



Analyses and optimization of electrolyte concentration on the electrochemical performance of iron-chromium flow battery

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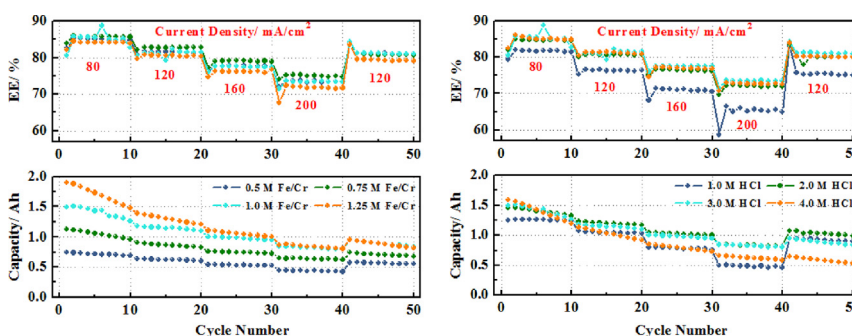
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HIGHLIGHTS

- Effect of electrolyte concentration of Fe/Cr flow battery is firstly investigated.
- Electrolyte of 1.0 M FeCl₂, 1.0 M CrCl₃ and 3.0 M HCl shows the best performance.
- This work can provide a direct guidance to the application of Fe/Cr flow battery.

GRAPHICAL ABSTRACT

Effect of FeCl₂, CrCl₃ and HCl concentration on the electrochemical performance of iron-chromium flow battery is systematically investigated, and the optimized electrolyte exhibits excellent battery efficiency (energy efficiency: 81.5%) at 120 mA cm⁻².



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ABSTRACT

In order to improve the electrochemical performance of iron-chromium flow battery, a series of electrolytes with x M FeCl₂ + x M CrCl₃ + 3.0 M HCl ($x = 0.5, 0.75, 1.0, 1.25$) and 1.0 M FeCl₂ + 1.0 M CrCl₃ + y M HCl ($y = 1.0, 2.0, 3.0, 4.0$) are prepared, and the effect of electrolyte concentration on the electrochemical performance of iron-chromium flow battery are firstly investigated. The viscosity of electrolyte increases along with the increasing concentration of FeCl₂, CrCl₃ and HCl, however, the corresponding conductivity decreases with the increasing concentration of FeCl₂ and CrCl₃ but increases with the increasing HCl concentration. It is worth noting that the electrolyte with 1.0 M FeCl₂, 1.0 M CrCl₃ and 3.0 M HCl presents the best electrochemical performance due to the synergistic effect of viscosity, conductivity and electrochemical activity. Most importantly, iron-chromium flow battery with the optimized electrolyte presents excellent battery efficiency (coulombic efficiency: 97.4%; energy efficiency: 81.5%) when the operating current density is high up to 120 mA cm⁻². This work can improve the battery performance of iron-chromium flow battery more efficiently, and further provide theoretical guidance and data support to its engineering application.

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1. Introduction

Due to the limited fossil fuel resource and growing environmental pollution, the renewable energy including wind energy and solar energy has been widely developed in the past few years [1]. However, the intermittent and unstable output characteristics of such renewable energy make it difficult to meet the requirement of power quality and safe operation of power grid [2]. One effective way is to match with a large-scale energy storage system in the whole renewable energy system [3]. Flow batteries, one of the most promising large-scale energy storage technologies, can store electrical energy in redox couples in electrolytes and realize the energy conversion between the electrical energy and chemical energy when flowing the electrolytes through the electrodes by pumps [4]. Based on the advantages of high safety, long cycle life, and deep discharge ability, especially for the design flexibility in decoupling energy and power [5], flow batteries have been widely developed in the energy storage demonstration project around the world [6]. In particular, iron-chromium (Fe/Cr) flow battery, which uses cheaper $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Cr}^{3+}/\text{Cr}^{2+}$ redox couples in hydrochloric acid solution as the catholyte and anolyte electrolytes respectively, becomes one of the promising candidates for large-scale energy storage application [7].

As the first applicable flow battery, Fe/Cr flow battery was proposed by the National Aeronautics and Space Administration (NASA) in the mid-1970s [8]. Subsequently, Lewis Research Center also studied the chromium electrode behavior during the charge and discharge process at room temperature [9]. It was found that there were three inner-sphere complex ions ($\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ and $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^{+}$) in CrCl_3 solution, and a dynamic equilibrium existed between the electrochemically active $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ and inactive $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. In general, the transformation process from $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ to $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ was relatively slow, but that kinetics would be promoted with the existence of Cr^{2+} [9]. So, the electrolyte deactivation was a key issue for Fe/Cr flow battery. Fortunately, the conversion of inactive $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ to active $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ can solve the electrolyte deactivation by raising the electrolyte temperature to 65 °C. However, it also brings in a serious cross contamination [8]. Aiming to solve such issue, a mixed electrolyte of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Cr}^{3+}/\text{Cr}^{2+}$ redox couples in hydrochloric acid solution as both catholyte and anolyte was proposed [10]. Furthermore, Zeng *et al.* investigated the effects of operating temperature on electrochemical performance of the Fe/Cr flow battery [11] and enhanced the energy efficiency by employing interdigitated flow fields with carbon papers coated bismuth [12].

Although the electrochemical performance of Fe/Cr flow battery was improved in some extent with a higher operated temperature and mixed electrolyte, the sluggish kinetics of $\text{Cr}^{3+}/\text{Cr}^{2+}$ in halide solution as well as the serious hydrogen evolution were still not solved, which greatly limited the overall battery performance [13]. Lots of researchers have been devoted to solving these problems by electrode modification, such as introducing Au [14], Bi [15], Pb [16] as catalyst onto the electrodes, and adjusting the precursor materials of electrodes [17] and the corresponding pre-treatment technology [18]. However, none of them demonstrated their superiorities in commercial application because of tedious treatment procedures, unfavorable stability, and the limited improvement in the electrochemical performance of Fe/Cr flow battery.

