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Effect of fluoride addition on electrochemical behaviors of V(III) in molten LiCl−KCl

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Abstract: X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were used to analyze the complexes in LiCl−KCl eutectic salt containing VCl_3 and KF. The additional fluoride ions would replace chloride ions and combine with V(III) to form VF_6^{3-}. The electrochemical behavior of V(III) was evaluated under condition of the molar concentration ratio of F^- to V^{n+} (α) equal to 0:1, 1:1, 2:1, 5:1, 20:1 and 50:1, respectively. The results showed that a new reduction step appeared: $VF_6^{3-}\rightarrow V^{2+}$, and the reduction mechanism of vanadium ions became more complicated. The metallic vanadium was deposited on the tungsten electrode at −2.90 V in the LiCl−KCl melts for 6 h, and the products were characterized by SEM−EDS. It was indicated that the particle size of the product decreased with adding fluoride ions for the forming of the coordination compound VF_6^{3-}.

Key words: V(III) ion; molten salt; electrochemical behavior; reduction mechanism; complex

1 Introduction

Vanadium metal has good performance under various environmental conditions due to its special physical and chemical properties, which leads to a wide application of fields such as alloys, medicine, batteries, and chemicals [1,2]. However, the production process of vanadium metal has some problems such as high energy consumption, environmental pollution, and low purity [3−5]. Among the present systems of vanadium metal production, molten salt electrolysis technology is the most promising method.

One of the largest obstacles to electrochemical route of vanadium production still comes from vanadium species with various valences dissolved in electrolyte. The vanadium ions with different valences in electrolytes would undergo different reoxidation reactions, which results in a low current efficiency. In the electrolysis process, the composition of electrolyte is a critical factor which should be considered, and the interaction between electrolyte anions and vanadium ions has been studied. The ultimate technological viability of this process, however, is contingent upon the identification of electrolyte.

At present, the electrolyte used in the research can be divided into chloride molten salt, fluoride molten salt and fluoride−chloride molten salt. Various types of chloride electrolytes including LiCl−KCl and NaCl−KCl have been used for vanadium electrolysis [6,7].

In our previous work [8], the electrochemical properties of vanadium ions in molten salts were investigated. SULLIVAN [9] has reported the electrorefining of vanadium in NaCl−VCl_2 firstly. TRIPATHY et al [10−12] performed vanadium

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refining through different anodes containing vanadium, including VN, (V,N), and (V,N,C,O). More literature was included in our recent review paper [13]. However, all previous studies were carried out in chloride systems, and they were not sufficient and systematic. In addition, although several studies have addressed the electrochemical behaviors of V(III), few discussion has been argued to the thermodynamics and kinetics.

As reported, the introduction of fluoride ions in molten salt will change the electrochemical properties and reduction process of metal ions. And the presence of fluoride ions might be effective in the energy consumption and product quality. One successful example is the widely known titanium ions. Disproportionation reactions were observed after fluoride ions were added to the melt [14], which was mainly due to the formation of the coordination compound TiF_i^{3-i}.

However, the influence of fluoride ions for vanadium is still unclear. With the aim of investigating the effect of fluoride ions on the reduction of vanadium ions in molten LiCl−KCl, fluoride ions were introduced into the melt by adding KF in-situ in this work. The electrochemical behavior of vanadium ions with different fluoride contents was investigated by various methods. The formation of complexes between vanadium and fluoride ions in molten salt was also discussed in detail. Furthermore, the electrodeposition of metallic vanadium was also conducted.

2 Experimental

The experimental equipment is shown in Fig. 1.

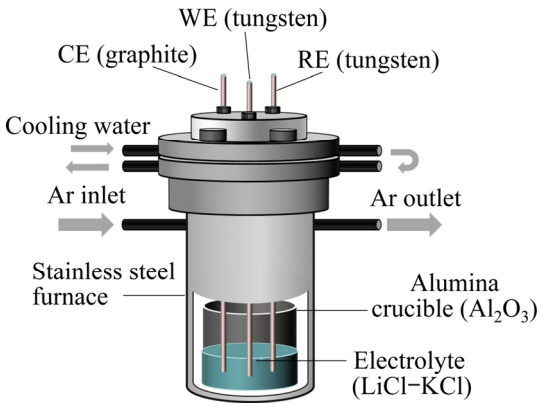

Fig. 1 Schematic of experimental apparatus used for electrochemical measurements

A three-electrode system was used for the experiment, and the whole process was carried out under argon atmosphere protection. The working electrode was a tungsten wire (1 mm in diameter, 99.94% in purity); the counter electrode was a graphite rod (6 mm in diameter, 99.99% in purity); a tungsten wire (1 mm in diameter, 99.99% in purity) was applied as a reference electrode. To be more comparable, the reference potential was converted to the potential of Cl_2/Cl^-. When determining the anodic polarization curve, a gold wire (diameter of 2 mm, purity of 99.99%) was used as the working electrode.

