. ED is simple, has a high deposition rate, and can meet the needs of industrial production at a low cost.

Various systems are used for the preparation of Ir coatings using ED, among which the ternary NaCl-KCl-CsCl molten salt system [28,29] is the most widely used; the Ir coatings deposited using this method are continuous, dense, and effective. Zhu [30–32] successfully prepared Ir coatings on a variety of substrate (molybdenum, rhenium, and a C/C composite) surfaces using this molten salt system. The electrodeposition temperature

and current density are related to the quality, morphology, and densities of the coatings. In addition, the Ir coatings showed better bonding on the rhenium (Re) matrix. Huang [33,34] investigated the electrochemical behavior of Ir^{3+} during the electrodeposition process. They found that the electrochemical reduction of Ir^{3+}/Ir is a diffusion-controlled irreversible reaction in the temperature range of 823 K to 883 K, but it transformed into a diffusion-controlled quasi-reversible reaction when the temperature increases to 913 K. However, regarding the high-temperature changes in molten salts, the electrochemical reduction of Ir^{3+}/Ir is a diffusion-controlled quasi-reversible reaction. However, there are fewer reports on the physicochemical properties and Ir^{3+} ion complexation law during the changes in molten salts at high temperatures. Research in this direction can lead to better-optimized molten salt structures and can improve the deposition quality of Ir coatings.

In this paper, NaCl-KCl-CsCl was used as the molten salt system, and IrCl_3 was used as the source of Ir^{3+} for the preparation of Ir coatings via electrodeposition. The complex structure of Ir in the molten salt system with Ir^{3+} ions and the influence of their concentration on the quality of the coatings prepared via electrodeposition were investigated, providing a reference and ideas for the optimization and preparation of molten salt systems. Firstly, the thermal stability of IrCl_3 was investigated via TG-DSC and in situ XRD. Based on this, the complex structure of Ir ions in the molten salt system and the effect of temperature were analyzed via in situ XRD and Raman spectroscopy. Finally, the influence of the concentration of Ir^{3+} ions in the molten salt system on the quality of the electrodeposited Ir coatings was investigated.

2. Materials and Methods

2.1. Preparation of Molten Salts

All the operations for the molten salts were carried out in a vacuum glove box. NaCl-KCl-CsCl (analytical grade 99.99%, aladdin, Shanghai, China) was used as the base molten salt, and IrCl_3 (analytical grade 99.99%, aladdin, Shanghai, China) was used as the main salt to build the molten salt system. A total of 100 g of NaCl-KCl-CsCl was weighed using an electronic balance, of which 32% of the total weight was NaCl and KCl (the molar ratio of NaCl-KCl was maintained at 1:1, with 14.1 g and 17.9 g, respectively), and 68% of the total weight was CsCl (68 g). The mass of IrCl_3 was 5% (5 g) of the total mass of the base molten salt. The weighed molten salt was placed in an agate mortar, thoroughly ground to produce a homogeneous mixture, placed in a corundum crucible, and dried under vacuum at 180 °C for 16 h to remove water.

2.2. Study of the Structure of Ionic Complexes in Molten Salt Systems

The molten salt system was studied using an X-ray powder diffractometer (in situ XRD) (model: Empyrean) from Malvern Panalytical, Almelo, Netherlands, under an argon atmosphere. The temperature range was 30 °C to 1000 °C, and the heating rate was 10 °C/min. The measurement angle of each test point ranged from 10° to 90° to study the changes in the physical molten salt system at high temperatures.

In situ Raman measurements of the molten salt system were taken using a Raman spectrometer (in situ Raman) (model: LabRAM HR Evolution) produced by Horiba, Kyoto, Japan, under an argon atmosphere. The temperature ranged from 30 °C to 800 °C. Combined with the in situ XRD test results, we studied the complex structure of the molten salts and the effect of temperature on this facet with a laser wavelength of 325 nm at wavenumbers ranging from 50 cm^{-1} to 1000 cm^{-1} .

The thermogravimetric analysis and differential scanning calorimetry of the molten salts were carried out using a simultaneous thermal analyzer (TG-DSC) (STA 449 F3) from Netzsch, Hanau, Germany. To measure IrCl_3 , a heating rate of 5 °C/min was used, and we used temperatures up to 800 °C to study the thermal stability of IrCl_3 .

The content of elements in the molten salt system was detected using inductively coupled plasma optical emission spectra (ICP-OES) (5110) from Agilent, Santa Clara, California, America. The samples were weighed and dissolved in an ablation solution

with a volume of 25 mL, and the concentration of the elements in the ablation solution was measured by the instrument. A total of three tests were performed, and the final results were averaged over the three tests.

2.3. Electrodeposition of Ir Coatings

Figure 1 shows a schematic diagram of the device used for the molten salt electrodeposition of the Ir coatings. The Ir coating was prepared on a rhenium substrate using Ir and rhenium sheets as the anode and cathode, respectively. (A graphite crucible was employed as an anode using a single electrode and a DC power supply positive pole, and the graphite crucible was connected to the electrode rod.) The dried molten salt was placed in a resistance furnace and heated to 600 °C at a rate of 10 °C/min, and this was maintained for 1.5 h to fully melt the salt. Subsequently, the electrode was placed into the molten salt system and electrodeposited at a cathodic current density of 0.2 A/cm² for 1 h. The experimental procedure was carried out in an inert protective gas argon environment. After electrodeposition, the DC power was turned off, and the electrode was removed from the molten salt and cooled to room temperature. The surface of the matrix was cleaned with deionized water and anhydrous ethanol and dried in a vacuum oven at 150 °C for 2 h.

