Investigation on the electrode process of the Mn(II)/Mn(III) couple in redox flow battery

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The Mn(II)/Mn(III) couple has been recognized as a potential anode for redox flow batteries to take the place of the V(IV)/V(V) in all-vanadium redox battery (VRB) and the Br2/Br\(^{-}\) in sodium polysulfide/bromine (PSB) because it has higher standard electrode potential. In this study, the electrochemical behavior of the Mn(II)/Mn(III) couple on carbon felt and spectral pure graphite were investigated by cyclic voltammetry, steady polarization curve, electrochemical impedance spectroscopy, transient potential-step experiment, X-ray diffraction and charge–discharge experiments. Results show that the Mn(III) disproportionation reaction phenomena is obvious on the carbon felt electrode while it is weak on the graphite electrode owing to its fewer active sites. The reaction mechanism on carbon felt was discussed in detail. The reversibility of Mn(II)/Mn(III) is best when the sulfuric acid concentration is 5 M on the graphite electrode. Performance of a RFB employing Mn(II)/Mn(III) couple as anolyte active species and V(III)/V(II) as catholyte ones was evaluated with constant-current charge–discharge tests. The average columbic efficiency is 69.4% and the voltage efficiency is 90.4% at a current density of 20 mA cm\(^{-2}\). The whole energy efficiency is 62.7% close to that of the all-vanadium battery and the average discharge voltage is about 14% higher than that of an all-vanadium battery. The preliminary exploration shows that the Mn(II)/Mn(III) couple is electrochemically promising for redox flow battery.

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1. Introduction

With the development of global economy, the need for energy increases extensively. Developing new type reproducible energy is an inevitable trend since the reserves of fossil energy such as petroleum and natural gas are limited. Renewable energy sources such as solar energy and wind energy which suffer from fluctuation and dispersed property and therefore need to be equipped with storage facilities, for example, secondary rechargeable batteries. Great efforts are being made to develop new types of redox flow batteries (RFB) [1–3], among others, all-vanadium (VRB), proposed by Skylas et al. [4–8], and sodium polysulfide/bromine (PSB) systems, put forward by Zhang and co-workers [9,10]. However, both batteries exhibit low voltage due to the low positive electrode potential. New positive coupled with higher potential are therefore of great interest. As for the electrode materials, in the history of the RFB study, graphite was the early adopted material. Subsequently, further study showed that carbon felt electrodes could provide more electrochemical active areas and decrease current density and overvoltage effectively. Gradually carbon felt electrodes have been widely used in RFB.

The standard electrode potential of the Mn(II)/Mn(III) couple is 1.51 V, which is higher than the V(IV)/V(V) in VRB and the Br2/Br\(^{-}\) in PSB. When it is coupled with a negative electrode, such as V(II)/V(III), the theoretical open circuit voltage could be 1.77 V in sulfuric acid which is higher than Fe–Ti (0.67 V), Fe–Cr (1.18 V), all vanadium (1.26 V) and PSB (1.52 V). But until now, the electrochemical behavior of the Mn(II)/Mn(III) couple has not been thoroughly investigated for the poor stability of Mn(III) due to the spontaneous disproportionation reaction producing Mn(II) and manganese dioxide. It was reported that Mn(III) could exist in the sulfuric acid with concentrations between 4.60 and 7.50 M, and the disproportionation reaction rate of Mn(III) was the lowest in 6.3 M sulfuric acid. A solution of 6.3 M sulfuric acid containing 0.25 M manganous sulfate was used as the electrolyte [11].

Recently, some electrochemical properties of Mn(II)/Mn(III) couple on Pt in the manganese system have been investigated [12,13]. But adopting the Pt is not practical due to the high cost. And no reports about the cheaper electrode material in manganese system were found. Furthermore, suitable concentration of supporting electrolyte was not determined [13]. In a word, selecting suitable electrode material and determining the concentration of
manganese sulfate and sulfuric acid were the key issues for the manganese system in practical using. Therefore, in this paper, various electrochemical and physical measurements were conducted to explore suitable electrode material and supporting electrolyte [14–18] on carbon felt and spectral pure graphite electrode. At the same time, the electrochemical reaction mechanism was also discussed extensively.

2. Experimental

The electrolytes in this paper were composed of manganous sulfate and sulfuric acid. All chemicals used were reagent grade without further purification and deionized water was used throughout. All tests were carried out at room temperature.

