Electrochemical Properties and Nucleation Morphology of Yttrium on Tungsten Substrate in Molten Salt

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Electrochemical Properties and Nucleation Morphology of Yttrium on Tungsten Substrate in Molten Salt

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In this work, the diffusion coefficient and electrocrystallization of yttrium in LiCl-KCl eutectic are typically investigated using different electrochemical techniques such as cyclic voltammetry (CV), chronopotentiometry (CP) and chronocoulometry (CA) techniques. At temperature from 673 to 823 K, the diffusion coefficients of two yttrium concentrations (YCl	extsubscript{3} (99.999% Ar, H	extsubscript{2}O < 0.5 ppm, O	extsubscript{2} < 1 ppm). A programmable...
electric furnace (Juichen, GR2–270) with a stainless steel (ϕ64 × 150 mm) and corundum crucible (ϕ50 × 100 mm) inside was placed in the glove box. The furnace maintained the temperature with an accuracy of ±1 °C. An Omega thermometer (HH806AU) was used to measure the actual temperature of the melt system. The electrochemical workstation (Gamry 3000 Reference) was used to apply voltage or current for electrochemical measurements.

The scheme of the electrochemical cell has been described in our previous work.17 Two kinds of working electrodes were applied. One is the widely used tungsten wire (ϕ = 1 mm) cathode, and another is a tungsten disk (9 mm D × 1 mm l) electrode encapsulated by a cylinder boron nitride (BN) shroud which is made up of a fastening screw rod and a lock nut.18 The disk inside is clamped between the BN lock nut and a stainless steel (SS) cylinder connecting a SS wire sealing in the BN screw rod as current collector. At the end of the lock nut, a small hole (2~5 mm) was previously drilled in order to contact and conduct with the melt. Both the upper and lower surfaces of the W disk was carefully polished (2000 and 3000 mesh sand paper, 1.2 micron SiC and 1.0 micron and 0.05 micron Al₂O₃ were used in succession) to a mirror like condition. Carbon rod (ϕ = 4 mm) was used as a counter electrode. Tungsten wire and carbon rod were polished by emery papers and then cleaned by diluted hydrochloric acid, ultrapure water and alcohol prior to the experiments. For a reference electrode, an alundum tube containing a silver wire (ϕ = 0.5 mm) was used, which was filled with LiCl-KCl-(1 wt%) AgCl salt. The bottom of the corundum tube was polished by a sander to provide a very thin diaphragm which can promote ionic conduction in the high temperature molten melt.

Electrochemical techniques and sample characterization.— Three different electrochemical techniques, cyclic voltammetry (CV), chronopotentiometry (CP) and chronoamperometry (CA), were employed to study the electrochemical redox reactions of YCl₃ in LiCl-KCl eutectic from 673 K to 823 K. To guarantee the consistency and reproducibility of the electrochemical test at each temperature, each of these electrochemical techniques was programmed several times by Gamry workstation software. All the electrochemical data were analyzed by Matlab R2019b. For the electrodeposition of yttrium sample, potentiostatic electrolysis was carried out on the tungsten disk electrode at different overpotential at 773 K. After deposition, the cooled tungsten disk can be readily detached. Its mirror-like surface enabled the solid salt in the hole at the end side of the BN lock nut to be easily stripped off and only kept the yttrium deposits staying without adhering too much salt. To characterize the surface morphology and composition of the deposits, the detached disk was firstly adhered on a copper sample stage by using conducting resin in a glove box and placed in an airtight canister. Then, the airtight canister was transferred to the scanning electron microscopy (SEM)-energy dispersive X-ray (EDX) (Quanta 400 FEG) at ambient humidity <30%RH. After open the canister, the copper stage was rapidly placed in the vacuum chamber within 5 s to avoid the oxidation of initial yttrium deposits as much as possible.

Results and Discussion

Electrochemical properties of yttrium in LiCl-KCl eutectic.— The electrochemical behaviors, diffusion coefficients and apparent standard potentials of yttrium in LiCl-KCl eutectic were studied by cyclic voltammetry (CV), chronopotentiometry (CP) and open circuit potential (OCP) at different temperatures ranging from 673 to 823 K.