In fact, both the electrochemical reaction and hydrogen evolution reaction (HER) are occurred on the electrode/electrolyte interface, and the above-mentioned modifications on the electrode or electrolyte can solve these problems to a certain extent [19]. For example, N-alkylamines [20] or NH_4Cl [21] was used as the additive in the $\text{HCl}-\text{CrCl}_3$ solution and exhibited a desired ability to prevent the $\text{Cr}^{3+}/\text{Cr}^{2+}$ couple from deactivation. Moreover, chromium (III) acetylacetonate redox couples [22] or other chelated chromium electrolyte [23] have been investigated in the electrolyte with a low concentration of Cr^{3+} and delivered a higher voltage. In addition, the preliminary studies of

the electrolytes were also developed from the viewpoint of thermodynamic stability [24] or electrochemical kinetics [25]. Definitely, the above-mentioned research results are of great significance to deepen the insights into the reaction process of Fe/Cr flow battery, but it is difficult to expand into mass production due to its relatively high cost and technical uncertainty.

In our previous work, the electrochemical performance of vanadium flow battery was improved by optimizing the concentration of the electrolyte [26], which has been successfully applied to 250 kW VFB energy storage system [27]. However, there is no systematic research about the optimization of the electrolyte concentration of Fe/Cr flow battery, resulting in the lack of the data support and theoretical guidance to its application in engineering. Furthermore, there is no tedious procedure and expensive modification involved in the preparation of electrolyte. Thus, it is facile to realize the scale implement of the results based on the optimization of the electrolyte concentration for the engineering amplification. Herein, a systematic study of the mixed electrolyte with different FeCl_2 , CrCl_3 and HCl concentration was carried out to determine the optimum electrolyte concentration. Firstly, the main physico-chemical properties and electrochemical behaviors of the electrolytes with different concentration were systemically investigated. Secondly, the rate and cycling performances of Fe/Cr flow batteries with different electrolytes were undertaken to further verify the electrochemical properties. And finally, the electrolyte with the optimized concentration of FeCl_2 , CrCl_3 and HCl was proposed, which will provide significantly scientific guidance for the practical application of Fe/Cr flow battery.

2. Experimental

2.1. Preparation of the electrolytes

The electrolytes of x M Fe/Cr (x = 0.5, 0.75, 1.0, 1.25) + 3.0 M HCl and 1.0 M Fe/Cr + y M HCl (y = 1.0, 2.0, 3.0, 4.0) were prepared by the dissolution of stoichiometric $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in concentrated HCl solution and then quantitatively diluted with deionized water at room temperature. Herein, x M Fe/Cr means that the electrolyte contains x M FeCl_2 and x M CrCl_3 . All chemicals were analytically pure agents and purchased from Sinopharm Chemical Reagent Co. Ltd as received. To keep experimental consistency, the prepared electrolytes would stand for 3 h before testing.

2.2. Physicochemical characterizations

The viscosity of the mixed electrolytes was measured by employing an Ubbelohde viscometer (1835, Shanghai Longtuo Instrument Co., LTD) at 65 °C, and the corresponding conductivity was measured with a conductivity meter (Shanghai REX Instrument Factory, China) at 65 °C.

2.3. Electrochemical behaviors

Electrochemical characteristics of the electrolytes with different concentrations were conducted on a Reference 600 electrochemical workstation (Gamry Instruments, USA) with a three-electrode system. In particular, a pyrographite electrode (PGE, Wuhan Gao-ss Union technology co., LTD, China) with a diameter of 6 mm was used as the working electrode, meanwhile a saturated calomel electrode (SCE) along with a saturated KCl salt bridge and a platinum sheet (4 cm²) acted as the reference electrode and counter electrode, respectively. In addition, the volume of electrolyte used during the test was 150 mL and the electrolyte was put into a thermostat for 20 min to ensure the temperature reached to 65 °C for all cases.

In order to evaluate the effect of electrolyte concentration on the electrochemical behaviors of the negative and positive process, cyclic voltammetry (CV) tests with the scan rate of 10 mV s⁻¹ were conducted in the potential range from -1.0 ~ 0 V and 0 ~ 1.0 V respectively. In

addition, electrochemical impedance spectroscopy (EIS) was performed using a 5 mV amplitude at a DC voltage of -0.5 V and 0.5 V with the frequency ranging from 100 kHz to 10 mHz, and the corresponding results were fitted with ZView software.

The charge/discharge behaviors of the Fe/Cr flow battery were evaluated by a single cell testing system (Neware CT-4008-5V12A-DB-F, Shenzhen, China) under different current densities from 80 to 200 mA cm $^{-2}$. Specifically, the flow battery system including a single cell, electrolyte banks, pipes and multi-channels peristaltic pump (BT100-1L, Longer Precision Pump Co., Ltd, China) was placed in an air drying oven, and the corresponding operating temperature was 65 ± 3 °C. The assembled single cell is composed of two pieces of polyacrylonitrile-based graphite felts (5 cm \times 10 cm \times 5.3 mm, Liaoning JinGu Carbon Fibre Sci-Tech Co., Ltd., China) with the compression ratio of 40% , an ion exchange membrane (60 μ m, Chaoyang Huading Energy Co., Ltd, China), two conductive plastic plates (0.8 mm, Weihai Nanhai Carbon Co., Ltd, China) coated copper foil as current collectors, some gaskets and compression clamps. Thereinto, the membrane was soaked in deionized water for 24 h at room temperature. Moreover, both catholyte and anolyte with a volume of 70 mL were pumped into the single cell under the flow rate of 200 mL min $^{-1}$, and the corresponding cut-off voltages were 0.7 and 1.2 V respectively.