Two kinds of electrodes were used in this paper. The first kind was polycyanonitrile (PAN) based carbon felt obtained from Lanzhou Carbon Works (China). The dimensions of carbon felt electrode is 1 cm x 1 cm. The average pore diameter of carbon felt is 3.5 nm and the diameter of carbon fiber is about 20 μm. To increase the wetting ability all carbon felts should be pretreated as follows: carbon felts were immersed in dense sulfuric acid for 5 h, then washed to neutral, dried to anhydrous and heat-treated for 2 h at 450 °C in tube furnace.

The other kind of electrode was spectral pure graphite obtained from Beijing Lvneng Power Sources Co. Ltd. (China). The area of disc graphite electrode is 0.5 cm². To get reproducible results, all the graphite electrodes were pretreated as follows: initially manual polished with 600 and 1200 grit paper, then polished with 0.3 and 0.05 μm alumina by a polisher at 100 rpm. Finally, electrodes were ultrasonic cleaned with acetone and deionized water for 5 min, respectively, to remove polishing residues.

All the electrochemical experiments were evaluated with a VMP2, Multichannel Potentiostat (Princeton Applied Research, USA). A conventional three-electrode cell was used with a carbon felt or graphite as the working electrode, a saturated calomel electrode as the reference electrode and a large area graphite bon felt or graphite as the counter electrode. X-ray diffraction patterns were recorded with an X-ray diffractometer (MAC MXP21VAHF) by using monochromatic CuKα radiation. Capillary viscosity meter was used to determine the electrolytes viscosity.

The performance of a test battery employing Mn(II)/Mn(III) as anolyte active species and V(III)/V(II), which has a standard reduction potential of −0.255 V, as catholyte ones were evaluated with constant-current charge–discharge experiments. The membrane used in the Mn–V test battery was Nafion 117 (DuPont, USA) and the electrode area was 6.25 cm². The anolyte was 20 ml of 0.3 M Mn(II) in 5 M H₂SO₄ medium while the catholyte was 20 ml of 0.3 M V(III) in 5 M H₂SO₄ medium. The current density is significant because of the common ion effect. Therefore, a compromise of above two effects should be considered. At the same time, different electrode materials may have different influences on the electrochemical reaction, e.g. the catalytic performance. So the electrochemical process on different electrodes was investigated firstly.

Two redox flow batteries employing carbon felt or spectral pure graphite as working electrode were assembled, respectively. The anolyte was 0.3 M Mn(II) in 5 M H₂SO₄ medium while the catholyte was 0.3 M V(III) in 5 M H₂SO₄ medium. After several repeated charge–discharge cycles two kinds of anolytes were, respectively, checked. The results showed that no deposition was found in the cell employing graphite, while some depositions were found in the cell employing carbon felt. These depositions were tested by X-ray diffraction and the result is revealed in Fig. 1. Then the characteristic diffraction peaks were found at about 22°, 37°, 42° and 55°. Compared to the standard cards [19], the existence of MnO₂ was confirmed. The reaction process producing MnO₂ and electrochemical mechanism on carbon felt was not clear and need be investigated in detail.

3. Results and discussion

Mn(III) disproportionation reaction is a fatal shortcoming confining the application of manganese system redox flow battery. Mn(III) spontaneously turns into Mn(II) and manganese dioxide as follows:

\[ 2\text{Mn}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+ \]  \hspace{1cm} (1)

From reaction (1), it can be seen that, with the increase of the concentration of sulfuric acid, the equilibrium will move towards left and the Mn(III) disproportionation reaction will be restrained.

![Fig. 1. X-ray diffraction result for deposition in the anolytes of the battery employing carbon felt after repeated charge–discharge cycles. The characteristic diffraction peaks for MnO₂ are noted with (●).](image)

However, the solubility decrease in sulfuric acid with high concentration is significant because of the common ion effect. Therefore, a compromise of above two effects should be considered. At the same time, different electrode materials may have different influences on the electrochemical reaction, e.g. the catalytic performance. So the electrochemical process on different electrodes was investigated firstly.