Figure 1a presents the comparison of the cyclic voltammograms recorded in the blank LiCl–KCl eutectic (blue curve) and in the LiCl–KCl-(9.816 × 10⁻⁵ mol ml⁻¹) YCl₃ melt (orange curve) recorded on a tungsten wire electrode at 723 K. The baseline (blue curve) of LiCl–KCl eutectic shows only the current responses of the reduction of Li⁺ and the release of Cl₂ at ∼2.407 and ∼1.26 V, respectively. The orange curve illustrates a sharp redox couple with cathodic peak at approximately −2.08 V and it associated anodic peak at −1.884 V, indicating the feature of a formation and dissolution of a new solid phase on the surface of the electrode. The inset in Fig. 1a shows more details about the baseline, and the current response of the blank eutectic at the reduction potential range of Y³⁺ is ∼−0.001 A, which even became smaller after the introduction of YCl₃ and several hours of melt homogeneous equilibrium process. This phenomenon suggests that the influence of baseline on Y reductive current response is limited. It has been proved that the reduction of yttrium is a one-step reaction at the introduction of YCl₃ and several hours of melt homogeneous equilibrium process. This phenomenon suggests that the influence of baseline on Y reductive current response is limited. It has been proved that the production of yttrium is a one-step reaction at the introduction of YCl₃ and several hours of melt homogeneous equilibrium process. This phenomenon suggests that the influence of baseline on Y reductive current response is limited.

For a soluble-insoluble reversible couple system, the diffusion coefficient D of Y³⁺ in the melt can be deduced by employing the Berzins–Delahay equation,19

\[
\frac{I_p}{\sqrt{v}} = 0.61(nF)^{3/2}SC_y^{1/2}D_y^{1/2}
\]

Figure 1. (a) Comparison of the cyclic voltammograms recorded in the blank melt and the LiCl–KCl-(9.981 × 10⁻⁵ mol ml⁻¹) YCl₃ melt recording at 100 mV s⁻¹. (b) Scan rates dependence of cyclic voltammograms on tungsten wire electrode, S = 0.479 cm².

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where $I_p$ is the peak current of cathodic wave in Fig. 1, $v$ is the scan rate in V s$^{-1}$, $n$ is the number of electrons transferred, $F$ is Faraday’s constant, $C_{Y^{3+}}$ is the more concentration of $Y^{3+}$, $S$ is the surface area of the working electrode, $n$ is the number of exchanged electrons and $D$ is the diffusion coefficient of $Y^{3+}$ for different temperatures ($T$, 673 ~ 823 K).

Figures 2a and 2b present the linear relationships between peak current and square root of scan rate fitted by the Berzins–Delahay equation (dash line) and actual experimental trend (line) at different temperatures (from 673 to 823 K). In fact, the practical experimental trend does not strictly pass the zero point to match the Berzins–Delahay equation. One possible reason is the influence of Y nucleation on the W surface in the high temperature molten salt which highly affected the current response. It is reasonable and understandable for the experimental data and the theoretical model to have some discrepancies since the Berzins–Delahay equation was established and verified based on the data primarily collected in aqueous solution. This discrepancy was also found in many published works involving molten salt system, although all these works have been trying to fit a zero-passed linear relationship. Nevertheless, the dash line represents the calculated the diffusion coefficient of $Y^{3+}$ for a comparison with the one deduced by CP method and those in literature as shown in Table I.

Figure 3 illustrates the CP curves for YCl$_3$ (9.981 × 10$^{-5}$ mol ml$^{-1}$) recorded on a tungsten wire electrode in LiCl-KCl eutectic melts at 773 K at different applied currents. Under all current conditions from 40 to 70 mA, potential platforms for $Y^{3+}$/Y$^{0}$ always maintain at the same level regardless of current applied. This phenomenon suggests the possible reversible of $Y^{3+}$/Y$^{0}$ electrode reaction. Therefore, the reversibility of the $Y^{3+}$/Y$^{0}$ and the linear relationship between I and $\tau ^{-1/2}$ (Figs. 4a and 4b) guarantees the application of the Sand’s law:

$$I_{p} \sim \tau = 0.5nFC_{Y^{3+}}S^{1/2}\sqrt{D_{Y^{3+}}}$$

Figure 2. The linear relationships between I and the square root of the scan rate at different temperatures with (a) YCl$_3$ = 3.816 × 10$^{-5}$ mol ml$^{-1}$, $S^{-1}$ = 0.4475 cm$^2$ and (b) YCl$_3$ = 9.981 × 10$^{-5}$ mol ml$^{-1}$, $S^{-1}$ = 0.479 cm$^2$.