LiCl and KCl (LiCl, ≥99% in purity; KCl, ≥99.9% in purity) with a molar ratio of 0.59:0.41 were used as electrolyte. The 100 g mixed salt was held at 200 °C for 2 h to remove residual moisture, and then heated to 450 °C for experiment [15]. The experimental temperature was measured by a platinum-rhodium thermocouple with a deviation of ±1.5 °C.

VCl_3 (≥ 99.9% in purity) and KF (≥ 99% in purity) were used as the source of vanadium and fluoride ions. The concentration of vanadium ions was 0.034 mol/L, and the molar concentration ratio, $[F^-]/[V^{n+}]$ (α), was employed as a parameter to illustrate the influence of fluoride ions on the electrochemical behaviors of V(III), which was 1:1, 2:1, 5:1, 20:1 and 50:1, respectively.

All electrochemical tests were carried out by an AUTOLAB (PGSTAT 302N). Various transient electrochemical techniques were used to study the electrochemical behavior of V(III) in LiCl−KCl with various contents of fluoride. A quartz rod (diameter of 6 mm) was inserted into the melt with different concentrations of fluoride ions and quickly pulled out. The attached melt was cooled to solid state and collected. Then, the cooled salt was investigated using X-ray photoelectron spectroscopy and Raman spectroscopy. Electrolysis was performed using a regulated direct current power supply (TDK lambda). After the electrodeposition of vanadium, the working electrodes were cleaned with deionized water and dried, and then the product on the working electrode was collected. The microstructures and morphologies of the deposits were observed by scanning electron microscope and energy dispersive spectroscope.

3 Results and discussion

3.1 Redox behavior of vanadium ions in molten salt

A new form of trivalent vanadium ions, $VCl_iF_{6-i}^{3-}$, exists in the melt with the presence of fluoride ions. To prove this point, XPS spectroscopy was performed on the molten salt with various α. The V 2p region spectra are shown in Fig. 2.

A peak was situated at approximately 515.0 eV under the condition of no fluoride, which represented the bond of V^{3+} with Cl^- (V—Cl). After fluoride ions were added in the melt, a new peak at approximately 518 eV was observed, representing the bond of V^{3+} with F^- (V—F) [16−18]. This indicated that fluoride ions can react with V^{3+} and lead to forming of complexes $VCl_iF_{6-i}^{3-}$ in the melt due to the stronger binding force of F^-. Depending on the anions nature, the weaker V—Cl bond was replaced by the stronger V—F bond. Thus, the total concentration of vanadium ions in this work is referred to the sum of "free" ions and complexes.

To study the electrochemical behavior of V(III) with various α, cyclic voltammetry was carried out on a tungsten working electrode. Figure 3 shows the cyclic voltammogram with various α values.

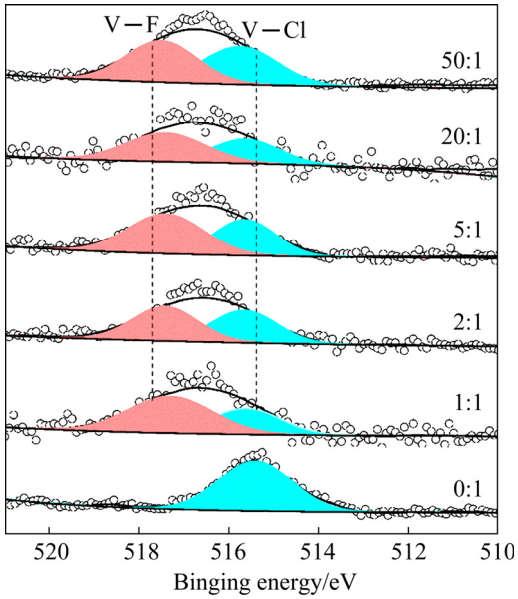

Fig. 2 XPS spectra of VCl_3 in LiCl−KCl−KF molten salt at 450 °C with various α

As shown in Fig. 3(a), there was not fluoride in the melt, and three pairs of redox peaks were observed. According to our previous study [6], the reduction paths of V(III) were V(III)/V(II), V(II)/V, and V(III)/V. When α increased to 1:1, a new reduction peak R1′ was found. As described in previous work, fluoride ions can react with vanadium ions and lead to the forming of complex