3.1. Electrochemical process analysis on carbon felt electrode

Cyclic voltammograms for 0.3 M manganous sulfate in 3 M sulfuric acid on carbon felt electrode at a scan rate of 5 mV s⁻¹ is shown in Fig. 2. The current density is calculated by the projected area of the carbon felt. From Fig. 2 a single anodic peak was observed at potential of about 1.29 V. And two cathodic peaks were, respectively, observed when scanning toward cathodic direction and the potential attained 1.11 V and 0.76 V. The mechanism of oxidation and reduction process will be discussed, respectively.

First of all, the standard electrode potentials among Mn^{2+}, Mn^{3+} and MnO₂ with the saturated calomel electrode (SCE) as reference were found and shown as bellows [20]:

\[ \begin{align*}
\text{Mn}^{2+} & \quad 0.1268 \text{V} \\
\text{Mn}^{3+} & \quad 0.708 \text{V} \\
\text{MnO}_2 & \quad 0.988 \text{V}
\end{align*} \]
There are two kinds of possible mechanisms of the oxidation process according to above potentials data. The first possible process is a two stepwise oxidation from Mn$^{2+}$ to Mn$^{3+}$ and then to MnO$_2$. In this process Mn$^{3+}$ is just an intermediate product. If this reaction happens, two anodic peaks should be observed in the positive scan when the scan rate is slow enough. But in this work only one anodic peak was observed even if the scan rate was 0.166 mV s$^{-1}$. Therefore, this two stepwise oxidation mechanism can be excluded.

The other possible process is either an oxidation from Mn$^{2+}$ to Mn$^{3+}$ or an oxidation from Mn$^{2+}$ to MnO$_2$. If the potential separation of these two anodic peaks is small enough, these two peaks would be likely to overlap each other. To distinguish the oxidation process clearly steady polarization curve was adopted to determine the electron transfer number of the oxidation process. In the steady polarization the scan rate was 0.166 mV s$^{-1}$ and the potential scan range was from 0.6 V to 1.6 V. The polarization curve of oxygen. Because the concentration of MnSO$_4$ in the steady polarization curve was low enough, the diffusion step would be the control step in the whole electrochemical process. The electrode potential can be obtained according to Heyrovsky–Ilkovic equation [21]:

$$E = E_{1/2} - \frac{RT}{nF} \ln \left( \frac{I_d - i}{i} \right) = E_{1/2} - \frac{0.059}{n} \log \left( \frac{I_d - i}{i} \right)$$  (2)

where $E$ is the electrode potential, $E_{1/2}$ is the half-wave potential, $R$ is the universal gas constant (8.314 J K$^{-1}$ mol$^{-1}$), $T$ is the Kelvin temperature, $n$ is the number of electrons transferred in the reaction, $F$ is the Faraday constant [96,487 C (Coulombs)], $i_d$ is the limit diffusion current density, and $i$ is the current density. It can be followed from this equation that a plot of $E$ versus $\log([I_d - i]/i)$ should yield a straight line with a slope of 0.059$/n$ at 25°C. Such a plot offers a convenient method for the determination of $n$. According to (2) and Fig. 3, electron transfer number is calculated to be 0.97. That is to say the electron transfer number in the reaction is approximate 1. This result demonstrated the oxidation process was not the oxidation from Mn$^{2+}$ to MnO$_2$ but the oxidation from Mn$^{3+}$ to Mn$^{4+}$.

To confirm above process of the oxidation whether from Mn$^{2+}$ to MnO$_2$ or from Mn$^{2+}$ to Mn$^{3+}$, X-ray diffraction experiment was carried out to distinguish the oxidation product corresponding to the single anodic peak. Potentiostatic electrolysis was employed for electrolyte only containing 0.3 M Mn$^{2+}$ at 1.2 V for 10 min. After calculation, 10 min was long enough to obtain MnO$_2$ to reach the X-ray diffraction minimum detection limit. Then the carbon felt electrode was examined by X-ray diffraction. If the oxidation from Mn$^{2+}$ to MnO$_2$ happens, the characteristic diffraction peak of MnO$_2$ should be found in the X-ray diffraction spectrum. The result is shown in Fig. 4 and it can be seen the diffraction peak at 25° is corresponding to the carbon and there is no characteristic diffraction peak of MnO$_2$. This was the other evidence to demonstrate the oxidation reaction is not an oxidation of Mn$^{2+}$ to MnO$_2$.