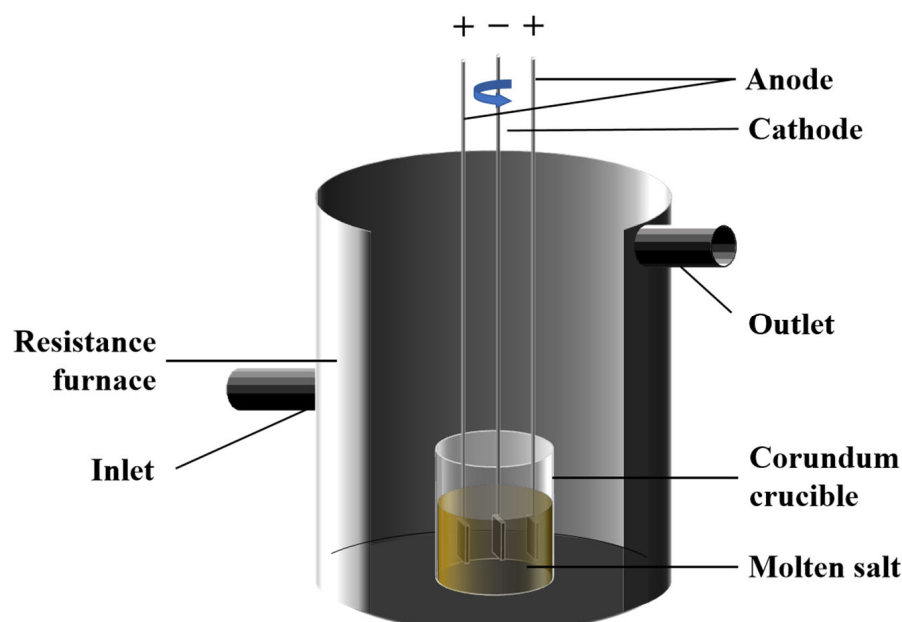


Figure 1. Experimental equipment used for electrodeposition of Ir coating with molten salt.

The microscopic morphology of the coatings was characterized using a German field emission scanning electron microscope (SEM) (GeminiSEM 300 from Zeiss, Oberkochen, Germany).

3. Results and Discussion

3.1. Thermal Stability of IrCl₃

Figure 2 shows the results of the in situ XRD analysis of IrCl₃. Ten test points from 30 °C to 800 °C were selected to study the changes induced in the physical phase of IrCl₃. Below 400 °C, Ir chloride shows good stability. When the temperature reaches 500 °C, a small amount of Ir peaks are detected. At 600 °C, the peaks of Ir were more obvious, corresponding to 41°, 47°, 69°, 83°, and 88°, respectively. Subsequently, the intensity of the peak of IrCl₃ gradually decreases with increasing temperature, while the intensity of the peak of Ir gradually increases. Therefore, it can be concluded that under high-temperature conditions, IrCl₃ will decompose into Ir and Cl₂, and more IrCl₃ is consumed due to decomposition as the temperature increases.

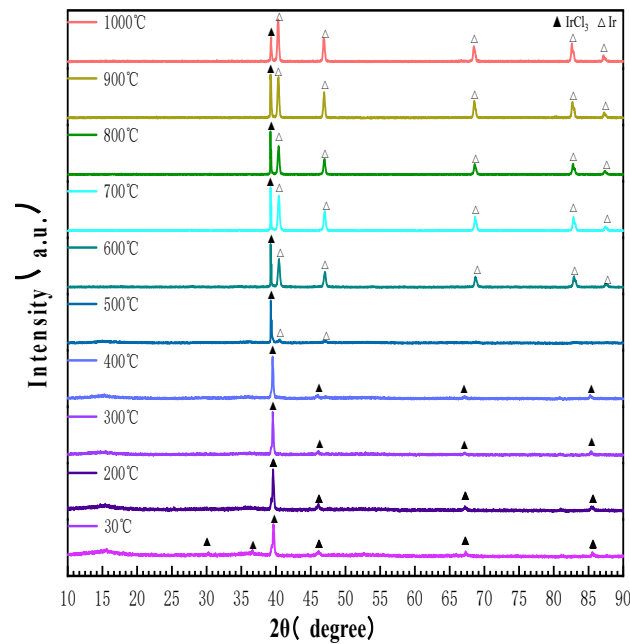


Figure 2. In situ XRD of IrCl_3 in an argon atmosphere.

Figure 3 demonstrates the TG-DSC analysis results of IrCl_3 . IrCl_3 is highly water-absorbent and exists mainly in the form of $\text{IrCl}_3(\text{H}_2\text{O})_3$ at room temperature. The loss of IrCl_3 below 400 °C is mainly due to dehydration, with the dehydrated weight accounting for 14.42% of the total weight, which corresponds to the water molecule content in the molecular formula. When the temperature is above 395 °C, the DSC curve of IrCl_3 gradually increases with the temperature increase, indicating a continuous increase in the heat flow rate of the sample, while the TG curve of IrCl_3 continues to decrease. Combined with the in situ XRD analysis of IrCl_3 , the weight loss of IrCl_3 at high temperatures in argon protection is mainly due to thermal decomposition to form Ir and Cl_2 . Therefore, we can ascertain that IrCl_3 starts to decompose at 395 °C. When the temperature reaches 647 °C, the weight loss of IrCl_3 is accelerated. The decomposition reaction rate increases exponentially with increasing temperature, following the Arrhenius equation. Moreover, when the temperature is 748 °C, the DSC curve exhibits an obvious heat absorption peak, indicating that IrCl_3 melts into a molten state at this time. This temperature is the melting point of IrCl_3 .