Table I. Diffusion coefficients (10$^5$D, cm$^2$ s$^{-1}$) of $Y^{3+}$ in LiCl-KCl-YCl$_3$ melts (YCl$_3$, $C_1 = 3.816 \times 10^{-5}$ mol ml$^{-1}$, $C_3 = 9.981 \times 10^{-3}$ mol ml$^{-1}$) at different temperatures.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>CP</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>4.81</td>
<td>1.55</td>
</tr>
<tr>
<td>723</td>
<td>5.96</td>
<td>1.79</td>
</tr>
<tr>
<td>773</td>
<td>7.10</td>
<td>2.19</td>
</tr>
<tr>
<td>823</td>
<td>8.25</td>
<td>2.58</td>
</tr>
</tbody>
</table>
Compared with the results in this work, the subtle differences are probably caused by different conditions in the experiments, such as temperatures, methods applied, molten salts system and so on. In addition, the possible presence of some additional contributions, such as concurrent electrochemical processes, convection, nucleation, dendritic growth etc, may also have an impact on the determination of diffusion coefficient.

In Fig. 5, the linear relationships between log D and T$^{-1}$ are fitted as Eqs. 3–6 for Y$^{3+}$ in the molten salt and compared them with that in literature. The comparable slopes between these lines in Fig. 4 guarantee the validity of these data.

In the CV experiments:

$$C_1 \log D_{Y^{3+}} = -3.79 - \frac{1771}{T}$$  \[3\]

$$C_3 \log D_{Y^{3+}} = -3.537 - \frac{1415}{T}$$  \[4\]

In the CP experiments:

$$C_1 \log D_{Y^{3+}} = -3.00 - \frac{891}{T}$$  \[5\]

$$C_3 \log D_{Y^{3+}} = -3.587 - \frac{829}{T}$$  \[6\]

Through these linear relationships (L1-L6) fitted in the Fig. 5, the validation of the Arrhenius law can be verified in our systems as follows,

$$D = D_0 e^{-\frac{E_a}{RT}}$$  \[7\]

where $D_0$ is the pre-exponential factor, $E_a$ presents the activation energy (kJ mol$^{-1}$), and T is the absolute temperature of K. The apparent activation energies can be calculated by applying the relationship of temperature and diffusion coefficient in Table I. The calculated results for YCl$_3 = 3.816 \times 10^{-5}$ mol ml$^{-1}$ are 17.06 and 33.90 kJ mol$^{-1}$ for CP and CV, respectively. For YCl$_3 = 9.981 \times 10^{-5}$ mol ml$^{-1}$, the corresponding values are 15.87 and 27.09 kJ mol$^{-1}$, respectively. These results are comparable to the data of 31.94 kJ mol$^{-1}$ reported in the literature.

By using the open circuit potential (OCP) techniques, the equilibrium potential and the apparent standard potential of Y$^{3+}$/Y can be calculated. In Fig. 6, at each studied temperature, an obvious stable plateau was obtained relating to the corresponding pseudo-equilibrium potential $E^{\text{eq}}_{Y^{3+}/Y}$ and the apparent standard potential $E^{\text{eq}}_{Y^{3+}/Y}$ by the Nernst relationship, as follows:

Figure 4. The linear relationships of I vs $\tau^{-1/2}$ for the chronopotentiometric data obtained in LiCl-KCl eutectic, (a)YCl$_3 = 3.816 \times 10^{-5}$ mol ml$^{-1}$, S$^{-1} = 0.4475$ cm$^2$ and (b) YCl$_3 = 9.981 \times 10^{-5}$ mol ml$^{-1}$, S$^{-1} = 0.479$ cm$^2$.

Figure 5. The linear relationships between log D and I/T for Y$^{3+}$ (with $C_1 = 3.816 \times 10^{-5}$ mol ml$^{-1}$ and $C_3 = 9.981 \times 10^{-5}$ mol ml$^{-1}$) determined respectively by CP ($\bigcirc$ and $\bigstar$) and CV($\blacktriangle$ and $\blacksquare$) in this work. Comparison of values in literature, $\triangle$ LiCl-KCF, $\square$NaCl-KCl, $\star$ LiCl-KCl.