In the course of reverse potential scan, two cathodic peaks appeared at 1.11 V and 0.76 V. There are three possible reduction processes of all the three valent manganese, which are the reduction from MnO$_2$ to Mn$^{2+}$, from MnO$_2$ to Mn$^{3+}$ and from Mn$^{3+}$ to Mn$^{2+}$. However, both reductions from MnO$_2$ to Mn$^{2+}$ and from MnO$_2$ to Mn$^{3+}$ could not happen at 1.11 V because the stand potentials of the two reductions are 0.988 V and 0.708 V. Therefore, the cathodic peak at 1.11 V is corresponding to the reduction of Mn$^{3+}$ to Mn$^{2+}$. But as for the cathodic peak at 0.76 V, there are still two possible reduction mechanisms on how to distinguish the reduction from Mn$^{3+}$ to Mn$^{2+}$ or the reduction from Mn$^{3+}$ to Mn$^{2+}$. In order to eliminate the disturbance of the reduction from Mn$^{3+}$ to Mn$^{2+}$, transient potential-step experiment was employed near the equi-
Fig. 5. Transient potential-step experiment of 0.15 M Mn$^{2+}$ + 0.15 M Mn$^{3+}$ in 3 M H$_2$SO$_4$ on carbon felt electrodes.

librium potential instead of steady polarization curve. At first, the electrolyte in which the ratio of Mn$^{2+}$/Mn$^{3+}$ was 1:1, was prepared by chronopotentiometry. Then, different overvoltage was applied to the electrode and the current–time response was determined. Because the duration time of step potential was very short, it is generally accepted that the thickness of diffusion layer was thin and electron transfer step was the control step in the whole electrochemical process. Here the overvoltage can be obtained according to the Butler–Volmer equation:

$$\eta_c = -\frac{2.3RT}{\alpha nF} \log i_0 + \frac{2.3RT}{\alpha nF} \log i_c$$

Where $\eta_c$ is cathodic overvoltage, $R$ is the universal gas constant (8.314 J K$^{-1}$ mol$^{-1}$), $T$ is the Kelvin temperature, $n$ is the number of electrons transferred in the reaction, $\alpha$ is the transfer coefficient, $F$ is the Faraday constant [96,487 C (Coulombs)], $i_0$ is the exchange current density, and $i_c$ is the cathodic current density.

Fig. 5 gives the transient potential-step experiment result of 0.15 M Mn$^{2+}$ + 0.15 M Mn$^{3+}$ in 3 M H$_2$SO$_4$ on carbon felt. According to (3), the product of transfer coefficient $\alpha$ and electron transfer number $n$ is calculated to be 1.04. It is known that transfer coefficient $\alpha$ is 0.5. So electron transfer number $n$ is 2.08. That is to say the electron transfer number in the reaction corresponding to the cathodic peak at 0.76 V is approximate 2. This result demonstrated the reduction corresponding the cathodic peak at 0.76 V is not the reduction from MnO$\textsubscript{2}$ to Mn$^{3+}$ but the reduction from MnO$\textsubscript{2}$ to Mn$^{2+}$. Since the oxidation at 1.29 V is not an oxidation of Mn$^{2+}$ to MnO$\textsubscript{2}$, then only one possible process, which is the disproportionation reaction of Mn$^{3+}$ according to the reaction (1), can produce MnO$\textsubscript{2}$ on carbon felt.

Cyclic voltammograms for 0.3 M manganous sulfate in 3 M sulfuric acid medium on carbon felt at different scan rate were carried out, too. Macdonald [22] has given the diagnostic criteria of different mechanism to distinguish variations of peak height, peak potential, etc. Variations of peak current function of the oxidation of Mn$^{2+}$ to Mn$^{3+}$ at 1.29 V of $i_p/v^{1/2}$ with different scan rate are shown in Fig. 6. According to the diagnostic criteria, it was concluded that this oxidation process obeyed the catalytic reaction mechanism. From another point of view, disproportionation reaction could be considered to be an especial form of catalytic reaction because the product of the electrochemical reaction, which is Mn$^{3+}$, would be converted into the reactant by disproportionation reaction, which is Mn$^{2+}$. These diagnostic criteria also confirmed the existence of disproportionation reaction of Mn$^{3+}$ in another way.