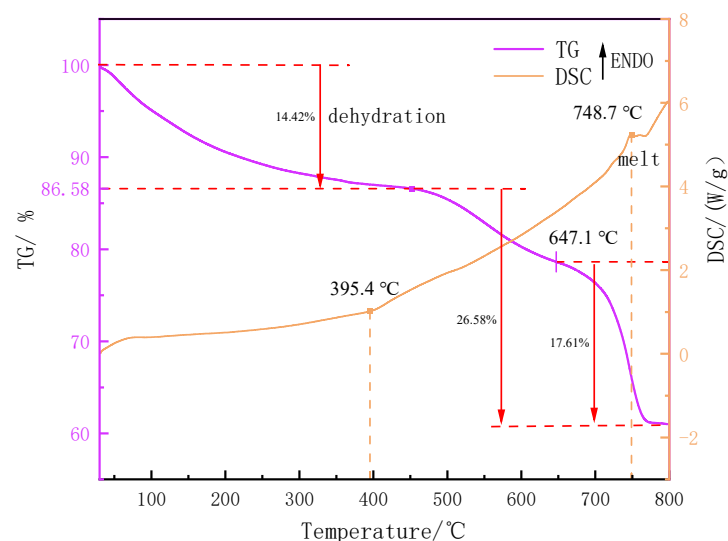


Figure 3. TG-DSC of IrCl_3 in an argon atmosphere.

To sum up, IrCl_3 is used as a source of Ir^{3+} ions in the electrolyte, and because of its strong water absorption, it dehydrates under vacuum conditions before electrodeposition to stop water from entering the molten salt, thereby affecting the electrodeposition reaction. IrCl_3 is highly stable below 400°C , but IrCl_3 decomposes to form Ir above 400°C . Since IrCl_3 is expensive, the structure of the molten salt system can effectively retain IrCl_3 due to decomposition at high temperatures before electrodeposition by reasonable proportioning, which can improve the electrodeposition efficiency and reduce the melting point of the salt at the same time.

3.2. Ir Complex Structure in the Molten Salt System

Figure 4 shows the results of the in situ XRD analysis of $\text{NaCl-KCl-CsCl-IrCl}_3$ in argon. Eight temperatures between 30°C and 800°C were selected to study the changes in the physical phase of the molten salt system. Below 400°C , the molten salt system shows no obvious phase change, and chloride exhibits good thermal stability. When the temperature reaches 500°C , the XRD spectrum of the molten salt shows bread-like diffraction peaks. At this point, the salt melts. At this time, the molten salt transforms from a crystal structure into an amorphous state. This is because NaCl , KCl , and CsCl are all ionic compounds in the molten salt system. As the temperature increases, the anions and cations gain enough energy to overcome the inter-ionic interactions. In the transformation process, many defects are generated in the crystal to raise its free energy, prompting amorphization. When the temperature is higher than 700°C , the diffraction peaks of Pt and Ir appear (the crucible that holds the molten salt is made of Pt). At this temperature, the molten salt volatilizes extensively, and X-rays penetrate it. A small amount of Ir is still present at high temperatures due to thermal decomposition.

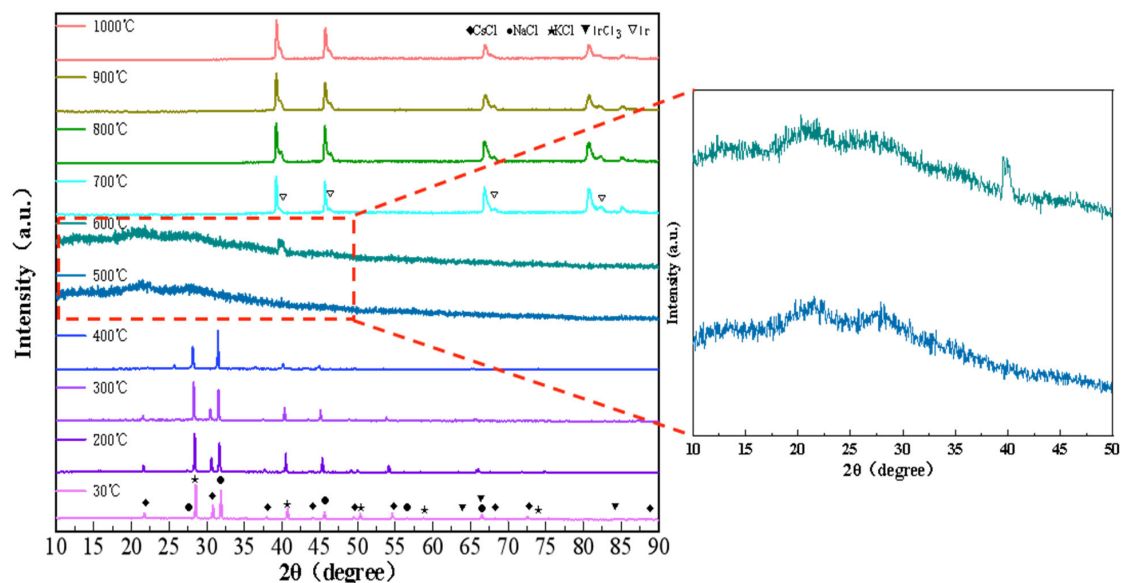


Figure 4. In situ XRD of $\text{NaCl-KCl-CsCl-IrCl}_3$ in an argon atmosphere.