Figure 6. Typical OCP curves recorded in LiCl-KCl-YCl$_3 = 1.8$ wt% at different temperatures.
\[ E_{\text{AgCl}/Y_{3+}}^{\text{eq}} = E_{\text{AgCl}/Y_{3+}}^0 + \frac{RT}{nF} \ln \left( \frac{a_{Y_{3+}}}{a_Y} \right) \]  
[8]

\[ E_{\text{AgCl}/Y_{3+}}^{\ast} = E_{\text{AgCl}/Y_{3+}}^0 + \frac{RT}{nF} \ln (\gamma_{Y_{3+}}) \]  
[9]

where \( E_{\text{AgCl}/Y_{3+}}^{\text{eq}} \) represents the standard potential at a hypothetical supercooled liquid reference of unit mole fraction and unit activity, \( a_{Y_{3+}} \) and \( a_Y \) are the activity of \( Y_{3+} \) ions and the metallic \( Y \). \( \gamma_{Y_{3+}} = \frac{n_{Y_{3+}}}{n_Y} \) represents the activity coefficient of \( Y_{3+} \) and \( x_{Y_{3+}} \) is the mole fraction of \( Y_{3+} \) in the melt. The activity of pure metal is assumed 1 by default.

To better compare these potentials with those in literature, the potentials mentioned above was recalculated vs \( \text{Cl}_2/\text{Cl}^- \) reference electrode according to the following equation:

\[ E_{\text{Ag}/\text{AgCl}(\text{vs } \text{Cl}_2/\text{Cl}^-)} = E_{\text{Ag}/\text{AgCl}}^0 + \frac{RT}{nF} \ln X_{\text{AgCl}} \]  
[10]

In the work of Yang et al.,\(^8\) the data obtained at a low \( \text{AgCl} \) concentration is extrapolated to infinite dilution. Subsequently, the potential of reference electrode employed in this work (0.0039 mole fraction \( \text{AgCl} \)) vs \( \text{Cl}_2/\text{Cl}^- \) is given by the following equation:

\[ E_{\text{Ag}/\text{AgCl}(\text{vs } \text{Cl}_2/\text{Cl}^-)} = -1.0910 - 1.855 \times 10^{-4} T(K) \]  
[11]

Based on Eqs. 8–10, \( E_{\text{AgCl}/Y_{3+}}^{\ast} \) can be expressed as:

\[ E_{\text{AgCl}/Y_{3+}}^{\ast} = E_{\text{AgCl}/Y_{3+}}^{\text{eq}} - \frac{RT}{nF} \ln (x_{Y_{3+}}) + E_{\text{Ag}/\text{AgCl}} \times (\text{vs } \text{Cl}_2/\text{Cl}^-) \]  
[12]

Using Eqs. 8–12, the values of the apparent standard potential and the equilibrium potential at different temperatures with two concentrations were calculated and summarized in Table II. Therefore, the relationships between temperature and apparent standard potential of \( Y_{3+}/Y \) are fitted in Fig. 7 as the following equations for \( 5.642 \times 10^{-5} \text{ mol ml}^{-1} \) and \( 9.981 \times 10^{-5} \text{ mol ml}^{-1} \) of \( \text{YCl}_3 \) in the melt, respectively, and these results were compared with those data calculated in different references.

\[ C_2 E_{\text{AgCl}/Y_{3+}}^{\ast}(\text{vs } \text{Cl}_2/\text{Cl}^-)/V = -3.56 + 5.87 \times 10^{-4} T(K) \]  
[13]

\[ C_3 E_{\text{AgCl}/Y_{3+}}^{\ast}(\text{vs } \text{Cl}_2/\text{Cl}^-)/V = -3.477 + 5 \times 10^{-4} T(K) \]  
[14]

In Fig. 7, values of apparent standard potential derived from others’ works are compared with ours in \( \text{LiCl-KCl} \) eutectic. Except data 4, the literature is very close to the values in this work.

**Nucleation mechanism of yttrium electrodeposition.**—To further study the nucleation and initial growth of yttrium on the tungsten electrode, the fundamental method—chronoamperometry was applied. Moreover, the application of corresponding dimensionless theoretical equation can deduce typical modes for \( Y \) nuclei formation and growth. Before each CA test, two equilibrium conditions were carried out on the cell system to guarantee the consistency and reproducibility of data collection. First, a CV curve covering the redox potential of \( Y_{3+} \) and \( \text{Cl}^- \) was applied to the system with the starting and ending potentials of 0 vs \( \text{Ag}/\text{AgCl} \). Then, a potentiostatic electrolysis was done at 0 vs \( \text{Ag}/\text{AgCl} \) for 30 s for further electrode cleaning and system equilibrium. Finally, the CA test was performed at an initial applied potential which was little more anodic than the reduction potential of \( Y_{3+} \) on the \( \text{YCl}_3 \) concentration, covering the reductive peak potential range of \( Y_{3+} \) with a step potential of 0.005 V.