From above analysis of the cyclic voltammograms, the mechanism could be concluded that, when scan begins toward positive and the potential gradually increases and Mn$^{2+}$ will be continually oxidized into Mn$^{3+}$. Then a spontaneous disproportionation reaction of Mn$^{3+}$ happens according to reaction (1). Therefore, when scan sets out toward negative, manganese in the electrolyte actually exists in three forms which are Mn$^{2+}$, Mn$^{3+}$ and MnO$\textsubscript{2}$. In the course of the reverse scan, there are two reduction processes which are from Mn$^{3+}$ to Mn$^{2+}$ and from MnO$\textsubscript{2}$ to Mn$^{2+}$.

Fig. 7 shows the cyclic voltammograms for 0.3 M manganous sulfate in sulfuric acid with different concentrations on carbon felt electrode. It can be seen that the peak potential separation for the redox reactions decreased with the increase of sulfuric acid concentration and the current peak increased attributing to the improvement of electrolyte conductivity. But the current peak of cathode peak from MnO$\textsubscript{2}$ to Mn$^{2+}$ was also higher with the increase of sulfuric acid concentration. When the sulfuric acid concentration attained 5 M, the cathodic peak current of cathodic peak from MnO$\textsubscript{2}$ to Mn$^{2+}$ was quite clear while the cathodic peak from Mn$^{3+}$ to Mn$^{2+}$ was not obvious. That is to say, disproportionation reaction of Mn$^{3+}$ does not become less obvious on carbon felt with the increase of sulfuric acid concentration. The disproportionation reaction of
Mn$^{3+}$ is so complete that cannot be restrained by means of increasing the sulfuric acid concentration on carbon felt. This possible reason is that carbon felt is porous and the product of disproportionation reaction can diffuse into the solution through numerous holes rapidly. The porous characteristic of carbon felt with plentiful active sites may accelerate the disproportionation reaction of Mn$^{3+}$. Therefore, carbon felt is not suitable for the electrode in Mn$^{2+}$/Mn$^{3+}$ redox battery.

### 3.2. Influence of different supporting electrolytes concentration on Mn$^{2+}$/Mn$^{3+}$ reaction on graphite electrode

Fig. 8 shows the cyclic voltammograms for 0.3 M manganous sulfate in 3 M sulfuric acid on graphite electrode at a scan rate of 5 mV s$^{-1}$. Potential scan range was from 0.4 V to 1.4 V. From Fig. 8, only a couple of oxidation and reduction peaks at each sulfuric acid concentration were, respectively, found and no cathodic peak of MnO$_2$ to Mn$^{2+}$ was found. Some data obtained from Fig. 8 are summarized in Table 1.

From Table 1, it was concluded that the influence of sulfuric acid concentration mainly concerned two aspects, (1) with the increase of the sulfuric acid concentration from 0.5 M to 5 M, the redox peak currents decreased obviously for the reason that the increase of the sulfuric acid concentration also led to the proportional increase of the electrolyte viscosity and the mass transfer resistance. The mass transfer resistance gradually played the leading role in the whole electrochemical process. The viscosity data of the electrolyte in sulfuric acid with different concentrations were, respectively, found and no cathodic peak of MnO$_2$ to Mn$^{2+}$ was found. Some data obtained from Fig. 8 are summarized in Table 1.

In order to make out the effect of the sulfuric acid concentration on the graphite electrode process thoroughly, steady polarization curves for 0.3 M manganous sulfate in sulfuric acid with different concentrations were employed to determine the polarization resistance, exchange current density, and electrochemical reaction rate constant. Before the polarization, chronoamperometry method was used to prepare the electrolyte in which the ratio of Mn$^{2+}$/Mn$^{3+}$ was 1:1. Overvoltage less than 25 mV near the equilibrium potential was then applied on the electrode and the potential scan rate was 0.5 mV s$^{-1}$. In this low overvoltage area, current density and overvoltage should yield an approximate straight line. Polarization resistance could be calculated by the slope of the line and other parameters such as exchange current density and electrochemical reaction rate constant could be calculated as follows:

$$ i_0 = \frac{RT}{nF}, \quad k_0 = \frac{i_0}{nFC_0} \quad (4) $$

where $i_0$ is the exchange current density, $R$ is the universal gas constant (8.314 J K$^{-1}$ mol$^{-1}$), $T$ is the Kelvin temperature, $n$ is the number of electrons transferred in the reaction, $F$ is the Faraday constant (96,487 C (Coulombs)), $R_p$ is the polarization resistance, $k_0$ is rate constant, and $C_0$ is the solution concentration.