To investigate the structure of the high-temperature molten salt's components, it was heated to 600°C in an argon environment; this was maintained for 30 min, and then it was removed and cooled to room temperature. Using XRD, we analyzed the composition of the molten salt. The results are shown in Figure 5. The new phase components Cs_3IrCl_6 , Na_3IrCl_6 , and Cs_2IrCl_6 were detected in the molten salts, but no IrCl_3 was detected. IrCl_3 generated new ionic compounds with CsCl and NaCl in the high-temperature molten salt. There are two main valencies for Ir ions, Ir(III) and Ir(IV), which mainly exist in molten salts in the form of two atomic groups: $(\text{IrCl}_6)^{3-}$ and $(\text{IrCl}_6)^{2-}$. The peak intensity of $(\text{IrCl}_6)^{3-}$ is higher than that of $(\text{IrCl}_6)^{2-}$, indicating that at 600°C , the content of $(\text{IrCl}_6)^{3-}$ is higher than that of $(\text{IrCl}_6)^{2-}$.

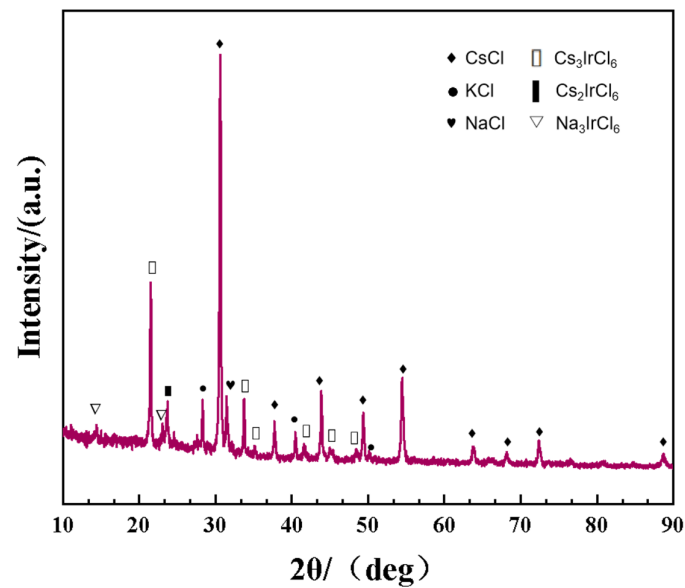


Figure 5. XRD of quenched NaCl-KCl-CsCl-IrCl₃ molten salt after being heated to 600 °C in an argon atmosphere.

In situ Raman spectroscopy was used to further investigate the variation in the Ir ionic complex structure with temperature. Figure 6 shows the Raman spectra of the molten salt system and each molten salt component at room temperature. There are two characteristic peaks of IrCl₃ near 173 cm^{−1} and 318 cm^{−1}, one characteristic peak of NaCl near 350 cm^{−1}, one characteristic peak of CsCl near 188 cm^{−1}, and one characteristic peak of KCl near 290 cm^{−1}. NaCl, KCl, and CsCl are all diatomic molecules with only one vibrational frequency along the direction of the chemical bond, corresponding to one Raman peak; their test results basically correspond to the existing data, and the deviation of the displacements is due to the different test instruments and conditions [35]. The structure of IrCl₃ is similar to that of AlCl₃, which is monoclinic α polycrystalline. There are fewer reports related to the Raman peak of IrCl₃. Referring to the vibrational frequency of the chemical bond of AlCl₃, there are vibrational bands near 393 cm^{−1} and 150 cm^{−1} [36], which are similar to the test results of IrCl₃.

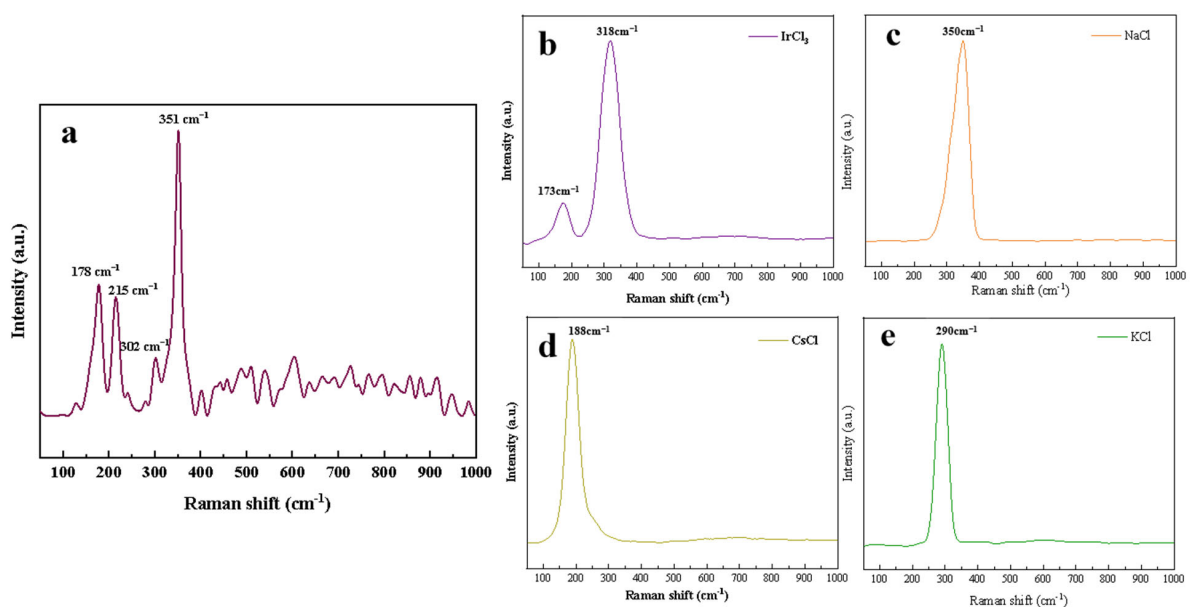


Figure 6. Raman spectra of molten salts at room temperature: (a) NaCl-KCl-CsCl-IrCl₃; (b) IrCl₃; (c) NaCl; (d) CsCl; and (e) KCl.