3. Results and discussion

3.1. Conductivity and viscosity of electrolytes with different concentrations

The electrolyte of Fe/Cr flow battery consists of the redox couples ($\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Cr}^{3+}/\text{Cr}^{2+}$) as well as supporting electrolyte (HCl), where the former couples provide active reactants for electrochemical redox reactions, while the latter offers proton to construct an ion conduction loop. For flow batteries, ions transmission is very important for the electrode process, so the ion conductivity and viscosity of the electrolyte, which directly depend on the speed of ions transmission [28], are initially investigated in this work. In general, a higher conductivity is beneficial for the ions transmission, which could reduce battery resistance and enhance efficiency [26]. However, a larger viscosity always means a larger flow resistance, which will cause a larger mass transfer resistance [29] and higher energy consumption [30]. Therefore, it is necessary to make a balance between conductivity and viscosity of the electrolytes. On this basis, the conductivity and viscosity of electrolytes with different concentration were measured and shown in Fig. 1. According to Fig. 1(a), as the Fe/Cr concentration increases from 0.5 to 1.25 M in 3.0 M HCl solution, the conductivity of electrolytes gradually decreases from 785 mS cm $^{-1}$ to 453 mS cm $^{-1}$. By contrast, the corresponding viscosity gradually increases in initial section and then rapidly increases with the increase of Fe/Cr concentration, and the viscosity of electrolyte with 1.25 M Fe/Cr increases 87% compared with 0.582 mm 2 s $^{-1}$ of 0.5 M Fe/Cr electrolyte. The

conductivity of electrolytes is determined by the ions transmission speed to a great extent, which is affected by hydrated ion radius, concentration, temperature and viscosity [31]. At a low concentration, the increasing concentration is in favor of the electrolyte conductivity, however, with the electrolyte concentration increases, the ionic interaction in electrolyte also increases in accompany with the ions transmission speed decreases, which will decrease the conductivity to a great extent. Meanwhile, a higher concentration often results in a higher viscosity [28]. Therefore, with the increasing Fe/Cr concentration, the viscosity of electrolytes increases while the conductivity decreases. Furthermore, it is believed that the electrolyte with 0.5 M Fe/Cr concentration has the highest conductivity and the lowest viscosity. However, we have to augment the concentration of the active reactants to improve the energy density of Fe/Cr flow battery. So it is necessary to sacrifice some ions transmission properties to obtain an acceptable energy density and discharge capacity. Based on the above views, the electrolyte with 1.0 M Fe/Cr, is selected in the following measurement.

In addition, the conductivity and viscosity of 1.0 M Fe/Cr electrolyte with various y M HCl ($y = 1.0, 2.0, 3.0, 4.0$) were also measured and the corresponding data was presented in Fig. 1 (b). The results show that both conductivity and viscosity increase with the increasing concentration of HCl from 1.0 to 4.0 M. In contrast to the changing tendency of conductivity for Fe/Cr concentration, the free protons gradually increase with the increasing HCl concentration, resulting in the much faster ions transmissions compared with that of other ions [31]. Therefore, the electrolyte conductivity increases with the increasing HCl concentration. However, when the HCl concentration is higher than 3.0 M, the conductivity increases slightly while the viscosity increases rapidly, indicating the interaction force among the ions plays a dominate role when the HCl concentration reaches to a certain degree, and this is harmful to the conductivity of the electrolyte. In short, electrolyte with the HCl concentration of 3.0 M exhibits a high conductivity and an acceptable viscosity, so the electrolyte is selected in the measurements with different Fe/Cr concentration.

3.2. Electrochemical behaviors of electrolytes with different concentrations

3.2.1. Effect of Fe/Cr concentration

Firstly, CV tests of PGE in the x M Fe/Cr + 3.0 M HCl ($x = 0.5, 0.75, 1.0, 1.25$) electrolytes were carried out to investigate the effect of Fe/Cr concentration on the electrochemical behaviors of negative and positive reactions. Fig. 2 is the CV curves corresponded to the negative and positive reactions, and the detailed CV parameters such as peak current (i_{pa} or i_{pc}), ratio of the peak current ($-i_{pa}/i_{pc}$) and onset potential (E_o) are listed in Table 1. Generally, peak potential separation (ΔE_p), $-i_{pa}/i_{pc}$ and E_o are usually used to evaluate the electrochemical behaviors of the electrode reactions [32]. However, ΔE_p often contains the ohmic potential drop (i^*R), so ΔE_p can't accurately estimate the electrochemical activity of the electrode especially when the peak

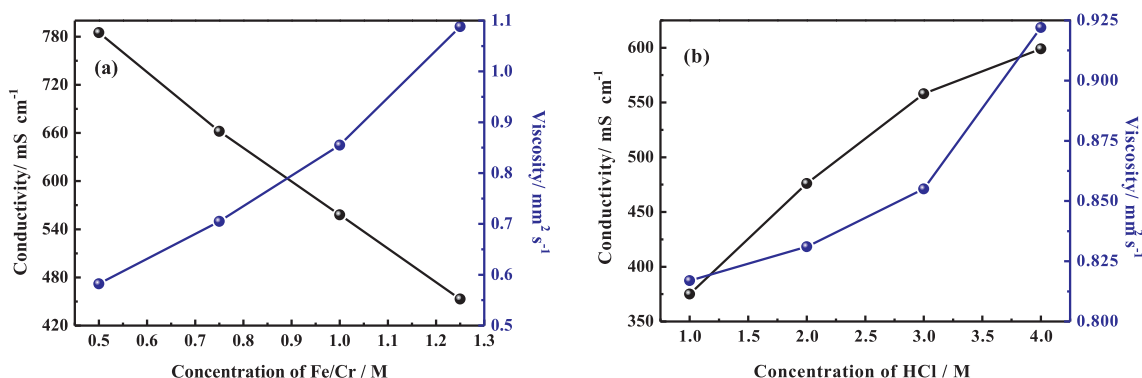


Fig. 1. Conductivity and viscosity of electrolytes with different concentration at 65 °C: (a) x M Fe/Cr + 3.0 M HCl ($x = 0.5, 0.75, 1.0, 1.25$) and (b) 1.0 M Fe/Cr + y M HCl ($y = 1.0, 2.0, 3.0, 4.0$).