As an example, the steady polarization curve for 0.3 M manganous sulfate in 5 M sulfuric acid is shown in Fig. 9. The polarization resistance, exchange current density and electrochemical reaction rate constant for 0.3 M manganous sulfate in sulfuric acid with different concentrations are summarized in Table 3. From

| Table 1 Cyclic voltammograms data for 0.3 M MnSO$_4$ in sulfuric acid with different concentrations on graphite electrode |
|-----------------|-----------------|-----------------|
| $C$(H$_2$SO$_4$: M) | Peak potentials separation ($\Delta E_p$, mV) | Peak current ratio ($i_{pa}/i_{pc}$) |
| 0.5             | 140             | 1.465           |
| 1               | 135             | 1.197           |
| 3               | 105             | 1.138           |
| 5               | 106             | 1.036           |

| Table 2 Viscosity data for 0.3 M MnSO$_4$ in sulfuric acid with different concentrations |
|-----------------|-----------------|
| $C$(H$_2$SO$_4$: M) | Viscosity ($\times 10^3$ Pa s) |
| 0.5             | 1.048           |
| 1               | 1.550           |
| 3               | 2.031           |
| 5               | 2.831           |

Fig. 8. Cyclic voltammograms for 0.3 M MnSO$_4$ in sulfuric acid with different concentrations at scan rate of 5 mV s$^{-1}$ on graphite electrodes. Concentrations of the sulfuric acid, (1) 0.5 M; (2) 1 M; (3) 3 M; (4) 5 M.

Fig. 9. Steady polarization curve for 0.3 M MnSO$_4$ in 5 M H$_2$SO$_4$ on graphite electrode at scan rate of 0.5 mV s$^{-1}$. In this low overvoltage area, current density and overvoltage should yield an approximate straight line. Polarization resistance could be calculated by the slope of the line and other parameters such as exchange current density and electrochemical reaction rate constant could be calculated as follows:

$$ i_0 = \frac{RT}{nF}, \quad k_0 = \frac{i_0}{nFC_0} \quad (4) $$

where $i_0$ is the exchange current density, $R$ is the universal gas constant (8.314 J K$^{-1}$ mol$^{-1}$), $T$ is the Kelvin temperature, $n$ is the number of electrons transferred in the reaction, $F$ is the Faraday constant (96,487 C (Coulombs)), $R_p$ is the polarization resistance, $k_0$ is rate constant, and $C_0$ is the solution concentration.
Table 3
Polarization resistance ($R_p$), exchange current density ($i_0$) and rate constant ($k_0$) by way of steady polarization 0.3 M MnSO$_4$ in sulfuric acid with different concentrations on graphite electrode

<table>
<thead>
<tr>
<th>$C$(H$_2$SO$_4$: M)</th>
<th>Exchange current density $i_0$ $(10^{-4}$ Acm$^{-2}$)</th>
<th>Polarization resistance $R_p$ $(Ω)$</th>
<th>Rate constant $k_0$ $(10^{-2}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>6.15</td>
<td>41.8</td>
<td>0.212</td>
</tr>
<tr>
<td>1</td>
<td>8.18</td>
<td>31.4</td>
<td>0.283</td>
</tr>
<tr>
<td>3</td>
<td>12.8</td>
<td>20.0</td>
<td>0.442</td>
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<tr>
<td>5</td>
<td>18.6</td>
<td>13.8</td>
<td>0.642</td>
</tr>
</tbody>
</table>

Fig. 10. Electrochemical impedance spectroscopy for 0.3 M MnSO$_4$ in sulfuric acid with different concentrations on graphite electrodes and equivalent circuit.

Table 3, it can be concluded that with the increase of sulfuric acid concentration from 0.5 M to 5 M, polarization resistance gradually decreased and exchange current density increased. The higher the exchange current density is, the stronger the depolarization ability is. The electrode reaction is easier to occur and shows better reversibility. When the concentration of sulfuric acid reached 5 M, the polarization resistance was smallest and exchange current density and rate constant were highest. These results were consistent with the results of the cyclic voltammograms. Therefore, these results also support the selecting of 5 M sulfuric acid.