As shown in Figure 6a, Since NaCl, KCl, and CsCl are all ionic crystals, and after mixing, their Raman spectra have a lower signal/noise ratio (SNR) and exhibit more stray peaks. The presence of four major characteristic peaks near 178 cm^{-1} , 215 cm^{-1} , 302 cm^{-1} , and 351 cm^{-1} . The characteristic peak near 178 cm^{-1} is formed by superimposing the characteristic peak of IrCl_3 near 173 cm^{-1} with the characteristic peak of CsCl near 188 cm^{-1} . The characteristic peak near 302 cm^{-1} is formed by superimposing the characteristic peak of IrCl_3 near 318 cm^{-1} with the characteristic peak of KCl near 290 cm^{-1} . The characteristic peak near 351 cm^{-1} is the characteristic peak of NaCl. The characteristic peak near 215 cm^{-1} has no salt counterpart in Figure 6, and its formation may be related to the Metal–Metal bond (M–M bond). Because the metal bond is weak and the mass of metal atoms is large, the M–M bond of compounds containing halogen bridges usually occurs in the low-frequency region between 200 cm^{-1} and 250 cm^{-1} , and it is very susceptible to thermal decomposition [35,37].

The salt is a solid powder below $400\text{ }^\circ\text{C}$; however, above $700\text{ }^\circ\text{C}$, it is molten due to serious volatilization, which is unfavorable for electrodeposition. Therefore, for the in situ XRD, we focused on the temperature range of $450\text{ }^\circ\text{C}$ – $700\text{ }^\circ\text{C}$, when the Ir ionic complex structure changes. Seven temperature points were selected (450 , 500 , 550 , 600 , 650 , 700 , and $800\text{ }^\circ\text{C}$). Figure 7 demonstrates the in situ Raman spectra of NaCl–KCl–CsCl– IrCl_3 . There are more stray peaks in the Raman spectra at $450\text{ }^\circ\text{C}$ when most of the molten salts are still solid. Compared with those at room temperature, the intensity of the Raman peaks is slightly reduced. After the molten salts begin to melt at high temperatures, the original characteristic peaks near 178 cm^{-1} , 215 cm^{-1} , and 351 cm^{-1} are slightly shifted. The original peak near 302 cm^{-1} disappears, and in its place, the two new peaks appear near 292 cm^{-1} and 312 cm^{-1} , and the characteristic peak near 292 cm^{-1} is more pronounced. There are two possibilities for the origin of peaks near 292 cm^{-1} and 312 cm^{-1} . The first one is due to temperature change: the peak near 302 cm^{-1} splits into two peaks near 292 cm^{-1} and 312 cm^{-1} , and peaks near 292 cm^{-1} correspond to the KCl, while the peak near 312 cm^{-1} corresponds to the peaks of IrCl_3 . The second one is that the structure of IrCl_3 has been transformed in the molten salt system, and in combination with the XRD analysis, these two peaks may be related to $(\text{IrCl}_6)^{3-}$ and $(\text{IrCl}_6)^{2-}$. When the temperature reaches $500\text{ }^\circ\text{C}$, the salts become molten. It can be seen from Figure 7 that the characteristic peak changes significantly from $450\text{ }^\circ\text{C}$ to $500\text{ }^\circ\text{C}$. The peaks near 178 cm^{-1} , 215 cm^{-1} , and 351 cm^{-1} all disappeared, leaving only peaks near 169 cm^{-1} , 292 cm^{-1} , and 312 cm^{-1} . In addition, there is an inflexion point at the shoulder of peak 312 cm^{-1} corresponding to frequency shift at 352 cm^{-1} , where a less well-defined Raman peak may exist.

The characteristic peaks in the Raman spectra are related to the degree of chemical bond polarization. In the molten state, the ionic Na–Cl, K–Cl, and Cs–Cl bonds break. It is hard to detect the characteristic peaks of NaCl, KCl, and CsCl at this moment. Asuhiko also proved through light scattering experiments that there is no ionic bond in molten salt at high temperatures [38]. The Ir–Cl bond is a polar covalent bond with strong thermal stability and does not break significantly at $500\text{ }^\circ\text{C}$. The electron arrangement of Ir is $[\text{Xe}]4f145d76s2$, where the electrons of the 5d layer are not occupied, which makes it easy to form an ortho-octahedral structure. Ir^{3+} and Cl^- are close to each other in the molten salts, and due to the action of their own electric fields, ion polarization occurs, forming $(\text{IrCl}_6)^{3-}$ and $(\text{IrCl}_6)^{2-}$. Ortho-octahedral structures have six vibrational modes; of these modes, v_1 (A_{1g}), v_2 (E_g), and v_5 (F_{2g}) are Raman active [39]. According to the existing literature, the three Raman activity modes of $(\text{IrCl}_6)^{3-}$ are v_1 near 320 cm^{-1} to 323 cm^{-1} , v_2 near 295 cm^{-1} to 303 cm^{-1} , and v_5 near 161 cm^{-1} [39,40]. The three Raman activity modes of $(\text{IrCl}_6)^{2-}$ are v_1 near 341 cm^{-1} to 352 cm^{-1} , v_2 near 278 cm^{-1} to 295 cm^{-1} , and v_5 near 161 cm^{-1} to 188 cm^{-1} [39–42]. The Raman vibrational modes of $(\text{IrCl}_6)^{3-}$ and $(\text{IrCl}_6)^{2-}$ are similar, and some of the differences that exist are due to the different valence of Ir. Ionic bonding is absent in the molten state, and IrCl_3 also undergoes a complexation reaction, thus above $500\text{ }^\circ\text{C}$, ruling out that 292 cm^{-1} and 312 cm^{-1} correspond to KCl and IrCl_3 . Combined with XRD studies, $(\text{IrCl}_6)^{3-}$ and $(\text{IrCl}_6)^{2-}$ co-exist in the molten salt. The

