Study on kinetics behavior of the graphite felt electrode in the lead acid flow battery

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ABSTRACT

This paper described the liquid flow battery system with graphite felt electrode and a single electrolyte, lead (II) in methanesulfonic acid. The kinetics and cyclic voltammetry behavior of graphite felt electrode and effects of modifying graphite felt on them were studied. The results show that the dynamic characteristics of graphite felt electrode in strong polarization region was better than that in weak polarization region. The oxidation and reduction peak potentials were basically unchanged with the increase of cycle number, and the redox reversibility of the graphite felt electrode was good. The graphite felts soaked by methanesulfonic acid (99.8%) had more excellent cyclic voltammetry behavior.

INTRODUCTION

Within the next few years, large redox flow batteries have been proposed for large scale energy storage including load levelling and reserve electricity supplies as well as power sources for traction. Such batteries have been based on several chemistries including Fe/Cr, V and Zn/Br₂. All require the employment of cells with membranes. Such membranes are expensive, increase the complexity and cost of the cell and introduce issues associated with unwanted transport processes through the membrane.

In recent papers, a novel flow battery based on the electrode reactions of lead (II) in methanesulfonic acid has been reported[1-2]. The system differs from traditional lead acid battery because lead (II) is highly soluble in methanesulfonic acid. It also differs from all reported flow batteries in that it requires only a single electrolyte and hence no separator is required; this reduces the cost of the batteries significantly[3-6].

Previous papers described preliminary studies of the electrode reactions and the lead negative electrode and lead dioxide positive electrode, the influence of additives and the determination of relevant solution properties, allowing the selection of an appropriate battery electrolyte[7-9]. While there is almost no literature describing the selection of negative and positive electrode materials and the kinetics behavior of Pb (II)/Pb and PbO₂/Pb (II) couples in graphite felt electrode. This paper reports the kinetics and cyclic voltammetry behavior of Pb (II)/Pb and PbO₂/Pb (II) couples and effects of treatment methods on them in PAN-graphite
felt electrode, which has a favorable stability, good conductivity and electro-catalytic activity for Pb (II)/Pb and PbO₂/Pb (II) couples.

**EXPERIMENTAL**

The graphite felts were soaked by methanesulfonic acid (99.8%) and heated at 550°C for 2 hours to modify electrode materials. The modified PAN-graphite felt was cutted into a Ø10 circular slice, and embedded in the polyethylene plate with dimensions 15mm × 25mm. Copper gauze was pressed against the back of the plate to decrease the resistance of electrode. The polyethylene plates soften at 160°C for 20 minutes in the dry trunk. Then it was cooled and solidified in the natural air.

All solutions were prepared with water from a Analyst Purifier. Unless otherwise stated, throughout this paper the experiments were commenced with the battery in the uncharged state containing an electrolyte solution with the composition, lead methanesulfonate (0.01M) + methanesulfonic acid (0.01M).

The voltammetry was carried out in a two compartment, glass cell with a volume of 250 cm³ and it was immersed in a water thermostat at a temperature of 293K. The disc working electrodes and the graphite counter electrode were in the same compartment but the saturated calomel reference electrode (SCE) was separated from the working electrode by a Luggin capillary. The tip of the Luggin capillary was placed 1 mm from the surface of the disc working electrodes. The voltammetry was carried out with a model CS3000 potentiostat/galvanostat produced by Wuhan CorrTest Instrument Co. Ltd. coupled to a PC, and the system was controlled and data recorded using the CorrTest software package.

**RESULTS AND DISCUSSION**

The polarization characteristics of the graphite felt electrode

Figure 1 showed that a cathodic and anodic polarization curves recorded at a graphite felt electrode in the solution of lead (II) (10 mM) in aqueous methanesulfonic acid (10 mM). The scan potential ranges were between 0 V and -1.0 V vs. SCE in cathode and between 0.5 V and 1.6 V vs. SCE in anode respectively, and the scan rate was 10 mV·s⁻¹. The cathodic and anodic current increased rapidly when the scan potential arrived at -0.474 V and 1.0 V vs. SCE respectively, and the deposition of lead and lead dioxide reactions on the graphite felt electrode happened. On the scan towards more negative potentials in cathode and more positive potentials in anode, a reduction and oxidation wave were observed at E_p –0.694V vs. SCE and E_p 1.55 V vs. SCE. From theoretic analysis, the negative and positive electrode reactions are:

\[
Pb^{2+} + 2e^{-} \xrightarrow{\text{disch arg e}} Pb \quad \phi^0 = -0.367 \text{V} \text{ vs. } \text{SCE} \quad (1)
\]

\[
Pb^{2+} + 2H_2O - 2e^{-} \xrightarrow{\text{disch arg e}} PbO_2 + 4H^+ \quad \phi^0 = 1.214 \text{V} \text{ vs. } \text{SCE} \quad (2)
\]

**Figure 1**: Polarization curves of graphite felt electrode in 0.01mol·L⁻¹Pb(CH₃SO₃)₂ + 0.01mol·L⁻¹CH₃SO₃H solution, scan rate: 10mV·s⁻¹