Figure 8 plots a series of typical CA curves at 773 K at different over-potentials on \( W \) wire electrode in \( \text{LiCl-KCl}-9.981 \times 10^{-5} \text{ mol ml}^{-1} \text{ YCl}_3 \) melts. In this plot, two distinct current evolutions can be clearly observed. The first one is a gradual rise of current to reach a maximum value (peak, \( I_m \)) because of the formation and subsequent growth of yttrium crystals resulting from the increase in active cathodic surface. The second one is that the current follows a typical \( t^{1/2} \) decay as in the Cottrell equation, which is controlled by the mass transfer process of \( Y_{3+} \).

Scharifker and Hills\(^{29,30}\) proposed two dimensionless theoretical modes (S-H mode) based on a 3D nucleation and growth process which are controlled by diffusion of electroactive species. The nucleation mode of the electrodeposition can be distinguished by applying this theory. The mathematical models are expressed in two cases as follows:

1. **Instantaneous nucleation** which means all the yttrium nuclei are generated at the beginning of electrolysis at the same time and grew over the time;

<table>
<thead>
<tr>
<th>T(K)</th>
<th>( C_2 ) vs (Ag/AgCl)/V</th>
<th>( C_3 ) vs (Ag/AgCl)/V</th>
<th>( C_2 ) vs (Cl_2/Cl^-)/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>-2.023</td>
<td>-1.988</td>
<td>-1.853</td>
</tr>
<tr>
<td>723</td>
<td>-2.005</td>
<td>-1.960</td>
<td>-1.822</td>
</tr>
<tr>
<td>773</td>
<td>-1.951</td>
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<tr>
<td>823</td>
<td>-1.932</td>
<td>-1.897</td>
<td>-1.724</td>
</tr>
</tbody>
</table>

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**Table II. Summary of the equilibrium potentials and the apparent standard potentials of \( Y_{3+}/Y \) in \( \text{LiCl-KCl-YCl}_3 \) melts (\( \text{YCl}_3, C_2 = 5.642 \times 10^{-5} \text{ mol ml}^{-1}, C_3 = 9.981 \times 10^{-5} \text{ mol ml}^{-1} \)) at different temperatures.**
overpotentials and temperatures. Accordingly, yttrium nuclei are generated at the same time on all active sites available at the initial stage of electrolysis. Castrillejo et al. also suggested that the nucleation of yttrium on tungsten is an instantaneous mode. In addition, Fig. 9 also suggests that the studied range of Y concentrations, temperatures and overpotential have a limited effect on the nucleation mechanism. It should be mentioned that the experimental data cannot meet a good fitting to the instantaneous mode. The data published in many works also present this discrepancy. One possible reason might be the different experimental protocols such as different electrodes, cell configurations, data collection and processing, etc. Moreover, it should be mentioned that the Eqs. 15 and 16 were derived for a specific and simple situation: the diffusion controlled three-dimensional nucleation of electroactive species with fast electron transfer kinetics, in the absence of any other contributing process. The fast electron transfer kinetics in the high temperature molten salt system is very easy to figure out. It is found that in the high temperature molten salt system, a severe adsorption behavior was found on the electrode surface accompanied with a metal electrochemical reduction process, which highly affected the potential and current response. Researchers are trying to establish a nucleation mode considering the adsorption behavior in the high temperature molten salt system. It is quite clear that more works need to be done to get a good understanding on this issue.

**Morphology evolution of yttrium electrodeposition.** As mentioned before, the initial stage of yttrium nucleation and following growth can be predicted by applying theoretical electrochemical models of (15) and (16) to fit CA curves. However, the visual information of nucleus morphology and growth evolution, which are very important for understanding the subsequent deposition, are still needed to confirm the mode. It is a challenge to obtain the early stage of nuclei samples in molten salt electrodeposition. The early nuclei generally are deposited during a very short time; therefore, the sample quantity is minimal. More troublesome, micro-sized nucleus samples are very sensitive to water and oxygen, especially to those active elements such as lanthanides, and generally attach larger amount of solid salts after electrodeposition. Thus, it is problematic to be obtain the initial nuclei by solvent cleaning. In the references, Tang and Pesic given a

\[
\frac{I(t)}{I_m} = \frac{1.97542}{t_m} \left[ 1 - \exp \left( -1.2564 \frac{t}{t_m} \right) \right]^2 \quad [15]
\]