peaks near 169 cm^{-1} and 292 cm^{-1} may correspond to either $(\text{IrCl}_6)^{3-}$ and $(\text{IrCl}_6)^{2-}$ or an overlap of the two. The characteristic peak near 312 cm^{-1} may be $(\text{IrCl}_6)^{3-}$. The position of 352 cm^{-1} on the shoulder of the peak near 312 cm^{-1} corresponds to an inflection point that may be the ν_1 mode of $(\text{IrCl}_6)^{2-}$. However, the signal of the vibrational mode is not clear, which may be related to the experimental conditions or interference. At 450°C , melting of the molten salt partially occurs, and because the KCl and ν_2 bond of $(\text{IrCl}_6)^{3-}$ and $(\text{IrCl}_6)^{2-}$ have similar Raman shifts, 290 cm^{-1} may be a superposition of the $(\text{IrCl}_6)^{3-}$, $(\text{IrCl}_6)^{2-}$, and KCl. The peak near 312 cm^{-1} may be a superposition of the $(\text{IrCl}_6)^{3-}$ and IrCl_3 at this temperature. Table 1 compares the change in the Raman peak from 30°C to 500°C .

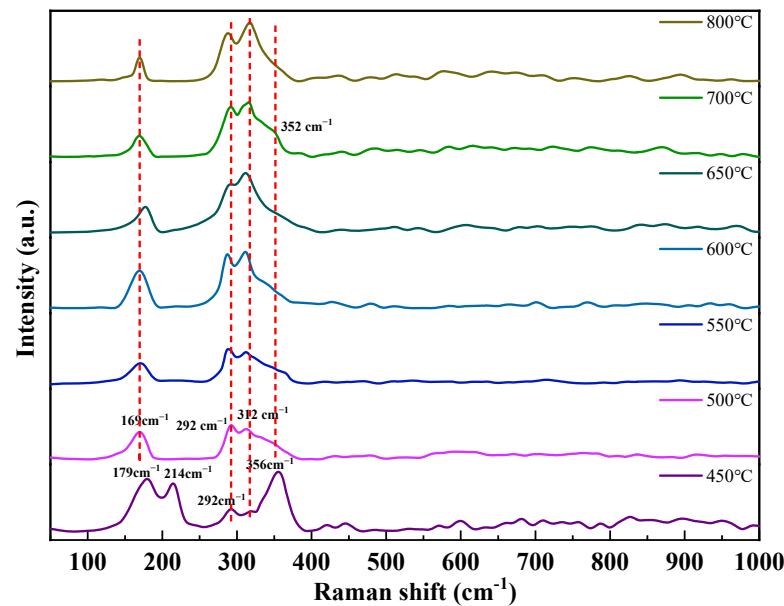


Figure 7. In situ Raman of NaCl-KCl-CsCl-IrCl₃ in an argon atmosphere.

Table 1. Change in Raman peak in molten salt system from 30°C to 500°C .

	30°C	450°C	500°C	Reasons for Changes
178 cm^{-1}	IrCl_3 CsCl	IrCl_3 CsCl	-	Chemical bond breaking
215 cm^{-1}	M-M	M-M	-	Thermal decomposition
302 cm^{-1}	IrCl_3 KCl	-	-	Chemical bond breaking
351 cm^{-1}	NaCl	NaCl	-	Chemical bond breaking
169 cm^{-1}	-	-	$(\text{IrCl}_6)^{2-}$ $(\text{IrCl}_6)^{3-}$	Complex formation
292 cm^{-1}	-	$(\text{IrCl}_6)^{2-}$ $(\text{IrCl}_6)^{3-}$ KCl	$(\text{IrCl}_6)^{2-}$ $(\text{IrCl}_6)^{3-}$	Complex formation
312 cm^{-1}	-	$(\text{IrCl}_6)^{3-}$ - IrCl_3	$(\text{IrCl}_6)^{3-}$	Complex formation

Below 600°C , the intensity of the Raman peak near 292 cm^{-1} is higher than the other peaks. At 650°C , the intensity of the Raman peak near 312 cm^{-1} exceeds that of the peak near 292 cm^{-1} . As the temperature rises, the Raman peak near 312 cm^{-1} becomes the main peak. Experiments have shown that temperature can affect the complex structure of Ir in molten salts. However, the intensity of the Raman peaks at 169 cm^{-1} and 292 cm^{-1} did not change significantly. In the molten salt, the total amount of element Ir is certain, and

the increase in the intensity of the peak near 312 cm^{-1} indicates that the concentration content of $(\text{IrCl}_6)^{3-}$ is elevated at this time, and $(\text{IrCl}_6)^{2-}$ can be reduced to $(\text{IrCl}_6)^{3-}$ in a high-temperature environment. In the process of preparing Ir coatings by electrodeposition, it is $(\text{IrCl}_6)^{3-}$ formed by Ir^{3+} , which plays a major role [34]. The $(\text{IrCl}_6)^{3-}$ concentration in the molten salt system was adjusted by controlling the magnitude of the temperature to optimize the electrodeposition reaction and enhance the quality of the Ir coating.