The equilibrium electrode potentials of Pb (II)/Pb and PbO₂/Pb (II) couples in a electrolyte consisting of 10 mM Pb (CH₃SO₃)₂ + 10 mM CH₃SO₃H are -0.425V vs. SCE and 1.04 V vs. SCE calculated by the Nernst equation. The test result was close to the theoretic equilibrium electrode potential, and the difference was due to the electrochemical polarization on the graphite felt electrode caused by the exchange current density and charge transfer coefficient which calculated by the Butler-Volmer equation,
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\[ I = i^0 \left\{ \exp \left( \frac{\alpha nF}{RT} \eta \right) - \exp \left( \frac{\beta nF}{RT} \eta \right) \right\} \]

(3)

Where \( I \) is the net cathodic or anodic current density, \( i^0 \) is the exchange current density, \( \alpha \) and \( \beta \) are the charge transfer coefficient of cathode and anode respectively.

When \( |\eta| \ll \frac{RT}{\alpha nF} \) and \( |\eta| \ll \frac{RT}{\beta nF} \), the equation 3 is approximated to express as

\[ I = i^0 \frac{nF}{RT} \eta \]

(4)

There is a linear relationship between the net current density and overpotential, and the ratio of overpotential and net cathodic current density is charge transfer resistance \( R_{ct} \), that is

\[ R_{ct} = \frac{RT}{nF i^0} \]

(5)

couple calculated by the equation 5 were \( 1.075 \times 10^{-5} \) A cm\(^{-2}\) and \( 1.625 \times 10^{-4} \) A cm\(^{-2}\), which showed that the dynamic characteristics of graphite felt electrode at equilibrium state was good, especially for \( \text{PbO}_2/\text{Pb} \) (II) couple of anode electrode.

Figure 2 : Linear relationships between net current density and overpotential

According to the test data of cathodic and anodic polarization curves of graphite felt electrode in electrolyte, Figure 2 showed that the linear relationship between net current density and overpotential. The linear relationships were expressed as

\[ \eta_c = 0.0239 + 1173.58 \times I_c \]

(6)

\[ \eta_a = -0.2897 + 77.66 \times I_a \]

(7)

According to the slope of the linear equations, the charge transfer resistances \( R_{ct} \) of cathode and anode were 1173.58 \( \Omega \) cm\(^2\) and 77.68 \( \Omega \) cm\(^2\) respectively. The exchange current density of reduction reaction of \( \text{Pb} \) (II)/\( \text{Pb} \) couple and oxidation reaction of \( \text{PbO}_2/\text{Pb} \) (II)

Figure 3 : Linear relationships between logarithmic net current and overpotential in Tafel region

Charge transfer coefficient of electrode was a parameter of influence degree of electrode potential on oxidation or reduction reaction activation energy, and depended on the electrode reaction properties. When the electrochemical polarization was control step, the anode reaction could be neglected since the initial solution without oxidizing state particle \( \text{PbO}_2 \) during the cathode polarization, and the cathode reaction could be neglected since the initial solution without oxidizing state particle \( \text{PbO}_2 \) during the anode polarization. The net cathodic or anodic current density and overpotential met with the Tafel relationship, which expressed as,

\[ \eta = a + b \lg I \]

(8)

With \( a = -\frac{2.3RT}{anF} \lg i^0 \) and \( b = \frac{2.3RT}{anF} \) for cathode polarization, and \( a = -\frac{2.3RT}{\beta nF} \lg i^0 \) and \( b = \frac{2.3RT}{\beta nF} \) for anode polarization.

Figure 3 showed that the linear relationships between logarithmic net current density and overpotential, and the linear relationships were expressed as,

\[ \eta_c = 0.69658 + 0.26246 \times \lg I_c \]

(9)

\[ \eta_a = 0.84606 + 0.35255 \times \lg I_a \]

(10)
The exchange current density $i_0$ and the charge transfer coefficient $\alpha$ of Pb (II)/Pb couple calculated were $2.218 \times 10^{-3}$ A cm$^{-2}$ and 0.1106 respectively, and them of PbO$_2$/Pb (II) couple were $3.983 \times 10^{-3}$ A cm$^{-2}$ and 0.0824. The exchange current density in strong Tafel polarization region was significantly greater than that in weak polarization region. This was because that deposition of lead or lead dioxide was controlled by electrochemical reaction in weak polarization region, and the reactant concentration increased in the liquid layer near the electrode surface during the electrode potential scanned from weak polarization region gradually to the strong polarization region, which led to increasing the exchange current density.

**The cyclic voltammetry characteristics of the graphite felt electrode**

Figure 4 and Figure 5 showed that the cyclic voltammogram characteristics of the lead negative and positive electrodes in electrolyte with soluble lead (II) (10 mM) in aqueous methanesulfonic acid (10 mM).

