

## Influence of $\text{Cr}^{3+}$ concentration on the electrochemical behavior of the anolyte for vanadium redox flow batteries

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The composition of electrolyte affects to a great extent the electrochemical performance of vanadium redox flow batteries (VRB). The effects of  $\text{Cr}^{3+}$  concentration in the anolyte on the electrode process of V(V)/V(IV) couple have been investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). It was found that  $\text{Cr}^{3+}$  causes no side reactions, but affects the electrochemical performance of V(V)/V(IV) redox reaction, including the reaction activity, the reversibility of electrode reaction, the diffusivity of vanadium ions, the interface film impedance, and the electrode reaction impedance. The experimental results show that  $\text{Cr}^{3+}$  within a certain concentration range can improve the reversibility of electrode reaction and the diffusion of vanadium ions. With the  $\text{Cr}^{3+}$  concentration increasing from 0 to 0.30 g L<sup>-1</sup>, the reversibility of V(V)/V(IV) reaction increases, while the diffusion resistance decreases. Correspondingly, the diffusion coefficient of vanadium ions increases from (5.48–6.77) × 10<sup>-7</sup> to (6.82–8.44) × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>, an increase of ~24%. However, the diffusion resistance increases and the diffusion coefficient decreases when  $\text{Cr}^{3+}$  concentration is over 0.30 g L<sup>-1</sup>, while the impedances of the interface, the film as well as the charge transfer increase continuously. As a result,  $\text{Cr}^{3+}$  with a certain concentration improves the diffusion and mass transfer process, but the resistances of the film, the interface, and the charge transfer rise. Furthermore,  $\text{Cr}^{3+}$  concentration of no more than 0.10 g L<sup>-1</sup> has few effect on the electrode reaction process, and that of no more than 0.30 g L<sup>-1</sup> is favorable to the diffusion of vanadium ions.

**vanadium redox flow batteries (VRB),  $\text{Cr}^{3+}$ , anolyte, cyclic voltammetry, electrochemical impedance spectroscopy**

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Vanadium redox flow batteries (VRB), a high efficient and clean rechargeable device for energy conversion and storage, have promising prospects in the fields of generating electricity using renewable power sources, peak regulation of electric networks, emergency power, remote supply and electric vehicles. They have unique advantages such as high power density, excellent cycling stability, high reliability, simple operation and convenient maintenance [1]. The process of energy storage and release of VRB is generally achieved through an interconversion of soluble redox couples like V(V)/V(IV) and V(III)/V(II) in a electrolyte. Thus, the electrolyte is both the electroactive species and the reservoirs for energy storage, and has a determining influence

on the electrochemical performance of VRB. The anolyte can be prepared directly by dissolving  $\text{VOSO}_4$  in a dilute sulfuric acid solution [2]. However, it is usually prepared by dissolving  $\text{V}_2\text{O}_5$  in a dilute sulfuric acid with a reduction treatment because of the high cost of  $\text{VOSO}_4$  [3].  $\text{V}_2\text{O}_5$  is an intermediate product in the smelting process for producing steel in Pangang Group, but it usually contains small amounts of impurities, such as  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  ions, which exist also in the  $\text{VOSO}_4$  prepared by using such  $\text{V}_2\text{O}_5$ . We have investigated the influence of  $\text{Mn}^{2+}$  concentration on the electrochemical behavior of  $\text{VOSO}_4$  anolyte for vanadium redox flow batteries in detail [4], however, to our knowledge, no research about the electrochemical behavior of the electrolyte with different  $\text{Cr}^{3+}$  concentrations has been reported.

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Herein, VOSO<sub>4</sub> anolyte was prepared by electrolyzing V<sub>2</sub>O<sub>5</sub> in a sulphuric acid solution. The electrochemical behavior of the anolytes with different Cr<sup>3+</sup> concentrations was investigated by CV and EIS. The effects of Cr<sup>3+</sup> concentration on the electrochemical characteristics and the mechanism of the redox reaction were discussed.