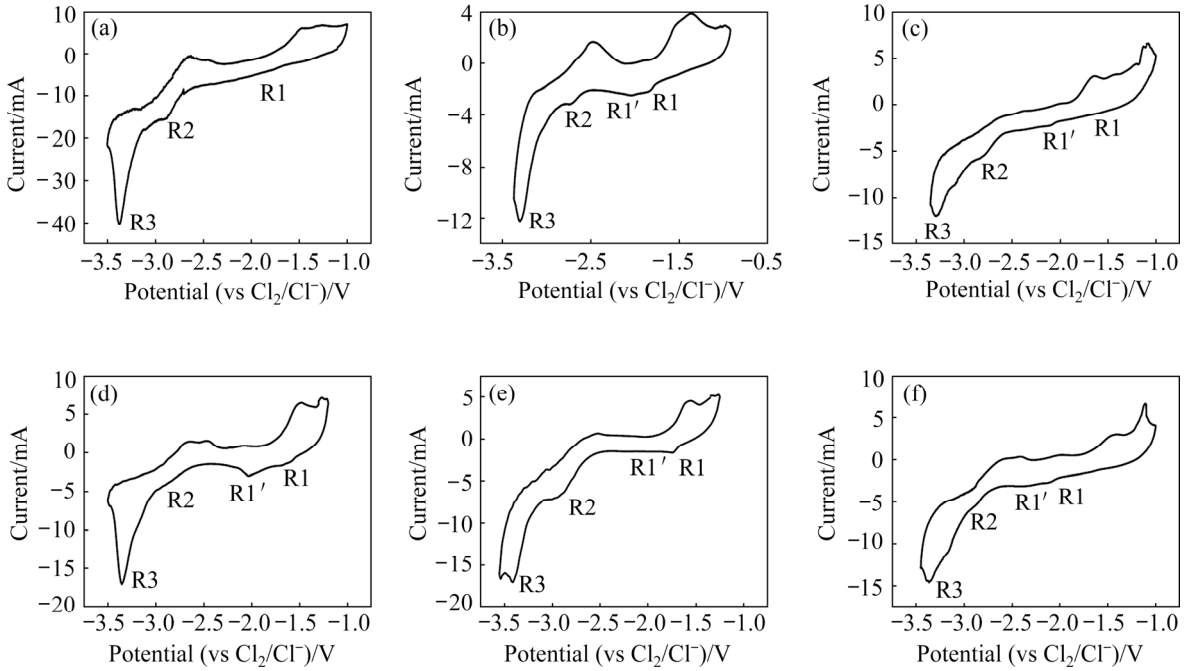

Fig. 3 Cyclic voltammograms of VCl_3 in LiCl−KCl−KF molten salt under scanning rate of 0.1 V/s at 450 °C with various α: (a) 0:1; (b) 1:1; (c) 2:1; (d) 5:1; (e) 20:1; (f) 50:1

$VCl_iF_{6-i}^{3-}$, so peak R1′ can be attributed to the reduction of $VCl_iF_{6-i}^{3-}$. With increasing of the fluoride ions in the melt, however, the reduction process had no obvious change.

According to the reduction step under fluoride-free conditions, there would be a peak corresponding to the reduction of $VCl_iF_{6-i}^{3-}$ to V in theory, but it was not observed in the electrochemical test results. One reason may be that the potential of reduction reaction is more negative than that of alkali metals precipitation. Thus, the corresponding peak cannot be observed in the electrochemical window. At the same time, V(II) may also react with fluoride ions to form the $VCl_iF_{6-i}^{4-}$ complex. However, no relevant peak was observed due to the low concentration of V(II) in the melt.

Cyclic voltammetry under different scan rates was carried out, as shown in Fig. 4. The number of reaction steps did not change with increasing the