(II) Progressive nucleation which indicates new yttrium nuclei are consecutively created throughout electrolysis;

\[
\frac{I(t)}{I_m} = \frac{1.2254}{t_m} \left[ 1 - \exp \left( -2.3367 \left( \frac{t}{t_m} \right)^{1.2} \right) \right]^2 \quad [16]
\]

Where \( I_m \) and \( t_m \) represent the maximum of transient current and time, respectively, which can be determined by Fig. 8 directly, \( t \) is the recorded time, and \( j \) the transient current density.

In Figs. 9a and 9b, the experimental CA curves are re-plotted in \( \left( \frac{I(t)}{I_m} \right) \) vs \( \frac{t}{t_m} \) relation for different overpotentials and temperatures, respectively, and compared with the dashed curve 1 and dotted curve 2 form the theoretical models described by Eqs. 15 and 16. In Fig. 9, the experimental data implies a tendency in terms of the dimensionless theoretical model (dashed curve 1) for instantaneous nucleation with 3D growth of the nuclei at all studied concentrations,
straightforward and smart idea to prepare a Mo disk electrode from a side-shielded 3 mm D × 10 mm l Mo cylinder.\textsuperscript{31} After carefully polished its open end, they found that the freshly and well-polished surface of Mo did not retain molten salt upon its withdrawal. As a result, they obtained high-quality SEM images for initial nuclei formation and growth of several lanthanides elements in molten salt electrolysis.\textsuperscript{3,31–37} However, due to the thick size and complex shielding of the Mo cylinder electrode, we need to design a special sample stage for the electron microscope. It is inconvenient in the process of sample preparation for SEM analysis. In addition, tungsten material, owing to its strong chemical stability and corrosion resistance performance in high temperature molten salt, has been widely used as cathode in molten salt electrochemical study. If we can obtain the initial nuclei morphology on the tungsten surface, it would be very helpful to better understand the yttrium electrochemistry. The tungsten disk (9 mm D × 1 mm l) electrode used in this study can readily solve these problems mentioned above.

By employing the tungsten disk electrode and scanning electron microscopy, the first few seconds of yttrium nucleation and growth can be visualized. Figure 10 presents the SEM images of tungsten disk electrode surface after electrodeposition of Y at −2.07 V vs Ag/AgCl in LiCl-KCl-9.981 × 10^{-5} \text{mol ml}^{-1} \text{YCl}_3 or 3.816 × 10^{-5} \text{mol ml}^{-1} \text{YCl}_3 melts at 773 K at 2 s and 5 s, respectively. Some individual circular regions range from dozens to hundreds of microns (Figs. 10a–10b) corresponding to the Y nucleation sites can be visualized on the tungsten surface. According to the previous study on Mo surface for Nd and Er deposition,\textsuperscript{3,37} this phenomenon is a typical characteristic for the case of instantaneous nucleation, where the nuclei are typically concentrated at the center and the following centrifugal diverging growth arranged to form lower density of dendrites. Even though our case firstly focused on the Y nucleation morphology on W surface, the emergence of some individual circular regions can still inspire our understanding in the Y nucleation. However, the mechanical or physical state after polishing, the magnetic field during the electrodeposition and the possible micro gas bubbles on the W surface after introduced in molten salt may also the possible reasons to cause such large cycles up to hundreds of microns.

Nevertheless, there are still some distinctive information for the yttrium nucleation on W surface. Here, high density nuclei seem gathered at the circular area and the sequential arrangement grown both at the peripheral and center-orientated directions. The obvious discrepancy is that no visible dendritic morphology is observed for Y deposition on the W surface, but circular chains arrangement clearly appears in the backscattered SEM images for the following growth (Figs. 10c–10d). It is believed that Y nuclei

![Figure 10. SEM images of tungsten disk electrode surface after electrodeposition of Y at −2.07 V vs Ag/AgCl in LiCl-KCl-9.981 × 10^{-5} \text{mol ml}^{-1} \text{YCl}_3 melts at 773 K. deposition time, (a) 2 s, (b) 5 s, (d) 10 s and LiCl-KCl-3.816 × 10^{-5} \text{mol ml}^{-1} \text{YCl}_3 melts, (c) 5 s, (c),(d) backscattered image.](image-url)
are highly mobile on the W surface during the deposition. Once a circular chain initially forms, the nuclei instantaneously form somewhere on the W surface, and migrate toward the circular nucleation sites to promote the following growth inside and at the peripheral of the circle. This explanation is supported by the observation in Fig. 11.