## 1 Experimental

### 1.1 Preparation of VOSO<sub>4</sub> anolytes with different Cr<sup>3+</sup> concentrations

The reference anolyte (1.45 mol L<sup>-1</sup> VOSO<sub>4</sub> + 3.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>) was prepared by electrolyzing the sulfuric acid solution containing V<sub>2</sub>O<sub>5</sub> (analytical reagent, AR) at a constant voltage. The ion content in the reference anolyte was determined by ICP-AES (IRIS Intrepid II XSP, Thermo Electron Corporation, USA) and the potential titration. The total content of vanadium in the reference anolyte was determined as 74.14 g L<sup>-1</sup> [4]. Adulterant solution consisting of 1 mol L<sup>-1</sup> Cr<sup>3+</sup> and 3 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> was prepared by the Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (AR) solution of 50 wt.% and the concentrated sulphuric acid of 98 wt.%. The VOSO<sub>4</sub> anolytes with different Cr<sup>3+</sup> concentrations were obtained by adding different amounts of adulterant solution prepared above to the reference anolyte. The determined composition is presented in Table 1. As the graphite electrode was dissolved into the acid solution in the process of electrolysis, many carbon particles come into existence in the electrolyte. To eliminate the effect of carbon, the as-obtained electrolyte was filtered after being rested for about 7 d, which is different from our previous work [4].

### 1.2 Electrochemical performance measurement

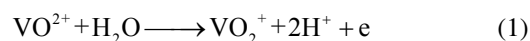
To avoid the graphite electrode degrading the measurements, the platinum foils of ~0.14 cm<sup>2</sup>, ~15 cm<sup>2</sup>, and the saturated calomel electrode (SCE) were applied as the working electrode, auxiliary electrode, and reference electrode, respectively. The platinum electrodes were treated with the chromium acid lotion and the dilute hydrochloric acid before each measurement [4]. The electrochemical behavior was investigated at room temperature by using the three-electrode system on an electrochemical station consisting of PAR273A and 5210 lock-in-amplifier. The potential range of the CV curves was 0.40–1.15 V. The scan rates were 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s<sup>-1</sup>, sequentially. In

the frequency range from 100 kHz to 10 mHz, EIS measurements were performed with a sinusoidal excitation voltage of 10 mV.

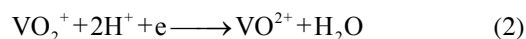
## 2 Results and discussion

### 2.1 CV analysis

The cyclic voltammograms of the VOSO<sub>4</sub> anolytes with different Cr<sup>3+</sup> concentrations at a scan rate of 50 mV s<sup>-1</sup> are shown in Figure 1. The curves are similar to each other in shape, and exhibit evidently only one couple of redox peaks. However, the potential difference between the oxidation peak and the reduction peak as well as the peak current intensity changes greatly as Cr<sup>3+</sup> concentration increases. The results show that the main redox reactions in all anolytes exist as V(V)/V(IV) couple, and addition of Cr<sup>3+</sup> has a great effect on the electrode reaction process. The oxidation peak at ~0.95 V is related to the oxidation of VO<sup>2+</sup> to VO<sub>2</sub><sup>+</sup>,



whereas the reduction peak at ~0.76 V is associated with the reduction of VO<sub>2</sub><sup>+</sup> to VO<sup>2+</sup> [5–9],