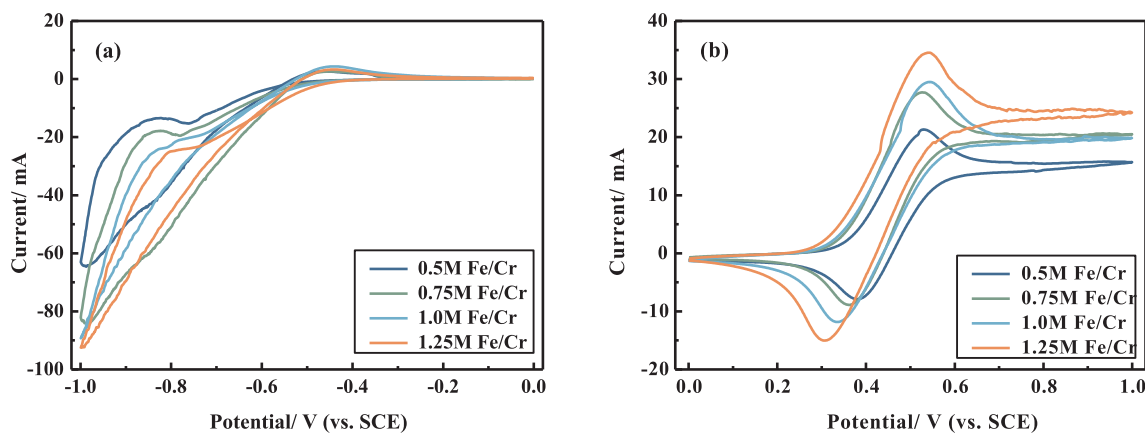


Fig. 2. CV curves of the electrolyte with x M Fe/Cr + 3.0 M HCl (x = 0.5, 0.75, 1.0, 1.25) as anolyte (a) and catholyte (b) at the scan rate of 10 mV s⁻¹.

Table 1

Electrochemical parameters resulting from the CV curves in Fig. 2.

$C_{\text{Fe/Cr}}/\text{M}$	$\text{Cr}^{3+}/\text{Cr}^{2+}$	$\text{Fe}^{3+}/\text{Fe}^{2+}$		
		E_0/V	i_{pa}/mA	$-i_{\text{pc}}/\text{mA}$
0.5 M	-0.541	20.825	-19.342	1.077
0.75 M	-0.518	26.378	-26.226	1.006
1.0 M	-0.508	28.590	-28.293	1.010
1.25 M	-0.472	33.988	-31.729	1.071

current and ohmic resistance are relatively large. Therefore, $-i_{\text{pa}}/i_{\text{pc}}$ is used to describe the electrochemical activity of the positive reaction. In addition, it is hard to correct its oxidation peak current due to the completely asymmetric CV curves responded to the negative reaction, so the onset potential of the reduction peak is used to evaluate its electrochemical activity. As expected, the apparently asymmetric redox peaks at about -0.5 V in Fig. 2(a) mean a completely irreversible reaction for the redox couple of $\text{Cr}^{3+}/\text{Cr}^{2+}$, which is ascribed to the sluggish kinetics as well as the coupled HER [18]. Additionally, despite of the little changes of the oxidation current, the reduction current is significantly enhanced with the increasing Fe/Cr concentration, meanwhile the onset potential gradually shifts to positive potential (from -0.541 to -0.472 V), which means a higher Fe/Cr concentration would help improve the electrochemical reversibility of negative reaction and the overall electrochemical performance. In addition, the current response at -1.0 V is composed of the reduction current of Cr^{3+} and HER, and the latter is because of the serious HER when the reduction potential is lower than -0.8 V. With the increase of Fe/Cr

concentration, the difference in the current response at -1.0 V is apparently larger than that at the reduction peak potential, indicating that HER is also promoted to some extent with the increasing Fe/Cr concentration. Therefore, it is necessary to select a suitable cut-off voltage to avoid the unwanted HER.

In contrast to the negative reaction, each CV curve responded to the positive reaction exhibits two symmetrical oxidation and reduction peaks (Fig. 2 (b)) whatever the Fe/Cr concentration changes, implying that $\text{Fe}^{3+}/\text{Fe}^{2+}$ possesses a preferable kinetics in HCl solution. In addition, both the oxidation and reduction peak currents (i_{pa} and $-i_{\text{pc}}$) gradually increase with the increasing Fe/Cr concentration, and the biggest peak currents are obtained when the concentration of Fe/Cr is 1.25 M, demonstrating that more active reactants and larger current response to the electrolyte are consistent with larger Fe/Cr concentration. Furthermore, the ratio of peak current ($-i_{\text{pa}}/i_{\text{pc}}$) first decreases and then increases, and the lowest value of 1.006, which is closest to 1, is achieved when the concentration of Fe/Cr is 0.75 M, indicating that electrolyte with the Fe/Cr concentration of 0.75 M exhibits the best electrochemical activity. Generally, the electrochemical activity will not change with different concentration for the active reactants, however, the change in the concentration will contribute to the change in the electrochemical environment (interface potential and its distribution, and so on) in the electrolyte [33], and further affect the electrode/electrolyte interface structure and electrochemical activity.