3.3. Effects of Ir^{3+} Concentration on the Microstructure of Ir Coatings

IrCl_3 is the source of Ir^{3+} ions in the molten salt system. However, it is expensive. Too much IrCl_3 in the molten salt system will lead to the oversaturation of IrCl_3 , resulting in decomposition at high temperatures and causing unnecessary consumption. Therefore, by studying the variation rule of the concentration of Ir^{3+} in the molten salt on the microstructure of the Ir coating, suitable control conditions are found to optimize the organization and compactness of the coating. In this section, we mainly study the influence of electrodeposition time and material of anode on the change rule of Ir^{3+} concentration in molten salt.

The ICP-OES test components are mainly soluble substances that can filter the metal element from molten salts. Using ICP-OES, we quantitatively measured the content of Ir in the deposited molten salt system with three sets of experimental data for each sample. According to Equation (1), we calculated the elemental content of Ir in the molten salt:

$$C_x = \frac{C_0 \times f \times V_0 \times 10^{-3}}{m \times 10^{-3}} = \frac{C_1 \times V_0 \times 10^{-3}}{m \times 10^{-3}} \quad (1)$$

where C_x is the content of the element to be measured, C_0 is the concentration of the element in the test solution, which is obtained by instrumental testing, f is the dilution factor, V_0 is the volume of the sample after digestion, C_1 is the elemental concentration of the sample in the original solution, measured by the apparatus, and m is the mass of the sample.

The test results are shown in Table 2. The molten salt was heated to $600\text{ }^\circ\text{C}$, maintained for 30 min at this temperature, and then stirred continuously to produce a fully melted and uniform mixture. Afterward, the molten salt was removed and cooled quickly to room temperature, and the elemental content of Ir in the molten salt was determined as a reference. The elemental mass of Ir was 2.1% of the total mass before electrodeposition. The amount of IrCl_3 added was 5% of the molten salt, and the initial content of elemental Ir was calculated to be 3.1%. During the heating process, some IrCl_3 decomposed into Ir metal due to the high temperature, and the content of this part of Ir accounted for 1%.

The Ir content was not supplemented during the electrodeposition when the graphite crucible was used as the anode; a total of 1.47% of Ir was consumed over 40 min. At 80 min of electrodeposition, the content of Ir in the molten salt was 0.15%, which was reduced by 1.95% and almost fully consumed.

Figure 8 demonstrates the microscopic morphology of the Ir coatings after different electrodeposition durations with graphite as an anode. The electrodeposition temperature was $600\text{ }^\circ\text{C}$, and the cathodic current density was 0.2 A/cm^2 . Figure 8a shows the microscopic morphology of the Ir coating electrodeposited for 40 min using a graphite crucible as the anode. Morphologically, the Ir coating is very dense, and the surface of the coating became flat during this process. Figure 8b shows the microscopic morphology of the Ir coating at higher microscopic magnification. The Ir coating is nanocrystalline, and it has an irregular block structure. Using the same electrodeposition conditions, the time was increased to 80 min. The microscopic morphology of the Ir coating is shown in Figure 8c,d. During this process, more holes appeared on the surface of the Ir coating, and the coating appeared to have different micro-morphological structures. Zoom in on different areas of Figure 8d to observe the surface microstructure. In Figure 8e, the grains have begun to show abnormal growth, and the grains begin to turn into a verrucous structure, while certain holes and crevices appear on the surface of the plating layer. In Figure 8f, the grain structure is growing in the form of a long strip, the densification and homogeneity

of the plating layer are poor, and the grains are more dispersed. Due to the long time of electrodeposition work, the concentration of Ir ions in the molten salt decreases, and when it is lower than a certain value, the grains will not grow or grow abnormally, resulting in holes in the coating and microstructural changes in the delamination, which is extremely unfavorable to the quality of the coating.

Table 2. Determination of Ir content in molten salt system by ICP-OES.

Type	Sample Weight m (g)	Sample Weight C_1 (mg/L)	Ir Content (%)
Before electrodeposition	0.058	48.990	2.1
		48.605	
		48.523	
Graphite as anode; electrodeposition of 40 min	0.044	11.091	0.63
		11.090	
		11.001	
Graphite as anode; electrodeposition of 80 min	0.073	4.457	0.15
		4.415	
		4.397	
Ir metal as anode; electrodeposition of 80 min	0.053	35.347	1.66
		35.171	
		35.164	