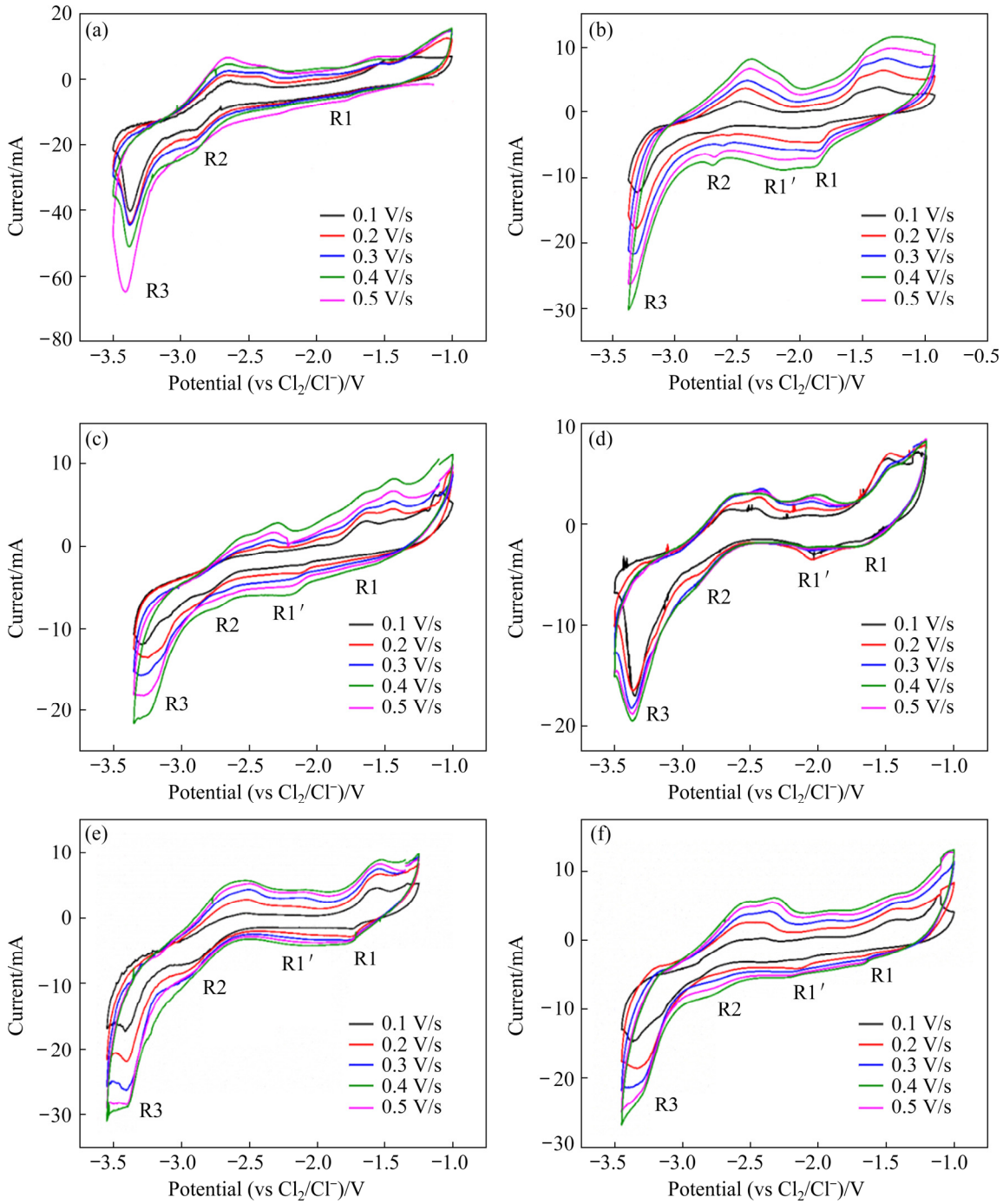

Fig. 4 Cyclic voltammograms of VCl_3 under different scanning rates in LiCl−KCl−KF molten salt at 450 °C with various α: (a) 0:1; (b) 1:1; (c) 2:1; (d) 5:1; (e) 20:1; (f) 50:1

scanning rate. Therefore, in the scanning rate range of 0.1−0.5 V/s, there was no concentration polarization phenomenon for all reaction steps, and the reduction potential change was caused by the properties of the complexes in the melt.

To investigate the details of the reduction of V(III), square wave voltammograms in the LiCl−KCl melt with various α were carried out, as shown in Fig. 5. The results were basically consistent with those of cyclic voltammetry testing. A significant difference was that the reduction potential of R1 was more obvious in square wave voltammetry, which was also the confirmation of the reduction potential of R1 by cyclic voltammetry mentioned above. The potential shift of redox peaks was not obvious, so it could be preliminarily confirmed that all reduction reactions under different conditions were quasi-reversible.

Gaussian fitting of square wave voltammetry at 25 Hz is shown in Fig. 6.