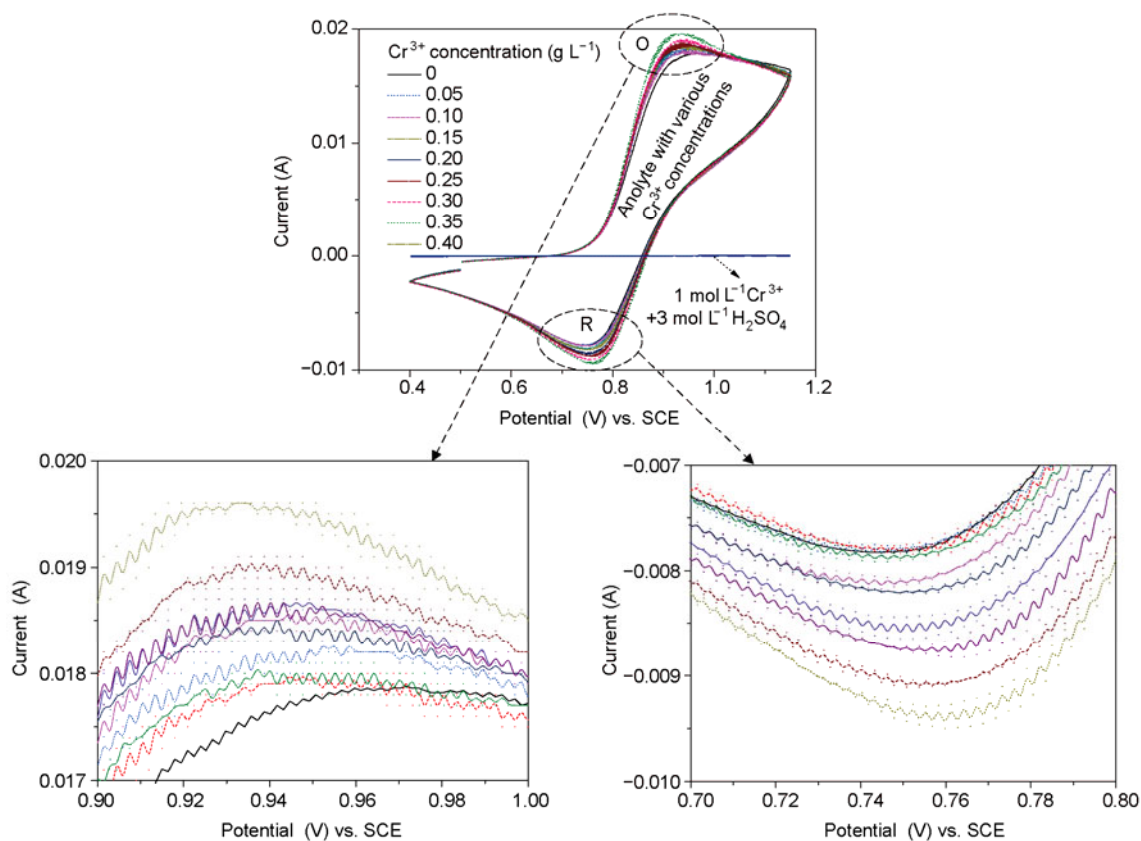


In order to investigate the influence of Cr<sup>3+</sup> concentration on the electrode polarization and reaction reversibility, the separation of peak potentials, ΔV<sub>p</sub>, and the ratio of peak current intensities of the oxidation peak (I<sub>po</sub>) to the reduction peak (I<sub>pr</sub>), I<sub>po</sub>/I<sub>pr</sub>, obtained from the CV measurements at different scan rates are summarized in Figure 2. With Cr<sup>3+</sup> concentration increasing from 0 to 0.35 g L<sup>-1</sup>, ΔV<sub>p</sub> shows a quasi decrease tendency. It indicates that Cr<sup>3+</sup> with a certain concentration reduces the electrode polarization, and improves the reaction activity [10–12]. On the other hand, the increase of Cr<sup>3+</sup> concentration results in the ratio of I<sub>po</sub>/I<sub>pr</sub> near to 1. It suggests that Cr<sup>3+</sup> can improve the reversibility of the V(V)/V(IV) redox reaction and the efficiency of VRB.

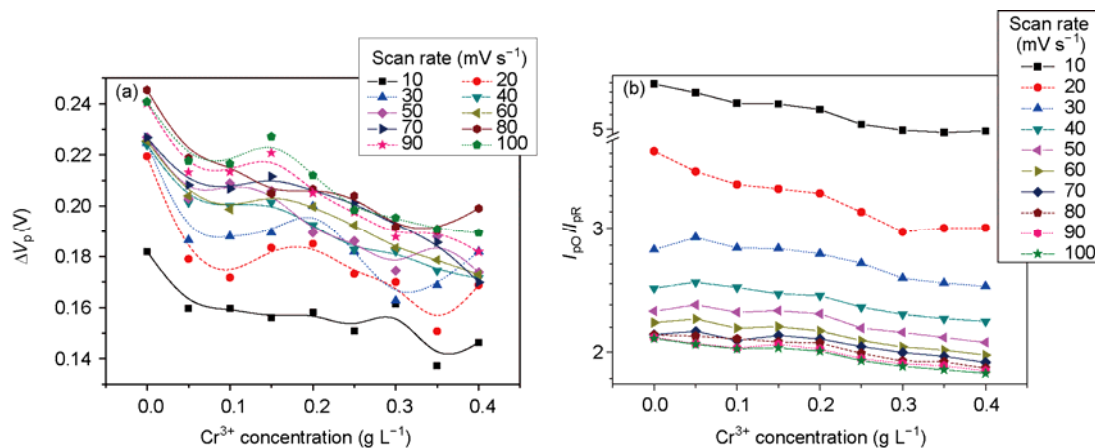
To study the influence of Cr<sup>3+</sup> concentration on the reaction activity of electrodes, the relationship between Cr<sup>3+</sup> concentration and the current intensities of the redox peaks is summarized in Figure 3. The absolute values of the peak current intensities obtained at different scan rates exhibit in whole an increase tendency with the increase of Cr<sup>3+</sup> concentration. The current intensity increases by ~3% with Cr<sup>3+</sup>

**Table 1** Concentration of the metal ions in the testing anolytes (g L<sup>-1</sup>)

Solution	Cr-only	Cr-p	Cr-a	Cr-b	Cr-c	Cr-d	Cr-e	Cr-f	Cr-g	Cr-h
Cr <sup>3+</sup>	52	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
V(IV)	0						66.56			
V(V)	0						7.58			



**Figure 1** CV curves of the analytes with different  $\text{Cr}^{3+}$  concentrations at a scan rate of  $50 \text{ mV s}^{-1}$ .