In order to further study the effect of Fe/Cr concentration on the electrochemical behaviors, EIS tests were performed using a 5 mV amplitude at a DC voltage of -0.5 and 0.5 V with the frequency ranging from 100 kHz to 10 mHz. Nyquist plots of electrolytes (x M Fe/Cr + 3.0 M HCl (x = 0.5, 0.75, 1.0, 1.25)) at the polarization potential

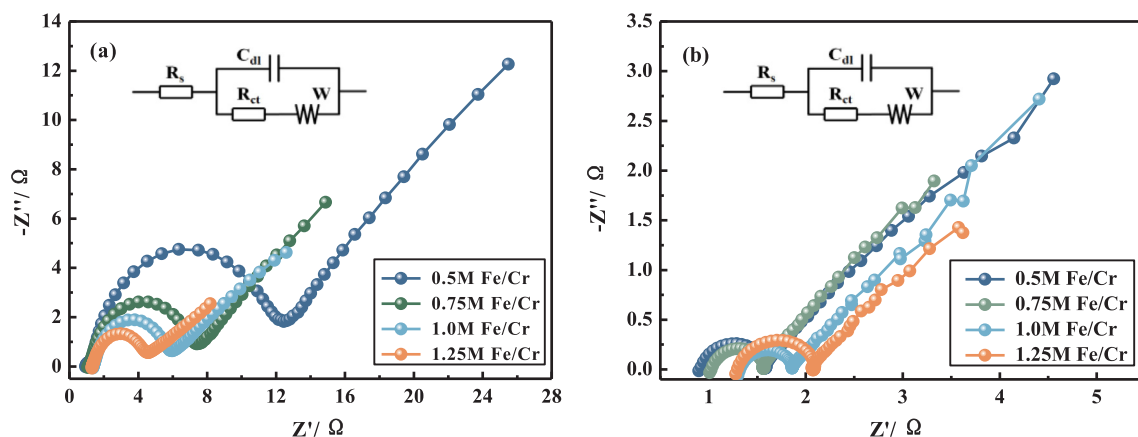


Fig. 3. Nyquist plots and the equivalent electric circuit recorded at the polarization potential of -0.5 V (a) and 0.5 V (b) in the electrolyte with x M Fe/Cr + 3.0 M HCl (x = 0.5, 0.75, 1.0, 1.25).

Table 2

The parameters resulting from fitting the impedance plots with the equivalent circuit model in Fig. 3(a).

$C_{Fe/Cr}/M$	R_s/Ω	R_{ct}/Ω	W/Ω
0.5 M	1.312	10.120	21.480
0.75 M	1.391	5.605	12.570
1.0 M	1.470	4.070	9.410
1.25 M	1.506	2.746	14.900

of -0.5 V, in addition to the corresponding equivalent electric circuit are displayed in Fig. 3(a). As shown in Fig. 3(a), Nyquist plots include a semicircle in the high frequency region and a straight line in the low frequency region. Specifically, the former means the charge transfer process, and the latter corresponds to the ion diffusion process [34]. Herein, R_s stands for the ohmic resistance of the electrolyte; C_{dl} represents the electric double-layer capacitance of electrode/electrolyte interface; R_{ct} means the charge transfer resistance at the electrode/electrolyte interface and W signifies the diffusion resistance attributed by the diffusion process of active reactants [26]. The fitting results which are obtained by simulating the plots with ZView software are listed in Table. 2. In accordance with the Fig. 3 (a), R_{ct} decreases obviously with the increasing Fe/Cr concentration, indicating that a higher electrochemical activity of the negative reaction could be obtained in the electrolyte with a higher Fe/Cr concentration, which is consistent with the CV results. The changing trend of R_s goes against that of R_{ct} as a result of the decreasing conductivity of the electrolytes. W first decreases and then increases and the smallest W is gained when the Fe/Cr concentration is 1.0 M, and such phenomenon might be ascribed to the increasing active reactants and flow resistance, both of which are caused by the increasing Fe/Cr concentration. In addition, compared with R_{ct} and W , the change of R_s in different Fe/Cr concentration electrolyte is unremarkable, suggesting the concentration and electrochemical polarization is more significant than ohmic polarization in the anolyte with different Fe/Cr concentration.

Similarly, Nyquist plots of catholyte with x M Fe/Cr + 3.0 M HCl ($x = 0.5, 0.75, 1.0, 1.25$) at a DC voltage of 0.5 V and the corresponding equivalent circuit are listed in Fig. 3 (b), and Table. 3 is the fitting parameters according to Fig. 3(b). As indicated by the EIS results, R_s gradually increases with the increasing concentration of Fe/Cr, complying with the conductivity results. R_{ct} first decreases and then increases, also indicating that electrolyte with the Fe/Cr concentration of 0.75 M exhibits the best electrochemical activity. In addition, the difference in R_{ct} in the catholyte is quite unremarkable compared with that in the anolyte, suggesting the electrochemical activity of Fe^{3+}/Fe^{2+} is much better than that of Cr^{3+}/Cr^{2+} . With regard to W , it gradually decreases with the increasing concentration of Fe/Cr, signifying a decreasing diffusion resistance. Generally, W is related to the diffusion driven force and diffusion coefficient, and the former depends on the concentration while the latter is related to the viscosity [30]. Due to the larger diffusion coefficient of Fe^{3+}/Fe^{2+} , the larger diffusion driven force resulting from the high Fe/Cr concentration plays a prominent role in reducing the diffusion resistance. Considering the above analysis, it might be concluded that the concentration and ohmic polarization are more significant than electrochemical polarization in the

Table 3

The parameters resulting from fitting the impedance plots with the equivalent circuit model in Fig. 3(b).

$C_{Fe/Cr}/M$	R_s/Ω	R_{ct}/Ω	W/Ω
0.5 M	0.959	0.586	6.012
0.75 M	1.080	0.454	5.758
1.0 M	1.365	0.467	1.954
1.25 M	1.384	0.681	1.661

catholyte with different Fe/Cr concentration.

In summary, compared with the ohmic polarization, Fe/Cr concentration has a greater influence on the electrochemical polarization and concentration polarization in the negative process, which is much higher than those in the positive process. Contrary to the negative process, Fe/Cr concentration has a greater influence on the concentration polarization in the positive process. In the light of the overall electrochemical performance of the negative and positive processes, it can be concluded that the electrolyte of 1.0 M Fe/Cr might exhibit the best electrochemical performance.