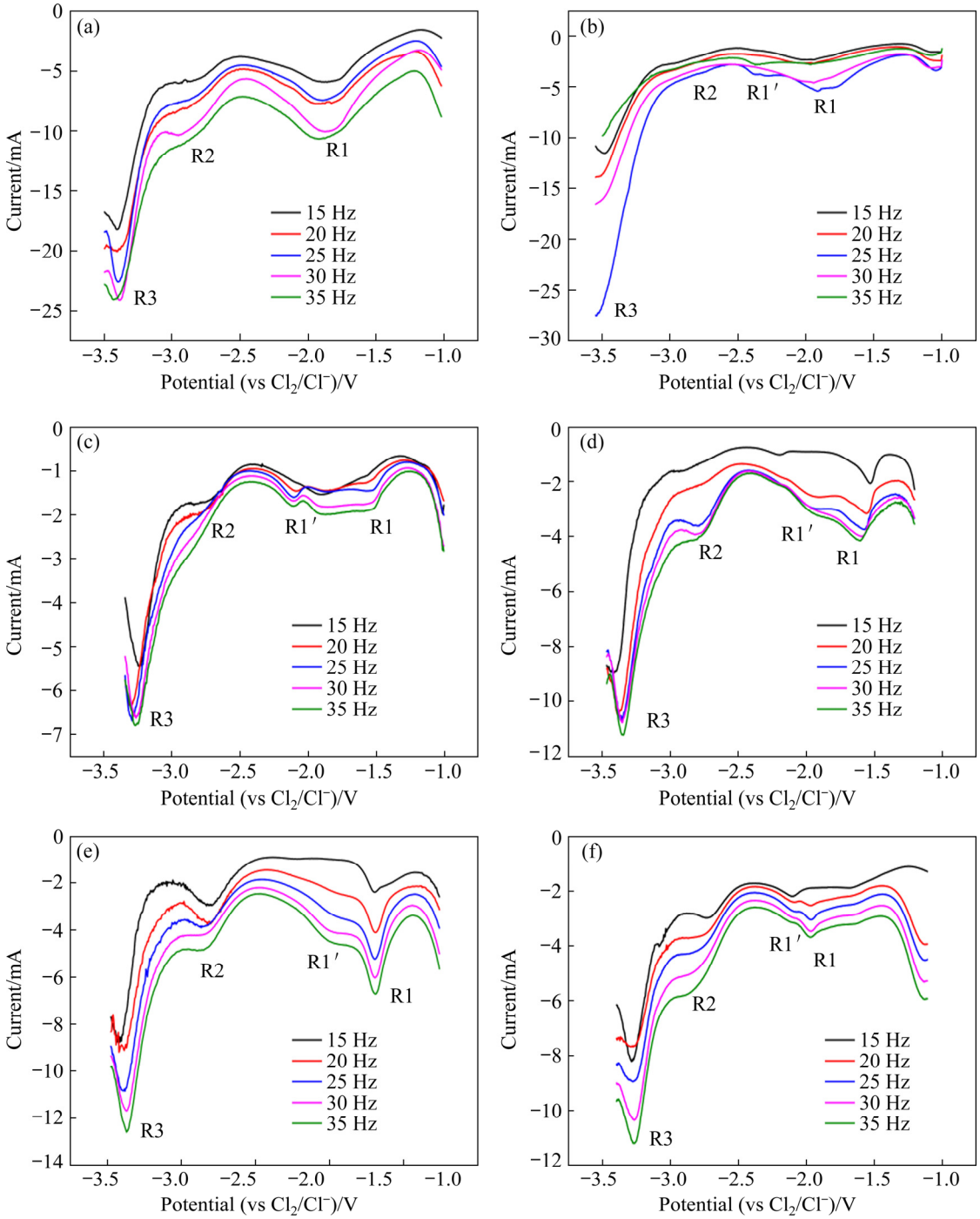

Fig. 5 Square wave voltammograms of VCl_3 in LiCl−KCl−KF molten salt at 450 °C under different frequencies with various α: (a) 0:1; (b) 1:1; (c) 2:1; (d) 5:1; (e) 20:1; (f) 50:1

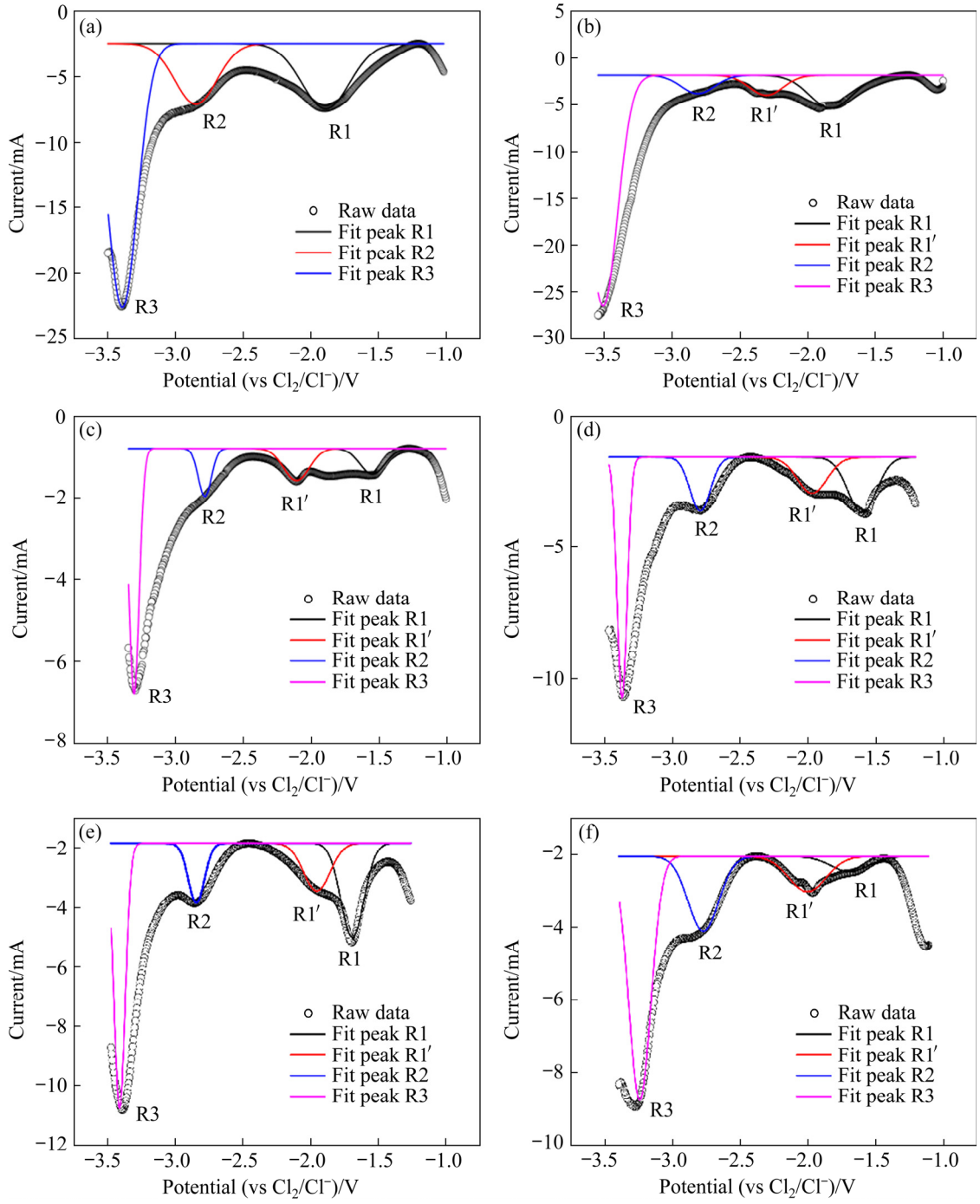

Fig. 6 Gaussian fitting of square wave voltammograms of VCl_3 in LiCl−KCl−KF molten salt at 450 °C under 25 Hz with various α: (a) 0:1; (b) 1:1; (c) 2:1; (d) 5:1; (e) 20:1; (f) 50:1