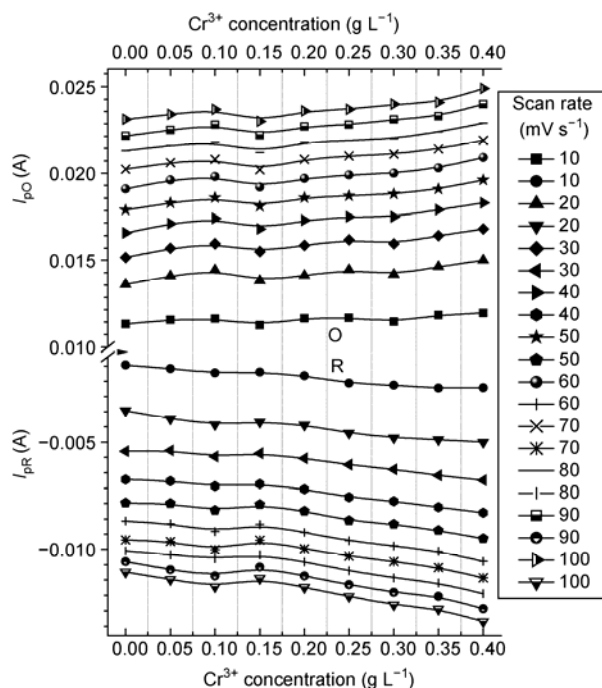


**Figure 2** Influence of  $\text{Cr}^{3+}$  concentration on the voltage difference (a) and the current intensity ratio (b) of the oxidation peak and the reduction peak.

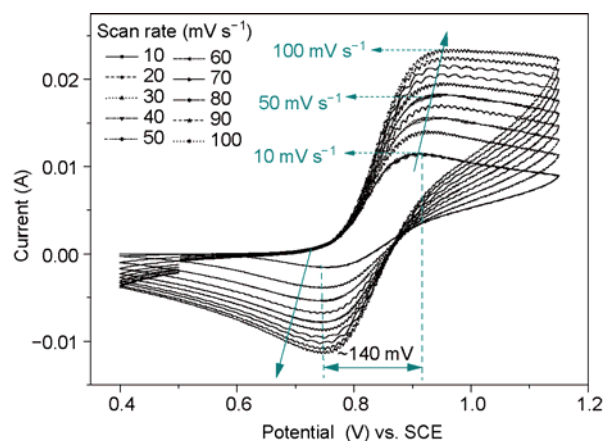
concentration rising from 0 to  $0.10 \text{ g L}^{-1}$ , whereas a fast growth of  $\sim 9\%$  from  $0.15$  to  $0.40 \text{ g L}^{-1}$ . It suggests that  $\text{Cr}^{3+}$  with high concentration increases the reaction capability of  $\text{V(V)}/\text{V(IV)}$  couple. Correspondently, the electrode activity is improved [10,11].

The CV curves of the analyte with  $0.05 \text{ g L}^{-1} \text{ Cr}^{3+}$  obtained at different scan rates are shown in Figure 4. With the scan rates increasing, the peak values of the current intensity are quite different, but the redox curves are comparative-

ly symmetric in shape. The potential difference between the oxidation peak and the reduction peak is about  $140 \text{ mV}$ , in the range of  $59\text{--}200 \text{ mV}$ , indicating the quasi-reversibility of the  $\text{V(V)}/\text{V(IV)}$  reaction on the Pt electrode [12–14]. Theoretically, the value of the diffusion coefficient for a quasi-reversible reaction ( $D$ ) is between that for a reversible ( $D_1$ ) one and an irreversible ( $D_2$ ) one. According to the experimental results of the CV curves obtained at different scan rates,  $D_1$  and  $D_2$  were determined by applying eqs.



**Figure 3** Influence of  $\text{Cr}^{3+}$  concentration on the current intensities of the oxidation peaks and the reduction peaks at different scan rates.