3.2.2. Effect of HCl concentration

CV curves of PGE in the anolyte and catholyte with 1.0 M Fe/Cr and different HCl concentration are shown in Fig. 4, and the corresponding electrochemical parameters are listed in Table. 4. Consistent with the CV curves with different Fe/Cr concentration, CV curves responded to the negative reaction in the anolyte with different HCl concentration also express asymmetric redox peaks (Fig. 4(a)). E_o positively shifts in initial and then negatively shifts, and that of 3.0 M HCl displays the most positive potential, which means electrolyte with 3.0 M HCl possesses the best electrochemical activity of the negative reaction. This is because the concentration of Cl^- would affect the complexation of Cr^{3+}/Cr^{2+} and its electrochemical behaviors to some extent, despite the fact that it does not participate in the electrode reaction [9]. Moreover, the current response at -1.0 V is larger than the reduction peak current for all the CV curves, meaning a serious HER at -1.0 V. With the increasing HCl concentration, the difference in the current response at -1.0 V is obviously larger than that at the reduction peak potential, also indicating that HER is promoted to some extent with the increasing HCl concentration. In comparison, the electrolyte containing 1.0 M Fe/Cr + 3.0 M HCl exhibits a better electrochemical behavior than the others.

Fig. 4 (b) displays the CV curves of the catholyte with different HCl concentration. It can be seen that both i_{pa} and $-i_{pc}$ first increase and then decrease with the increasing HCl concentration, and the biggest peak currents are obtained when the HCl concentration is 2.0 M. Meanwhile the change trend of the ratio of peak currents is consistent with the peak current, and the lowest value of 1.005 is acquired when the HCl concentration is 2.0 M, indicating that the electrolyte with 2.0 M HCl exhibits the best electrochemical activity.

EIS tests in 1.0 M Fe/Cr + y M HCl ($y = 1.0, 2.0, 3.0, 4.0$) electrolytes were also performed at DC voltage of -0.5 V and 0.5 V. As shown in Fig. 5, both Nyquist plots responded to the negative reaction (Fig. 5(a)) and positive reaction (Fig. 5(b)) include a semicircle in the high frequency region and a straight line in the low frequency region. Similarly, the semicircle means the charge transfer process, and the straight line corresponds to the diffusion process. And the detailed fitting parameters are listed in Table. 5 and Table. 6. Specifically, as observed in Fig. 5(a) and Table 5, R_s decreases rapidly with the increasing HCl concentration owing to the increasing conductivity of the electrolytes. While R_{ct} firstly decreases and then increases with the increasing HCl concentration, and the smallest R_{ct} is obtained when the HCl concentration is 3.0 M, indicating that electrolyte with 3.0 M HCl owns a better electrochemical activity toward to the negative reaction. Moreover, W firstly decreases and then increases, and the minimum value is obtained when the HCl concentration is 2.0 M, which might be attributed to the balance between the increasing concentration of active $Cr(H_2O)_5Cl^{2+}$ from the increasing Cl^- and increasing viscosity from the increasing concentration of HCl [9]. In other words, the anolyte with 3.0 M HCl expresses the lowest R_{ct} , as well as relatively lower R_s and W than those corresponded to other HCl concentration, demonstrating that the anolyte with 3.0 M HCl exhibits the best electrochemical behaviors, which is consistent with the CV results.

Furthermore, Fig. 5(b) is the Nyquist plots of the catholyte with 1.0 M Fe/Cr + y M HCl ($y = 1.0, 2.0, 3.0, 4.0$) at a DC voltage of 0.5 V as well as its equivalent circuit, and the corresponding fitting

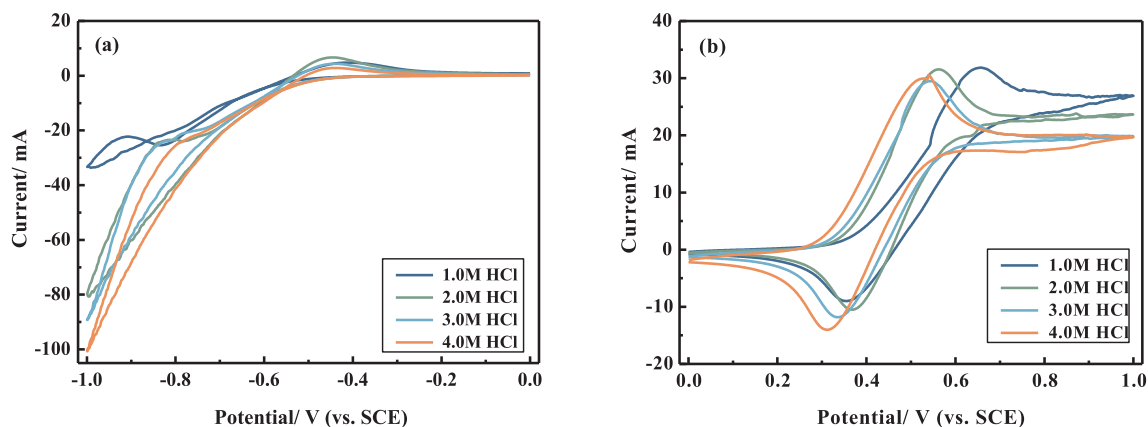


Fig. 4. CV curves of the electrolyte with 1.0 M Fe/Cr + y M HCl ($y = 1.0, 2.0, 3.0, 4.0$) as anolyte (a) and catholyte (b) at the scan rate of 10 mV s^{-1} .

Table 4

Electrochemical parameters resulting from the CV curves in Fig. 4.

C_{HCl}/M	$\text{Cr}^{3+}/\text{Cr}^{2+}$	$\text{Fe}^{3+}/\text{Fe}^{2+}$		
	E_o/V	i_{pa}/mA	i_{pc}/mA	$-i_{pa}/i_{pc}$
1.0 M	−0.577	29.751	−26.587	1.119
2.0 M	−0.513	30.209	−30.052	1.005
3.0 M	−0.508	28.590	−28.293	1.010
4.0 M	−0.517	28.155	−25.960	1.085

parameters are listed in Table 6. It can be clearly seen that the radius of all the semi-cycle in Fig. 5(b) is much smaller than that in Fig. 5(a), indicating a lower charge transfer resistance for $\text{Fe}^{3+}/\text{Fe}^{2+}$. Furthermore, R_s gradually decreases with the increasing HCl concentration due to the increasing conductivity, which is in consistent with that in the anolyte. R_{ct} firstly decreases and then increases, and the minimum is obtained when the HCl concentration is 2.0 M, accord with the CV results. In contrast to the anolyte, W responded to the catholyte increases with the increasing HCl concentration, which is caused by the increasing viscosity.