The number of exchanged electrons can be calculated by Gaussian fitting of square wave voltammetry by Eq. (1):

$$W_{1/2}=\left(3.53+\frac{3.46\zeta^2}{\zeta+8.1}\right)\frac{RT}{nF},\quad \zeta=\frac{nF\Delta E}{RT} \tag{1}$$

where $W_{1/2}$ is the half-wave width of the redox peak, F is the Faraday constant, T is the thermodynamic temperature, R is the molar gas constant, and ΔE is the amplitude of SWV. The calculated numbers of electrons transferred are shown in Table 1.

As can be seen from Table 1, in the alkali chloride melt, the electrode reduction reaction of V(III) were V(III)/V(II), V(II)/V, and V(III)/V. The number of electrons transferred for all reduction reactions did not change while containing fluoride.

Table 1 Calculated numbers of electrons transferred with various α

α	R1	R1′	R2	R3
0:1	0.89	−	1.69	2.76
1:1	1.12	0.95	1.68	2.92
2:1	1.04	0.99	1.99	2.74
5:1	0.91	0.87	1.56	2.79
20:1	1.09	0.95	1.68	2.63
50:1	0.91	0.87	1.59	2.74

And combined with the cyclic voltammetry results, it could be considered that R1 corresponds to $V^{3+}\rightarrow V^{2+}$, R1' corresponds to $VF_6^{3-}\rightarrow V^{2+}$, R2 corresponds to $V^{2+}\rightarrow V$ and R3 corresponds to $V^{3+}\rightarrow V$. The vanadium species would present in form of $VCl_iF_{6-i}^{3-}$, and in chloride−fluoride melts, the reaction would become more complicated. In a word, it could be considered that the initial reduction processes of V(III)→V(II)→V and V(III)→V did not change. At the same time, the addition of fluoride ions caused the formation of $VCl_iF_{6-i}^{3-}$, which was proven to be VF_6^{3-} later, and it would be reduced to V(II), that is a new reduction reaction of $VF_6^{3-}\rightarrow V^{2+}$.

The electrochemical behavior of vanadium ions was also studied by chronopotentiometry, as shown in Fig. 7. Several curvature changes were observed with different α. The chronopotentiometry results further confirmed the reduction process proposed previously.