![Figure 4: Cyclic voltammogram of graphite felt negative electrode in electrolyte with soluble lead (II)](image)

**Effect of treatment methods on cyclic voltammogram of the graphite felt electrode**

In order to improve the surface electrochemical activity of electrode, the graphite felts were soaked by methanesulfonic acid (99.8%), heated at 550°C, and both for 2 hours. The results from different treatment methods were compared in Figure 6, and the effect of the treatment method with soaking by methanesulfonic acid (99.8%) was the most obvious than that of treatment method with heat. The reduction peak potentials of Pb (II)/Pb couple on the graphite felts treated with methanesulfonic acid (99.8%) increased and the oxidation peak potentials decreased, which decreased the difference of the reduction and oxidation and was advantageous to oxidation and reduction reactions of Pb (II)/Pb couple on the graphite felts, while the trend was contrary to PbO$_2$/Pb (II) couple. The peak currents of PbO$_2$/Pb (II) couple on the graphite felts treated with methanesulfonic acid (99.8%) increased. Therefore, the
effect of treatment of negative electrode with soaking by methanesulfonic acid (99.8%) on graphite felts was significantly better than positive electrode. This was because that the effective graphite felt surface area increased, -C-O, -C=O oxygen-containing functional groups in graphite felt surface also increased, and the surface adsorption and wettability of graphite felt enhanced after the graphite felts were treated with methanesulfonic acid (99.8%), which increased the compatibility of electrode and active material, decreased the charge transfer resistance of electrode, and improved the reaction speed and activity of Pb (II)/Pb couple on the graphite felt electrode.

Pb (II)/Pb and PbO₂/Pb (II) couples, some additives, such as sodium ligninsulfonate \( (\text{C}_{20}\text{H}_{24}\text{Na}_2\text{O}_{10}\text{S}_2) \), triton X100 \( (\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n) \) and hexadecyltrimethylammonium bromide \( (\text{C}_{19}\text{H}_{43}\text{NBr}) \), were added to the electrolyte. A series of cyclic voltammograms were recorded at Pb (II)/Pb and PbO₂/Pb (II) couples in a solution of lead methanesulfonate (0.01M) + methanesulfonic acid (0.01M) + sodium ligninsulfonate (1gdm⁻³), triton X100 (1gdm⁻³) and hexadecyltrimethylammonium bromide (0.005M). The results from different effects of additives on cyclic voltammogram for Pb (II)/Pb and PbO₂/Pb (II) couples were showed in Figure 7 and Figure 8, respectively.

**Figure 5:** Cyclic voltammogram of graphite felt positive electrode in electrolyte with soluble lead (II)

**Effect of additives on cyclic voltammogram of the graphite felt electrode**

In order to improve the electrochemical activity of Pb (II)/Pb and PbO₂/Pb (II) couples, some additives, such as sodium ligninsulfonate \( (\text{C}_{20}\text{H}_{24}\text{Na}_2\text{O}_{10}\text{S}_2) \), triton X100 \( (\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n) \) and hexadecyltrimethylammonium bromide \( (\text{C}_{19}\text{H}_{43}\text{NBr}) \), were added to the electrolyte. A series of cyclic voltammograms were recorded at Pb (II)/Pb and PbO₂/Pb (II) couples in a solution of lead methanesulfonate (0.01M) + methanesulfonic acid (0.01M) + sodium ligninsulfonate (1gdm⁻³), triton X100 (1gdm⁻³) and hexadecyltrimethylammonium bromide (0.005M). The results from different effects of additives on cyclic voltammogram for Pb (II)/Pb and PbO₂/Pb (II) couples were showed in Figure 7 and Figure 8, respectively.

**Figure 6:** Effect of treatment methods on cyclic voltammogram of graphite felt electrode

Figure 7 showed that the effect of the triton X100 on cyclic voltammetry behavior of Pb (II)/Pb was the most obvious than that of the others, and Figure 8
showed that the effect of sodium ligninsulfonate on cyclic voltammetry behavior of PbO$_2$/Pb (II) was the most obvious than that of the others. The current peaks of the cyclic voltammogram were much higher with triton X100 and sodium ligninsulfonate present reflecting the faster kinetics of electron transfer when the additives are in the solution. Therefore, it can be concluded that the triton X100 and sodium ligninsulfonate are levelling agents for lead and lead dioxide in the battery electrolyte, respectively.

**CONCLUSIONS**

This work has focused on understanding the kinetics and cyclic voltammetry behavior of the lead negative and lead dioxide positive electrodes. In general, the following has been observed:

1. The exchange current density of reduction reaction of Pb (II)/Pb couple in weak and strong polarization region respectively, which showed that the dynamic characteristics of graphite felt electrode in strong polarization region was better than that in weak polarization region.

2. The oxidation and reduction peak potentials were basically unchanged with the increase of cycle number, and the redox reversibility of the graphite felt electrode was good.

3. The graphite felts soaked by methanesulfonic acid (99.8%) increased the compatibility of electrode and active material, decreased the charge transfer resistance of electrode, and improved the reaction speed and activity of Pb (II)/Pb and PbO$_2$/Pb (II) couples on the graphite felt electrode.

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