Similarly, compared with the ohmic polarization, HCl concentration has a greater influence on the electrochemical polarization and concentration polarization in the negative process, which is also much higher than those in the positive process. In contrast to the negative process, HCl concentration has a relatively greater influence on the ohmic polarization and concentration polarization in the positive process. Thinking of the overall electrochemical performance of the negative and positive processes, it can be concluded that the electrolyte of

Table 5

The parameters resulting from fitting the impedance plots with the equivalent circuit model in Fig. 5(a).

C_{HCl}/M	R_s/Ω	R_{ct}/Ω	W/Ω
1.0 M	3.849	7.911	14.810
2.0 M	1.746	4.199	8.845
3.0 M	1.470	4.070	9.410
4.0 M	1.203	4.897	10.910

Table 6

The parameters resulting from fitting the impedance plots with the equivalent circuit model in Fig. 5 (b).

C_{HCl}/M	R_s/Ω	R_{ct}/Ω	W/Ω
1.0 M	1.866	0.294	1.037
2.0 M	1.639	0.246	1.183
3.0 M	1.365	0.467	1.954
4.0 M	1.167	0.730	3.062

3.0 M HCl might exhibit the best electrochemical performance.

3.3. Charge/discharge behaviors of electrolytes with different concentrations

On the basis of the above-mentioned physicochemical characterizations and electrochemical measurements of electrolytes with different Fe/Cr and HCl concentration, the best electrochemical performance of PGE could be obtained in the electrolyte of 1.0 M Fe/Cr and

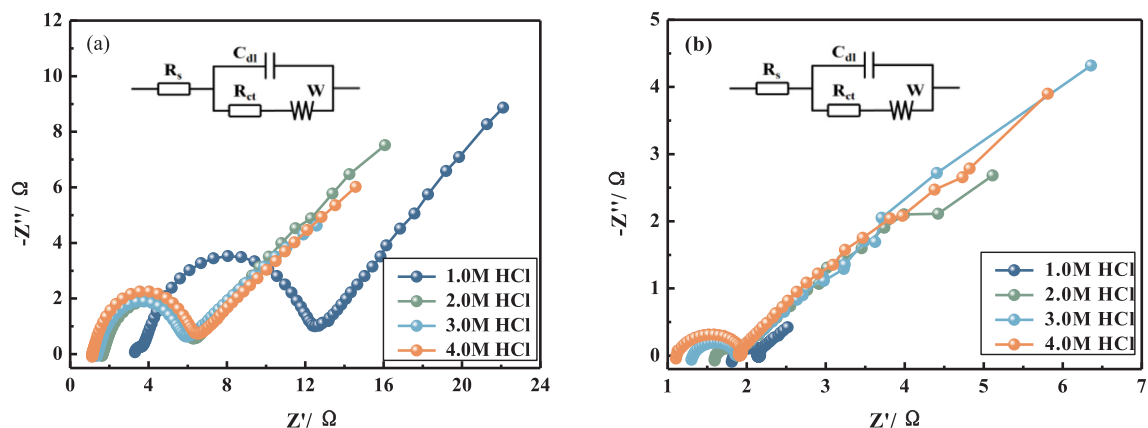


Fig. 5. Nyquist plots and the equivalent electric circuit recorded at the polarization potential of -0.5 V (a) and 0.5 V (b) in the electrolyte with 1.0 M Fe/Cr + y M HCl ($y = 1.0, 2.0, 3.0, 4.0$).