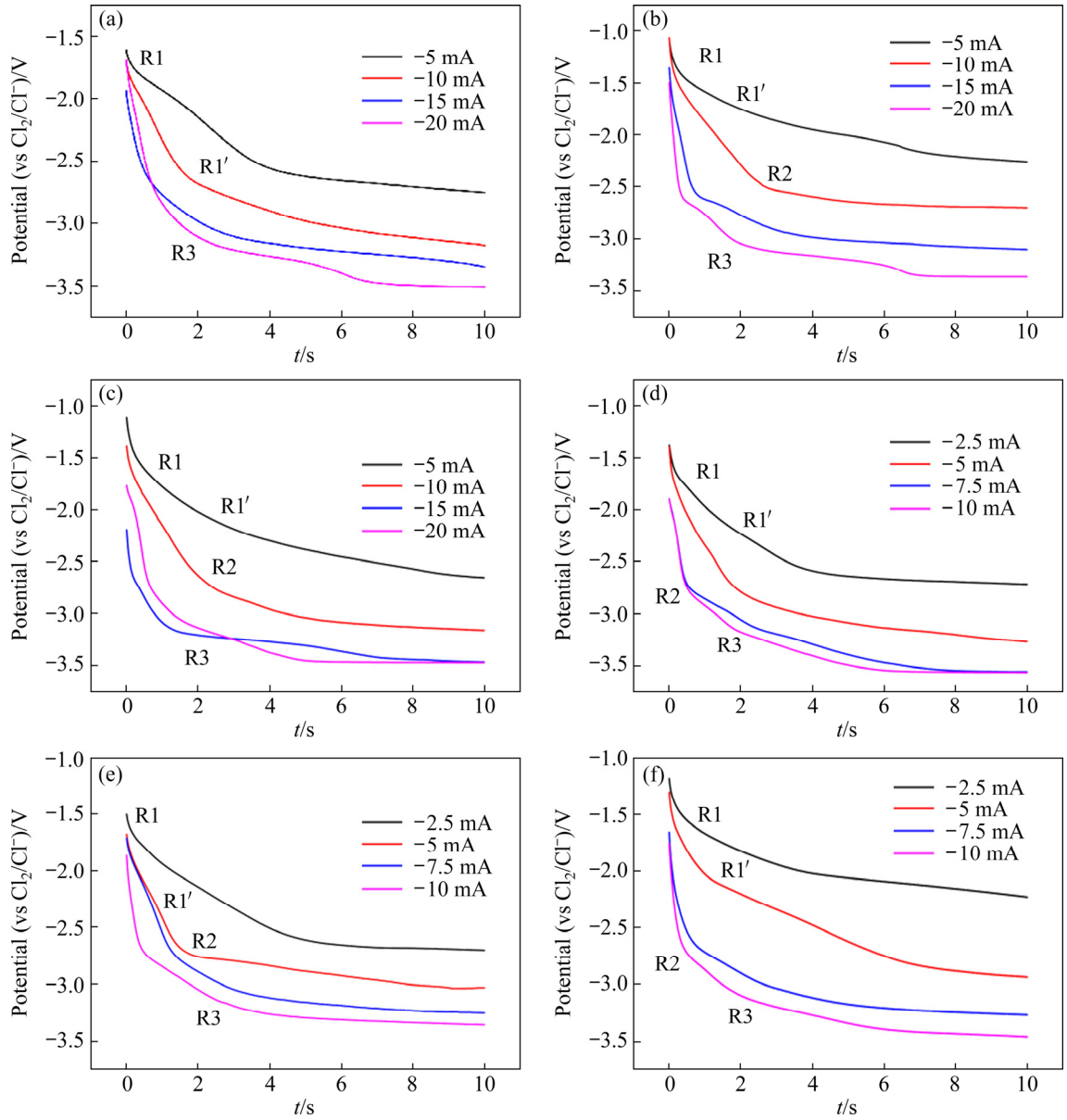

Fig. 7 Chronopotentiograms of VCl_3 in LiCl−KCl−KF molten salt at 450 °C with various α: (a) 0:1; (b) 1:1; (c) 2:1; (d) 5:1; (e) 20:1; (f) 50:1

To further investigate the specific form of fluoro—complex ions in molten salt, the solid molten salts under various α were collected and analyzed by Raman spectroscopy, and the results are shown in Fig. 8(a).

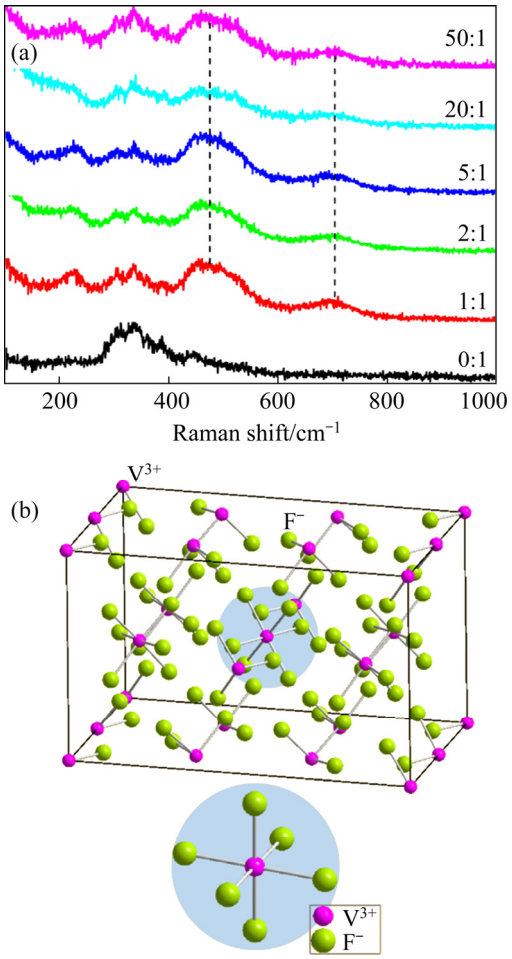

Fig. 8 Raman spectra of VCl_3 in LiCl−KCl−KF molten salt at 450 °C with various α (a) and geometric structure of VF_6^{3-} (b)

Only one Raman shift at 332 cm^{-1} in the spectrum was observed under the condition of α equal to 0:1. In this case, the molten salt system was LiCl−KCl−VCl_3, and thus the only complex ions in the system should be VCl_6^{3-} in theory [19]. Therefore, it could be considered that the Raman shift at 332 cm^{-1} corresponded to VCl_6^{3-}.

Two new characteristic peaks at 494 and 683 cm^{-1} were observed after adding fluoride ions. After the group theoretical analysis, the Raman spectrum of VF_6^{3-} consisted of three fundamental bands A_{1g}, E_g and F_{2g}. BECKER et al [20] calculated a theoretical A_{1g} mode value of 533 cm^{-1} on the basis of VF_6^{3-} in ideal O_h symmetry. The band at 335 cm^{-1} was attributed to the F_{2g} mode. Variations at the band positions could arise from different sites and correlation field effects as well as crystal packing. At the same time, it would also affect the position of the band since the main component of the sample for Raman spectroscopy analysis was eutectic LiCl−KCl. The band observed at 494 cm^{-1} could be assigned to be a component of the A_{1g} mode. It was noteworthy that the band at approximately 683 cm^{-1} was attributed to the presence of octahedral fluoride complexes. The geometric structure of VF_6^{3-} is shown in Fig. 8(b) [20−22].