3.3. Electrochemical impedance spectroscopy of 0.3 M MnSO$_4$ in sulfuric acid with different concentrations on graphite electrode

Electrochemical impedance spectroscopy was galvanostatically measured by applying an ac voltage of 20 mV over the frequency ranging from $10^{-3}$ Hz to $10^{5}$ Hz. The results are shown in Fig. 10 and analyzed by Zsimpwin software.

From Fig. 10, it can be seen that when the concentration of sulfuric acid are 0.5 M and 1 M, the conductivity of electrolyte was bad and the electrolyte resistance was high, so the electrochemical impedance spectroscopy showed a straight line and no electrochemical responsive semicircle appeared. With the sulfuric acid concentration increased, conductivity of electrolyte improved and electrolyte resistance decreased. The semicircle of electrochemical characteristic enhanced remarkably. When the sulfuric acid concentration attained 3 M and 5 M, electrochemical responsive semicircle and straight line were observed simultaneously. It can be seen that the electrochemical process in 3 M and 5 M sulfuric acid are together controlled by electrochemical reaction and diffusion step. Equivalent circuit model was also proposed in Fig. 10. In the equivalent circuit, $R_1$ stands for the electrolyte resistance and the CPE stands for the constant phase element of interface between the electrode and electrolyte. $R_2$ stands for the charge transfer resistance in the electrochemical process and $W$ stands for the Warburg resistance of diffusion step. Table 4 shows the simulation result by Zsimpwin software. It can be seen that charge transfer resistance $R_2$ are 1.127 $Ω$ and 0.980 $Ω$ when the sulfuric acid concentration are 3 M and 5 M. The charge transfer resistance of 5 M is the lowest. In addition, two resistances show little difference, which is consistent with the cyclic voltammetry and polarization curve results. All results confirmed 5 M is the suitable concentration of sulfuric acid.

3.4. Charge–discharge cycles performance of Mn–V redox flow battery

Performance of a RFB employing the Mn(II)/Mn(III) couple as anolyte active species and V(III)/V(II) as catholyte ones
was evaluated with constant-current charge–discharge tests. Charge–discharge circle results are shown in Fig. 11 and Table 5. When the current density is 20 mA cm$^{-2}$, the average columbic efficiency is 69.4% and the voltage efficiency is 90.4%. Accordingly the whole energy efficiency is 62.7%. Energy efficiency is close to that of the all-vanadium battery [24] and average discharge voltage is 1.66 V, which is about 14% higher than that of an all-vanadium battery (ca. 1.45 V) [25]. Furthermore, with the increase of circle times, the columbic efficiency and voltage efficiency keep stably.

4. Conclusions

Mn(II)/Mn(III) is capable of becoming the anodic couple because of its higher standard electrode potential. In this study, the electrode process, especially about the mechanism of the oxidation and reduction of Mn$^{2+}$ and Mn$^{3+}$, were investigated on the different electrodes such as carbon felt and spectral pure graphite. The following conclusions can be drawn.

On the carbon felt, the mechanism could be concluded that, the single oxidation reaction was not the oxidation from Mn$^{2+}$ to MnO$_2$ but the oxidation from Mn$^{2+}$ to Mn$^{3+}$. Then a disproportionation reaction of Mn$^{3+}$ occurred. However, the main cathodic reaction was the reduction of MnO$_2$ to Mn$^{2+}$. Owing to the Mn(III) disproportionation reaction, carbon felt is not suitable for the electrode material of RFB.

On the graphite electrode, the reversibility of Mn(II)/Mn(III) was optimized that when the sulfuric acid concentration was 5 M. At the same time manganous sulfate had the good solubility. The performance of a test battery employing 0.3 M Mn(II)/Mn(III) as anolyte active species and V(III)/V(II) as catholyte ones was evaluated with constant-current charge–discharge experiments. When the current density is 20 mA cm$^{-2}$, the average columbic efficiency is 69.4% and the voltage efficiency is 90.4%. The whole energy efficiency is 62.7%. Energy efficiency is close to that of the all-vanadium battery but average discharge voltage is about 14% higher than that of an all-vanadium battery. All above results show the Mn(II)/Mn(III) redox couple is an attractive system and electrochemically promising for use in RFB.

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References