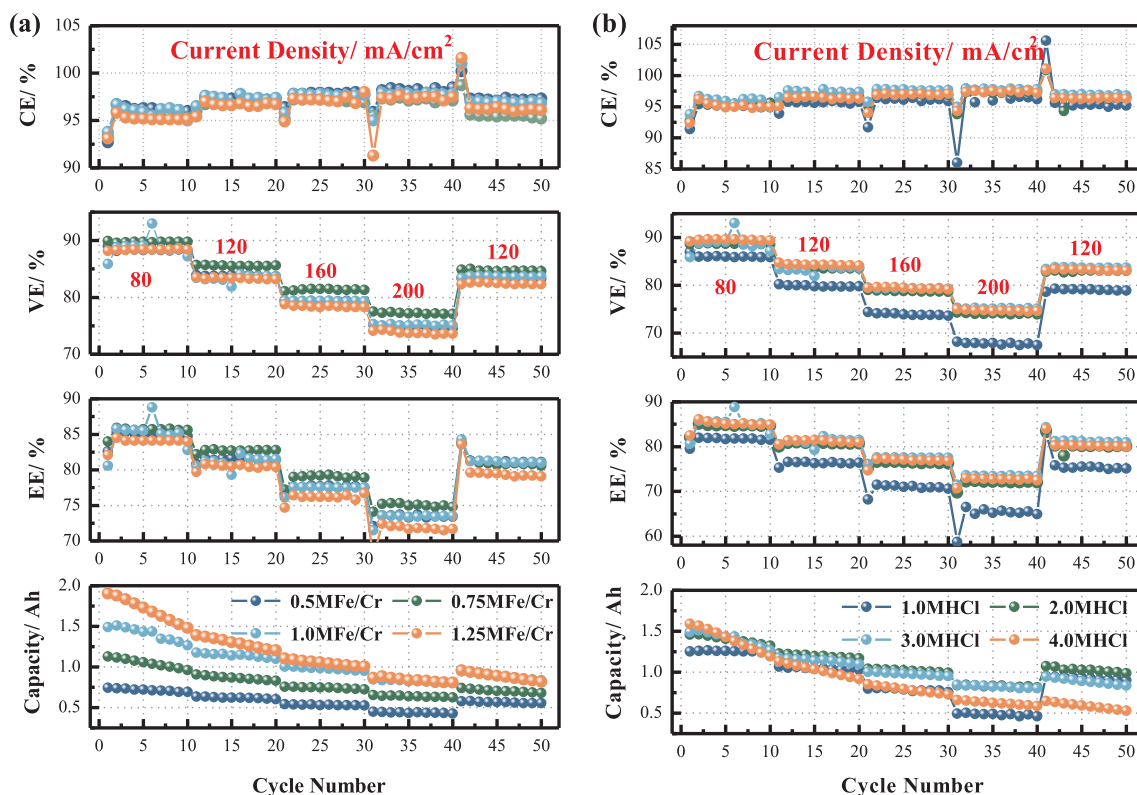


Fig. 6. Rate and cycling performances of single cells with electrolytes of different concentrations: (a) x M Fe/Cr + 3.0 M HCl ($x = 0.5, 0.75, 1.0, 1.25$); (b) 1.0 M Fe/Cr + y M HCl ($y = 1.0, 2.0, 3.0, 4.0$).

3.0 M HCl. With the consideration of the possible difference in the electrochemical behaviors of PGE and commercial graphite felt (GF), the charge/discharge tests of Fe/Cr flow battery with different electrolytes were carried out to further verify the results of the above electrochemical properties.

Herein, a series of single cells with the electrolytes of x M Fe/Cr + 3.0 M HCl ($x = 0.5, 0.75, 1.0, 1.25$) were assembled to evaluate the corresponding battery performance. And the detail parameters of battery performance including voltage efficiency (VE), coulombic efficiency (CE), energy efficiency (EE) and discharge capacity (DC) at the current density of 80, 120, 160, and 200 mA cm^{-2} are illustrated in Fig. 6 (a). Firstly, it can be witnessed that CE of single cells increases gradually, while the corresponding VE and EE decreases with the increasing current density. The former can be contributed to the reduced self-discharge by shortening the charge/discharge time, and the latter is ascribed to the enhanced polarization overpotential at a larger current density. Secondly, there is little change in CE with different Fe/Cr concentrations, while the corresponding VE and EE are different from each other especially at a larger current density. It is caused by Fe/Cr concentration having a greater influence on the electrochemical polarization and concentration polarization, especially for the negative process. Furthermore, DC decreases with the increasing current density and the electrolyte containing 1.0 M Fe/Cr exhibits a relatively higher discharge capacity and slower capacity decay rate than those of the others during the long cycle test. Besides, it can be seen that the discharge capacity decay rate is accelerated when the Fe/Cr concentration is higher than 1.0 M. This is because electrolyte with the higher Fe/Cr concentration (≥ 1.0 M) means a larger DC and a longer charging/discharging time, which also introduces more crossover between the catholyte and anolyte, as well as more serious side reaction of HER. Taken energy density, energy efficiency and capacity decay rate into consideration, it could be concluded that the single cell with 1.0 M Fe/Cr in electrolyte exhibits the best battery performance.

In addition, battery performances of single cells with the

electrolytes of 1.0 M Fe/Cr + y M HCl ($y = 1.0, 2.0, 3.0, 4.0$) were further investigated under the current density of 80, 120, 160, and 200 mA cm^{-2} respectively, just as shown in Fig. 6 (b). As expected, CE increases gradually while VE, EE and DC decrease rapidly with the increasing current density. In addition, there is a slight change in CE with different HCl concentrations, which is similar to that with different Fe/Cr concentrations. It is worth noting that VE and EE of the single cell under the same current density keep nearly the same values when the HCl concentration is no less than 1.0 M, and battery with the HCl concentration of 0.5 M exhibits the lowest VE and EE values, which is mainly due to its largest ohmic resistance and electrochemical polarization resistance. Besides, DC increases with the increasing HCl concentration in the initial stage, while the capacity decay rate is much larger along with a higher HCl concentration, especially under low current density, resulting from the serious HER for the electrolyte with a higher HCl concentration. Based on the above results, the electrolyte with 3.0 M HCl have relatively superior rate performance and a slower capacity decay rate, which can be operated at 120 and 200 mA cm^{-2} with an EE of 81.5% and 73.5%, respectively.

4. Conclusions

In this work, the physicochemical properties, electrochemical characteristics and charge/discharge behaviors of the electrolytes with different concentrations of FeCl_2 , CrCl_3 and HCl were investigated systematically and the optimal concentration of the electrolyte for the iron-chromium flow battery was obtained. Results show that the viscosity of electrolytes increases along with the increasing concentration of both FeCl_2 , CrCl_3 and HCl. However, the corresponding conductivity decreases with the increasing Fe/Cr concentration while increases with the increasing HCl concentration. The electrochemical measurements indicate that the electrochemical characteristics of the anolyte are particularly poor compared with those of catholyte, and the electrolyte with 1.0 M FeCl_2 , 1.0 M CrCl_3 and 3.0 M HCl presents the best

electrochemical performance as a consequence of the synergistic effect of the conductivity, electrochemical activity and transmission characteristics. In addition, battery tests further verified that iron-chromium flow battery with the electrolyte of 1.0 M FeCl₂, 1.0 M CrCl₃ and 3.0 M HCl presents the best battery performance, and the corresponding energy efficiency is high up to 81.5% and 73.5% with the operating current density of 120 and 200 mA cm⁻², respectively. This work not only gives data support to the fundamental research of iron-chromium flow battery, but also provide theoretical direction to its large-scale application.

CRediT authorship contribution statement

Shaoliang Wang: Conceptualization, Methodology, Visualization, Writing - original draft. **Zeyu Xu:** Writing - original draft, Visualization, Supervision. **Xiaoliang Wu:** Investigation, Validation. **Huan Zhao:** Investigation, Validation. **Jinling Zhao:** Investigation, Validation. **Jianguo Liu:** Supervision, Resources, Writing - review & editing. **Chuanwei Yan:** Resources, Funding acquisition. **Xinzhuang Fan:** Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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