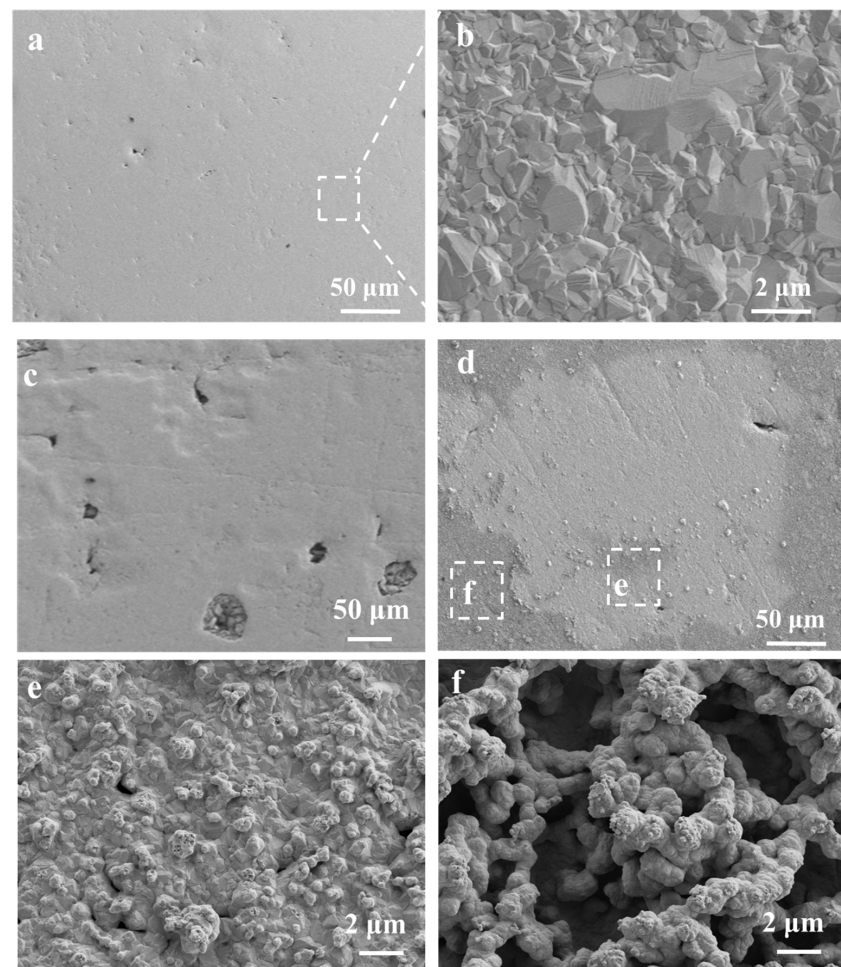


Figure 8. Microscopic morphology of Ir coatings after different electrodeposition durations with graphite as an anode: (a) 40 min; (b) 40 min at higher microscopic magnification; (c,d) 80 min; and (e,f) abnormal grain growth at higher microscopic magnification of 80 min.

Figure 9 demonstrates the microscopic morphology of the Ir coatings after 80 min electrodeposition with Ir as anode. The morphology of the Ir coating is very dense and smooth, and there are no obvious indications of concentration polarization. Compared with the graphite crucible as the anode, the phenomenon of abnormal grain growth did not occur at 80 min of electrodeposition. Using graphite as the anode, the reaction that occurs at the anode is mainly the loss of electrons of Cl^- ions to generate Cl_2 . Using Ir as the anode, the reaction at the anode is mainly the loss of electrons by Ir to generate Ir^{3+} , which enters into the molten salt and supplements the Ir^{3+} in the molten salt. It can also be seen from Table 2 that using Ir as the anode after 80 min electrodeposition, the change in Ir concentration is only 0.44%, which is 1.51% higher than that of graphite crucible as the anode. This indicates that Ir should be used as an anode when it is necessary to increase the thickness of Ir coating and electrodeposition for a long time.

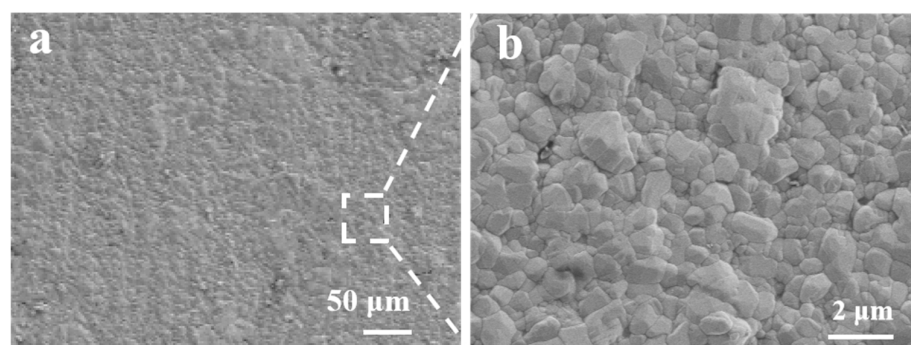


Figure 9. Microscopic morphology of Ir coatings after 80 min electrodeposition with Ir as anode: (a) microscopic morphology; (b) microscopic morphology at higher microscopic magnification.

In summary, the Ir ion concentration has an influence on the quality of the Ir coating electrodeposited using a molten salt system. When the concentration of Ir ion is low, the grain growth will stop, or abnormal growth will occur. Using Ir as an anode can supplement the Ir ions in the molten salt and improve this phenomenon.

4. Conclusions

The form of electrodeposited Ir ions in a molten chloride salt and the effect of different Ir concentrations were studied on the electrodeposition of Ir coating. IrCl_3 , as an added main salt, will thermally decompose to produce Ir above 400°C , and the decomposition rate accelerates with increasing temperature, which is consistent with the equation. By adding IrCl_3 to the molten salt system at above 500°C , the molten salt will melt into a molten state, at which time Ir exists in two forms, $(\text{IrCl}_6)^{3-}$ and $(\text{IrCl}_6)^{2-}$. At higher temperatures, part of $(\text{IrCl}_6)^{2-}$ is converted to $(\text{IrCl}_6)^{3-}$. The generation of the complexes not only reduces the thermal decomposition loss of IrCl_3 but also improves the quality of electrodeposited Ir coatings. The content of Ir in the molten salt also has a large impact on the electrodeposition reaction, when the content is low, it will cause phenomena such as Ir grain growth stopping or abnormal growth, resulting in rapid deterioration of coating quality. The use of Ir as the anode can supplement the content of Ir and improve this phenomenon.

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