**Figure 4** Cyclic voltammograms of the analyte with  $0.05 \text{ g L}^{-1} \text{ Cr}^{3+}$  at different scan rates.

(3) and (4) [5,8,10,13–18].

$$I_p = 2.69 \times 10^5 A n^{3/2} C_o D_1^{1/2} v^{1/2} \quad (25^\circ\text{C, reversible reaction}), \quad (3)$$

$$I_p = 2.99 \times 10^5 A n^{3/2} C_o \alpha^{1/2} D_2^{1/2} v^{1/2}$$

$$(25^\circ\text{C, irreversible reaction}), \quad (4)$$

where  $I_p$ ,  $n$ ,  $A$ ,  $D$ ,  $\alpha$ ,  $C_o$  and  $v$  refer to the current density of the reduction peak (A), the number of transferred electrons, the surface area of the working electrode ( $\text{cm}^2$ ), the diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ ), the transfer coefficient, the electrolyte concentration ( $\text{mol mL}^{-1}$ ), and the scan rate ( $\text{V s}^{-1}$ ), respectively.

Based on the above experimental results, eqs. (3) and (4) are transformed as follows:

$$\frac{I_p}{A} = 390.05 D_1^{1/2} \times v^{1/2} = k \times v^{1/2}, \quad (5)$$

$$\frac{I_p}{A} = 433.55 D_2^{1/2} \times v^{1/2} = k \times v^{1/2}. \quad (6)$$

In point of the linear function,  $k$  refers to the slope of the line, where the variables are the current density  $I_p/A$  and the square root of scan rate  $v^{1/2}$ , and can be determined by the linear regression.  $D_1$  and  $D_2$  calculated by using the following eqs. (7) and (8) are listed in Table 2,

$$D_1 = 6.57 \times 10^{-6} \times k^2, \quad (7)$$

$$D_2 = 5.32 \times 10^{-6} \times k^2. \quad (8)$$

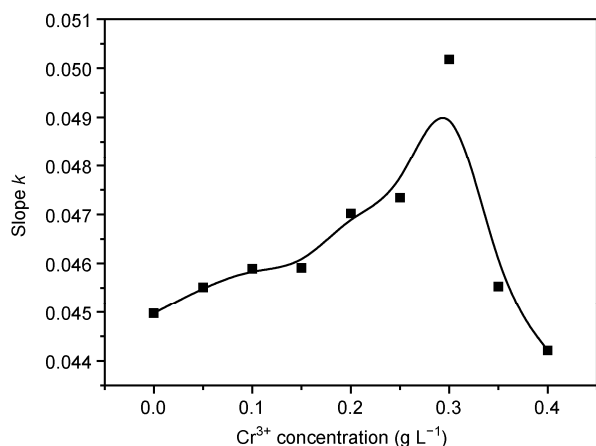
According to eqs. (7) and (8), with the slope  $k$  increasing, the diffusion coefficient  $D$  increases, which refers to the enhanced diffusivity of vanadium ions. Figure 5 indicates the relationship of  $k$  to  $\text{Cr}^{3+}$  concentration. With the increase of  $\text{Cr}^{3+}$  concentration,  $k$  increases firstly, and then decreases. The diffusion coefficient,  $D$ , rises to the maximum,  $(6.82\text{--}8.44) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , which is about 24% higher than that of the reference anolyte, when  $\text{Cr}^{3+}$  concentration is  $0.3 \text{ g L}^{-1}$ . Apparently,  $\text{Cr}^{3+}$  with a certain concentration improves the diffusivity of the vanadium ions and intensifies the processes of mass transfer and charge transfer. As a result, the reaction activity is improved. However, the diffusion process is blocked due to the increase of the polarization degree when  $\text{Cr}^{3+}$  concentration is over  $0.30 \text{ g L}^{-1}$ , which agrees well with the increase of the potential difference at the corresponding concentration shown in Figure 2.

## 2.2 EIS analysis

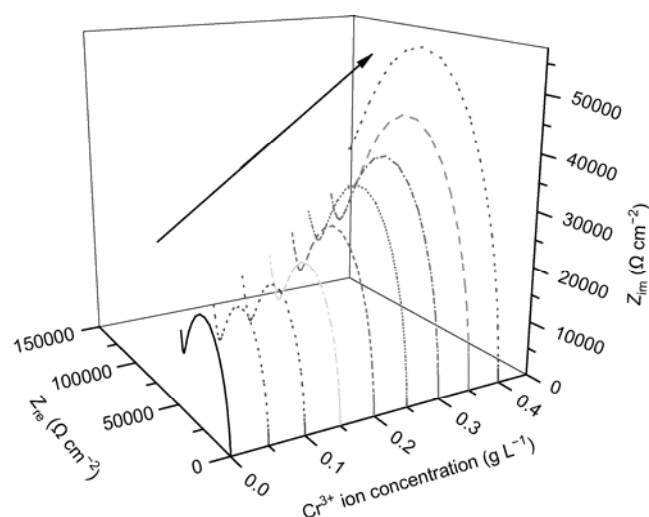
The influence of  $\text{Cr}^{3+}$  concentration on the electrode reaction process of the analyte was further investigated by EIS. The Nyquist plots are shown in Figure 6. In the range of 0–