3.2 Electro-deposition of vanadium

To investigate the effect of fluoride on the electro-deposition products, constant voltage electrolysis was carried out with various contents of fluoride. According to the results of electrochemical test, the reduction V(II)→V could occur at −2.90 V with different fluoride ion contents, and the deposition potentials would not change with the increase of fluoride ion content. So, −2.90 V could be used as the deposition potential. The electrolysis time was 6 h, and the deposits on the tungsten electrode were characterized by SEM and EDS, as shown in Fig. 9.

The inset of Fig. 9 shows the EDS analysis results of the deposits. Figure 9(a) shows that the product was a dendrite structure. A loose spongy structure was observed in Figs. 9(b, c). The particle size of the deposited product was approximately 200 nm when α was equal to 5:1. The particle size was reduced to approximately 100 nm with α of 20:1. The EDS analysis results in the inset revealed that metallic vanadium was deposited. This showed that fluoride ions had an effect on the nucleation process, resulting in a reduction in the particle size of the product.

4 Conclusions

(1) X-ray photoelectron spectroscopy showed that the V—Cl bond was replaced by V—F bond while adding fluoride in the molten salt, and $VCl_iF_{6-i}^{3-}$ was confirmed by both the electrochemical testing and Raman spectroscopy.

(2) The effect of fluoride ions on the electrochemical behavior of vanadium ions was investigated under condition of various α by cyclic voltammetry, square wave voltammetry and

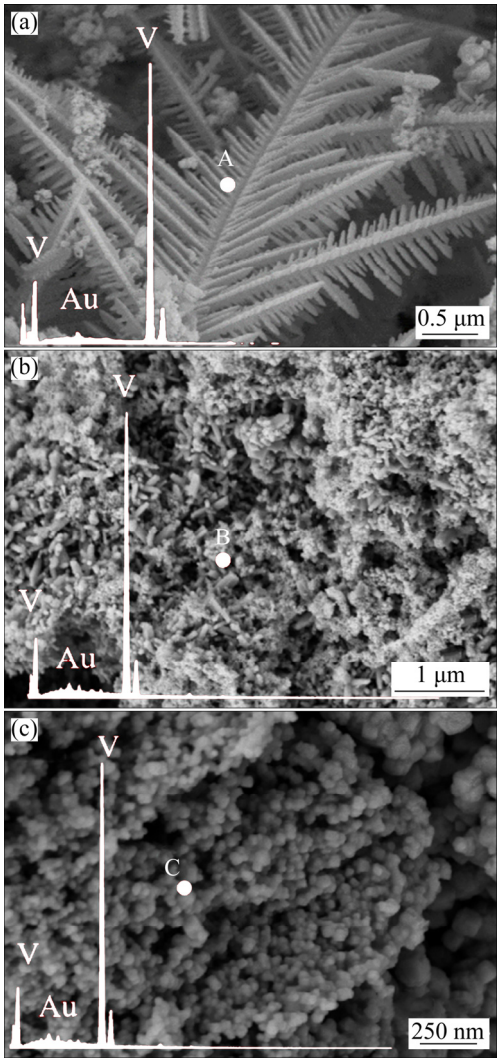

Fig. 9 SEM images of products of potentiostatic electrolysis with various α: (a) 0:1; (b) 5:1; (c) 20:1 (Inset: The EDS analysis results of Points A, B and C)

chronopotentiometry. The electro-reduction behavior of vanadium ions was more complicated due to the appearance of reduction step $VF_6^{3-} \rightarrow V^{2+}$.

(3) Metallic vanadium was obtained by long-term electrolysis. The deposition potential did not change with increasing the fluoride ion content; however, the particle size of vanadium was reduced.

Acknowledgments

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添加氟对 LiCl−KCl 熔盐中钒离子电化学行为的影响

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摘 要：利用 X 射线光电子能谱(XPS)和拉曼光谱分析含 VCl_3 和 KF 的 LiCl−KCl 共晶盐中钒离子的配位化合物形态。研究表明，氟离子会取代氯离子，与 V(III)结合形成 VF_6^{3-}。测试 F^-和 V^{n+}的摩尔浓度比(α)分别为 0:1、1:1、2:1、5:1、20:1 和 50:1 条件下钒离子的电化学行为。结果表明，相比未加氟的情况，出现新的还原步骤：$VF_6^{3-}\rightarrow V^{2+}$，钒离子的还原机制变得更加复杂。在 LiCl−KCl 熔盐中进行 6 h 电解，金属钒于 −2.90 V 在钨电极上沉积。SEM−EDS 分析结果表明，加入氟离子形成配位化合物 VF_6^{3-}后，电解产物的粒径减小。

关键词：V(III)离子；熔盐；电化学行为；还原机制；配位化合物

(Edited by Bing YANG)