On the same sample with Fig. 10b for 5 s of electrodeposition, a very compact and center-empty pentagonal area for Y film is also presented in the SEM images as shown in Figs. 11a–11b. This hollow compact film structure appears more in the following samples for a longer time of deposition. In Figs. 11c–11f for the 10 s and 20 s of deposition, several individual compact areas
The results conﬁrm that the subsequently formed nuclei migrate to the previous circular nucleation sites (Fig. 10) to further form a fully covered compact film.

Moreover, the subsequent formed nuclei seem have a partiality for further growth on fresh tungsten surface in a 2D mode instead of a 3D growth on the previously formed Y nuclei until the final formation of a uniform and compressed ﬁlm. Tang and Pesic reported that the formation of a very dense and thin ﬁlm of Nd and Er primarily on a Mo surface, primarily caused by the merge and overlapping of peripheric dendritic growth of the original nucleation sites. This overlapping leaded to a very high nuclei density of agglomerates promoting a very smooth and compact ﬁlm surface. In our case, no distinct dendritic structure is seen on the W surface for the Y nucleation and growth, but the phenomenon of overlapping is still visible in Figs. 11d–11e. We can see, the nuclei density (areas A) between the dense sites (red dotted cycle areas) is clearly higher than that in periphery (areas B) of a single compact site. As proposed in previous studies et al., the phenomenon mode of initial formation of 3D nucleus and subsequent peripheric 2D growth is the cause of the deviation between experimental data and theoretical instantaneous nucleation mode as shown in Fig. 9.

To further obtain a perfect Y ﬁlm, 60 s of deposition at a higher overpotential of −2.1 V vs Ag/AgCl was carried out on the tungsten disk electrode in LiCl-KCl-9.981 × 10⁻⁵ mol ml⁻¹ YCl₃ melts. As presented in Figs. 13a, a sharp SEM image for the dense and uniform Y ﬁlm is obtained. The element composition was also characterized by element mapping (Figs. 13b–13d) and EDS (Fig. 13e) analyses. The results conﬁrm a very pure and compact Y ﬁlm. A very small amount of salt was detected and primarily located at the regions with large nucleus size and rough areas as expected.

Conclusions

The diffusion coefﬁcient, apparent standard potential and electrocrystallization of yttrium in LiCl-KCl eutectic are investigated by different electrochemical techniques such as CV, CP and OCP. The diffusion coefﬁcients determined respectively by CP and CV methods at the temperature ranging from 673–823 K of two yttrium concentrations, YCl₃ = 3.816 × 10⁻⁵ mol ml⁻¹ and 9.981 × 10⁻⁵ mol ml⁻¹, are in a range from 0.453 × 10⁻⁵ cm² s⁻¹ to 8.25 × 10⁻⁵ cm² s⁻¹ and provide the apparent activation energies range from 15.87 to 33.9 kJ mol⁻¹.

Based on the CA technique and Scharifker-Hill models, the theoretical mode of Y nucleation is conﬁrmed to be instantaneous regardless the given temperature, over-potential and concentration.

With the application of W disk electrode and SEM-EDS techniques, the nucleation and initial growth of yttrium is visualized on the tungsten surface. Individual circular regions corresponding to the Y nucleation sites were ﬁrstly formed on the tungsten surface. Once a circular region formed, the continually formed nuclei migrate toward the initial circular nucleation sites to promote the following growth inside and peripheral of the circle. No dendritic structure for the Y deposition was observed on the W surface, but the overlapping of peripheric growth was still visualized to further form a very dense Y ﬁlm. The visualization of yttrium nucleation and growth phenomena broadens the scope of Y electrochemistry on the W surface and is of practical signiﬁcance for the electrochemical extraction and separation of lanthanides in preprocessing and the electrochemical preparation of thin Y ﬁlms in molten salt for material science.

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Figure 13. SEM images (a), element mapping analysis (b)–(d) and EDS (e) of Y film electrodeposited on tungsten disk surface at −2.1 V vs Ag/AgCl in LiCl-KCl-9.981 × 10⁻⁵ mol ml⁻¹ YCl₃ melts for 60 s.

References