**Table 2** Influence of  $\text{Cr}^{3+}$  concentration on the diffusion coefficient  $D_1$  and  $D_2$  of vanadium ions

Solution	Cr-p	Cr-a	Cr-b	Cr-c	Cr-d	Cr-e	Cr-f	Cr-g	Cr-h
$\text{Cr}^{3+}$ concentration ( $\text{g L}^{-1}$ )	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
Diffusion coefficient $D_1$ ( $\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ )	6.77	6.94	7.05	7.06	7.41	7.51	8.44	6.94	6.55
Diffusion coefficient $D_2$ ( $\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ )	5.48	5.61	5.71	5.71	5.99	6.07	6.82	5.62	5.30



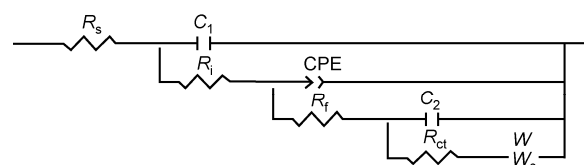
**Figure 5** Influence of  $\text{Cr}^{3+}$  concentration on the slope ( $k$ ) of the regression lines.



**Figure 6** Influence of  $\text{Cr}^{3+}$  concentration on the EIS of the analyte.

0.30  $\text{g L}^{-1}$  of  $\text{Cr}^{3+}$  concentration, the plots consist of a semi-circle part in the high frequency region and a linear part in the low frequency region. When the concentration of  $\text{Cr}^{3+}$  increases to 0.35 and 0.40  $\text{g L}^{-1}$ , the curves change to a uncompleted semi-circle part in the high frequency region,

while the linear part in the low frequency region disappears. The semicircle part in the high frequency region corresponds to the impedances of the solution, the interface, the electrode reaction and the electrolyte film altogether, while the linear part in the low frequency region corresponds to the Warburg impedance resulted from vanadium ions diffusion [18]. The equivalent circuit is illustrated in Figure 7, where the circuit model is described as  $R_s(C_1(R_i(Q_1(R_f(C_2(R_{ct}W))))))$ , where  $R_s$ ,  $R_i$ ,  $R_f$ ,  $R_{ct}$ , and  $W$  refer to the solution resistance, the interface resistance, the electrolyte film resistance on electrode surface, the charge transfer resistance, and the Warburg diffusion impedance, respectively. Because of the nonhomogeneity of the electrode surface, the interface capacitance  $C$  is substituted by the constant phase element (CPE). The parameters of the equivalent circuit are listed in Table 3, which were determined by simulating the EIS plots with ZSimpWin and Zview. With  $\text{Cr}^{3+}$  concentration increasing,  $R_s$  is nearly constant, while  $R_i$ ,  $R_f$ , and  $R_{ct}$ , as a whole, increase. The increase degrees of  $R_i$ ,  $R_f$ , and  $R_{ct}$  are small below 0.10  $\text{g L}^{-1}$   $\text{Cr}^{3+}$  concentration, and become notably large when the concentration is higher. The Warburg impedance  $W$  shows a minimum value at 0.30  $\text{g L}^{-1}$   $\text{Cr}^{3+}$  concentration. When the  $\text{Cr}^{3+}$  concentration is less than 0.30  $\text{g L}^{-1}$ , the Warburg impedance  $W$  decreases with  $\text{Cr}^{3+}$  concentration increasing, which is consistent with the CV results discussed above, which indicates  $\text{Cr}^{3+}$  enhances the diffusivity of vanadium ions. However, The Warburg impedance  $W$  increases when the  $\text{Cr}^{3+}$  concentration reaches 0.35  $\text{g L}^{-1}$ . The semicircle part in the high frequency region becomes uncompleted when the  $\text{Cr}^{3+}$  concentration is 0.40  $\text{g L}^{-1}$ , where the diffusion part disappears, as shown in Figure 6, indicating the charge transfer impedance is extremely high. Thus, the electrochemical reaction and the vanadium ion diffusion become difficult due to the increased electrolyte



**Figure 7** Equivalent circuits of the EIS fitting.

**Table 3** Influence of  $\text{Cr}^{3+}$  concentration on the parameters of EIS

$\text{Cr}^{3+}$ concentration ( $\text{g L}^{-1}$ )	$R_s$ ( $\Omega \text{ cm}^{-2}$ )	$R_i$ ( $\Omega \text{ cm}^{-2}$ )	$R_f$ ( $\Omega \text{ cm}^{-2}$ )	$R_{ct}$ ( $\Omega \text{ cm}^{-2}$ )	$W$ ( $\Omega \text{ cm}^{-2}$ )
0	0.67	86.41	$4.69 \times 10^4$	$3.45 \times 10^4$	$14.85 \times 10^{-5}$
0.05	0.59	93.52	$4.64 \times 10^4$	$3.45 \times 10^4$	$13.41 \times 10^{-5}$
0.10	0.60	95.91	$5.11 \times 10^4$	$3.80 \times 10^4$	$12.74 \times 10^{-5}$
0.15	0.60	144.36	$5.68 \times 10^4$	$3.98 \times 10^4$	$12.51 \times 10^{-5}$
0.20	0.60	160.25	$6.75 \times 10^4$	$5.01 \times 10^4$	$11.12 \times 10^{-5}$
0.25	0.60	175.62	$8.08 \times 10^4$	$5.99 \times 10^4$	$10.84 \times 10^{-5}$
0.30	0.59	188.65	$10.00 \times 10^4$	$6.83 \times 10^4$	$10.01 \times 10^{-5}$
0.35	0.59	202.96	$12.64 \times 10^4$	$7.69 \times 10^4$	$10.54 \times 10^{-5}$
0.40	0.60	254.83	$14.08 \times 10^4$	$9.70 \times 10^4$	—

film resistance and interface resistance resulted from high  $\text{Cr}^{3+}$  concentration. As a result, increasing  $\text{Cr}^{3+}$  concentration to a great extent (especially over  $0.10 \text{ g L}^{-1}$ ) has negative effects on the charge transfer reaction, the characteristics of the interface and the electrolyte film, and the vanadium ions diffusivity, which interfere with the electrode reaction and the power characteristics of VRB.

### 2.3 Mechanism analysis

Based on the results discussed above, it is suggested that  $\text{Cr}^{3+}$  affects the electrode process in respect of the charge transfer reaction, the electrode interface behavior, the surface electrolyte film impedance, and the vanadium ion diffusion. The electrode process of  $\text{V(V)/V(IV)}$  redox reaction is commonly controlled by the ion diffusion and the charge transfer reaction, where the influence factors of the electrochemical behavior are complicated, including the reactant concentration difference between the electrode surface and the bulk solution, the electric double-layer capacitance of the two-phase interface, the charge transfer and the electrolyte film on the electrode surface [19–24]. Consequently, the possible reasons for the influence of  $\text{Cr}^{3+}$  ions on the electrode process of  $\text{V(V)/V(IV)}$  redox reaction are as follows: (1) The valence electron configurations of V and Cr are  $3d^34s^2$  and  $3d^54s^1$ , respectively. Vanadium ion is thermodynamically active due to the existence of the empty  $d$  orbitals, which is easy to associate with each other in the anolyte [25–27]. However, Cr is comparably stable in view of thermodynamics because all  $d$  orbitals are occupied by electrons. On the other hand, addition of  $\text{Cr}^{3+}$  changes the original ionic circumstance, and leads to the change of the electric field interaction of vanadium ions. Therefore, the addition of  $\text{Cr}^{3+}$  in anolyte can hinder to some extent the association of vanadium ions, which results in the intensified diffusion process and the decreased concentration polarization. Because the number of the active vanadium ions for the electrode reaction increases, the electrode reaction activity is improved correspondingly. (2)  $\text{Cr}^{3+}$  makes the vanadium ions easy to diffuse by limiting the ion association. However, the collision probability of  $\text{VO}^{2+}$  with  $\text{Cr}^{3+}$  increases due to the larger radius of  $\text{Cr}^{3+}$  ( $0.63 \text{ \AA}$ ) [27] compared to that of  $\text{V(IV)}$  ( $0.46 \text{ \AA}$ ) [28]. Thus, the diffusion resistance of vanadium ions increases when large amount of  $\text{Cr}^{3+}$  ions exist in anolyte. (3) The valence of  $\text{Cr}^{3+}$  is lower than that of vanadium ions, and  $\text{Cr}^{3+}$  is competitive with vanadium ions for the adsorption on the electrode surface, leading to the composition of the electrolyte film on the electrode surface changes [29]. Simultaneously, the substitution of  $\text{Cr}^{3+}$  with low valence for vanadium ions with high valence will bring on the charge imbalance on the electrode surface, which alters the electric double-layer at the interface. Therefore, the electrolyte film impedance and the interface impedance increase with the increase of  $\text{Cr}^{3+}$  concentration. (4) The increased film impedance and interface

impedance will hinder the charge transfer and the diffusivity of vanadium ions. So, the high film impedance polarization and the electrochemical polarization will affect the diffusion impedance and the electrochemical reaction impedance. (5) Before the electrochemical reaction, the step of diffusion is the determined factor for the electrode process.  $\text{Cr}^{3+}$  intensifies the diffusion process and decreases the concentration polarization, resulting in the increase of the reaction current intensities, so the reaction activity is enhanced. However, the step of electrochemical reaction becomes the determined factor for the electrode process when the vanadium ions reach the Pt electrode.  $\text{Cr}^{3+}$  ions change the film composition and the interface status, inducing the increase of film impedance polarization and the electrochemical polarization. Consequently, the electrochemical reaction changes difficult.

According to the above possible reasons, it is not difficult to understand the influence of  $\text{Cr}^{3+}$  on the electrochemical behavior of the anolyte for VRB in a certain concentration. When  $\text{Cr}^{3+}$  concentration is as low as  $0.10 \text{ g L}^{-1}$ , the ionic atmosphere changes little, and the competitive adsorption between  $\text{Cr}^{3+}$  and vanadium ions is not severe. Therefore, the electrode surface status changes slightly and the increase of impedances of electrolyte film, interface and electrochemical reaction is not obvious. However, more  $\text{Cr}^{3+}$  ions will enhance the competitive adsorption and change the electric field. The large change of interface status will affect the processes of mass transfer and charge transfer, which hinders the electrochemical reaction. When  $\text{Cr}^{3+}$  concentration is no more than  $0.30 \text{ g L}^{-1}$ , the limited function for the association of vanadium ions is dominant. The decreased concentration polarization makes the diffusion coefficient of vanadium ions increase. However, when  $\text{Cr}^{3+}$  concentration is higher than  $0.30 \text{ g L}^{-1}$ , the changes of the collision probability, the ionic atmosphere and the competitive adsorption during the diffusion process become dominant. The increased diffusion resistance makes the diffusion coefficient of vanadium ions decline.

### 3 Conclusions

The effects of  $\text{Cr}^{3+}$  concentration on the electrode process of  $\text{V(V)/V(IV)}$  redox reaction were investigated by cyclic voltammetry and electrochemical impedance spectroscopy. It was found that  $\text{Cr}^{3+}$  affects to a great extent the electrochemical performance, including the electrode reaction activity and reversibility, the charge transfer process, the interface behaviour, the electrolyte film on the electrode surface and the ions diffusion. CV results show that  $\text{Cr}^{3+}$  with a certain concentration improves the diffusivity of vanadium ions, and lowers the electrode concentration polarization degree. Consequently, the reaction activity and reversibility are improved. Compared to the reference anolyte, ~24% decrease of the potential difference of redox peaks, ~24%

increase of vanadium ions diffusion coefficient, and ~10% increase of the current peaks are obtained when  $\text{Cr}^{3+}$  concentration is  $0.30 \text{ g L}^{-1}$ . EIS results suggest that the impedances of the electrolyte film, the charge transfer and the interface, increase with  $\text{Cr}^{3+}$  concentration increasing, but the increase extent is small when  $\text{Cr}^{3+}$  concentration is no more than  $0.10 \text{ g L}^{-1}$ . On the other hand, the diffusion impedance declines with the increase of  $\text{Cr}^{3+}$  concentration when the concentration is less than  $0.30 \text{ g L}^{-1}$ . According to the results of CV and EIS obtained in this work, it was concluded that  $\text{Cr}^{3+}$  with a certain concentration can enhance the processes of the diffusion and the mass transfer, but excessive amount of  $\text{Cr}^{3+}$  will increase the impedances of electrolyte film, charge transfer, ions diffusion and interface. Consequently,  $\text{Cr}^{3+}$  concentration of no more than  $0.10 \text{ g L}^{-1}$  has few effect on the electrode reaction process, while  $\text{Cr}^{3+}$  concentration of no more than  $0.30 \text{ g L}^{-1}$  facilitates the diffusion of vanadium ions.

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