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On-line mass spectrometry study of electrochemical corrosion of the graphite electrode for vanadium redox flow battery

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ABSTRACT

The electrochemical corrosion of the graphite electrode for vanadium redox flow battery is investigated by on-line mass spectrometry analysis. The results show that CO_2 and CO form and evolve more preferably than O_2 on the graphite anode, which lead to the electrochemical corrosion of the graphite electrode. Furthermore, the evolution rate of O_2 is the highest one among evolved gases if the polarization potential becomes too positive. The oxidation of VO^{2+} on the graphite electrode in 2 M H_2SO_4 + 2 M $VOSO_4$ hinders the carbon oxidation reaction and retards the electrochemical corrosion of the graphite electrode.

1. Introduction

Vanadium redox flow battery (VRB) is a promising technology that transforms unstable sources of energy such as wind and solar into a continuous, safe and reliable flow of electricity [1–5]. The reaction that occurs at the positive electrode of the VRB during charge and discharge processes can be expressed simply with Eq. (1.1),

$$VO_2^+ + 2H^+ + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} VO^{2+} + H_2O. \tag{1.1}$$

Side reactions including gas evolution and electrochemical corrosion of graphite electrodes in VRB have become a topic of increasing interest because these kinds of processes are considered as one of the critical factors determining the service life and energy efficiency of VRB [6–8]. In recent years there has been increased attention to gas evolution from the cathode and anode, but few of them have been available on the electrochemical corrosion of graphite electrodes and the effects of corrosion on the performance of VRB [9–11]. However, details of the mechanism of graphite corrosion and the composition of the gases evolved in VRB have only been speculated.

In fact, the gases evolved on the graphite anode may be composed of CO and CO_2 besides O_2 because of the carbon electrode used in VRB [12,13]. Furthermore, the amounts of CO and CO_2 in the gases evolved should correspond to extent of graphite corrosion. The composition of the gases evolved changes with time, polarization potential and concentration of ions (VO^{2+}) in the sulfuric acid solution, which may provide some useful information on the mechanism of electrochemical corrosion of the graphite electrode.

In this study, on-line mass spectrometry was applied to investigate the electrochemical corrosion behavior of the graphite electrode in 2 M H_2SO_4 + 2 M $VOSO_4$ and 2 M H_2SO_4. By monitoring and analyzing the composition of the gases evolved from the graphite anode during anodic polarization, it should be possible to gain some insight into the electrochemical corrosion of the graphite electrode for VRB.

2. Experimental

The electrolyte used was the $VOSO_4$ solution with different concentrations of VO^{2+} ranging from 0.1 to 2 M, in which the supporting electrolyte is 2 M H_2SO_4. The chemicals were of analytical grade, and deionized water was used for all experimental solutions. All electrochemical measurements were carried out using a PARSTAT 2273-potentiostat/galvanostat/FRA in a plexiglass cell containing 300 mL of the electrolyte at room temperature. A conventional three-electrode setup was utilized, in which the reference electrode was a saturated calomel electrode (SCE), the counter electrode was a graphite plate (5 cm × 6 cm), and the working electrode was a graphite disc electrode prepared from a graphite rod (spectroscopically pure) with a diameter of 12 mm as described in the literature [11]. The graphite rod was supplied by Sinosteel Shanghai Advanced Graphite Materials Company (China). The electrode potentials were given with respect to SCE. The surface morphology of graphite

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electrodes before and after corrosion was characterized by XL30FEG scanning electron microscopy (SEM).

A Hidden Analytical HPR 20 on-line mass spectrometer (MS) was used to analyze the gases evolved from the anodic graphite electrode in 2 M H_2SO_4 + 2 M $VOSO_4$ and 2 M H_2SO_4, respectively. Before on-line mass spectrometry measurements, the helium gas with flow rate of 10 mL min^{-1} was pumped into the electrolyte for 30 min to remove any air dissolved in the electrolyte. Then, a series of anodically polarized potentials were applied to the working electrode, with the duration of each polarization process being about 60 min. The gases evolved from the working electrode were collected in an upside-down funnel, which was placed above the electrode and the rim of the funnel was just below the surface of the electrolyte. Then, the collected gases were carried by helium gas with flow rate of 10 mL min^{-1} to MS. The partial pressure of evolved gas was monitored as a function of time by on-line mass spectrometry detection. Thereafter, the concentration of the evolved gas can be calculated by Eq. (2.1),

$$C_i = \frac{\frac{p_i}{N_{RSi}}}{\sum \frac{p_i}{N_{RSi}}} \times 100\%. \qquad (2.1)$$

Where C_i is the concentration for component i, p_i is the partial pressure for i, and N_{RSi} is the relative sensitivity coefficient for i. The values of N_{RSi} for O_2, CO and CO_2 were assessed at 0.028, 0.029 and 0.018, respectively, by experimental measurements.

3. Results and discussion

3.1. Effect of concentration of $VOSO_4$ on the potential of gas evolution

Fig. 1 shows potentiodynamic anodic polarization curves of graphite electrode in the $VOSO_4$ solution with different concentrations of VO^{2+} at the scan rate of 5 mV s^{-1}, in which 2 M H_2SO_4 serves as the supporting electrolyte. The curve $1^{\#}$ in Fig. 1 corresponds to the anodic potential excursion from 0 to 1.7 V in 2 M H_2SO_4 without any $VOSO_4$, and the significant increase in electrode current above 1.15 V can be attributed to carbon oxidation reaction of the graphite electrode. In comparison, the curves marked from $2^{\#}$ to $6^{\#}$ for the same potential excursion in the different concentrations of VO^{2+} show a peak around 0.9 V due to the oxidation of VO^{2+} to VO_2^+, and the peak current density increases with the concentration of VO^{2+}. Furthermore, the initial significant potential of giving rise to an increase in the anodic current for carbon oxidation reaction has a greater positive-shift in the electrolyte with higher concentration of $VOSO_4$ compared with that in the 2 M H_2SO_4. It can be deduced that oxidation of VO^{2+} on the graphite electrode can hinder carbon oxidation reaction.

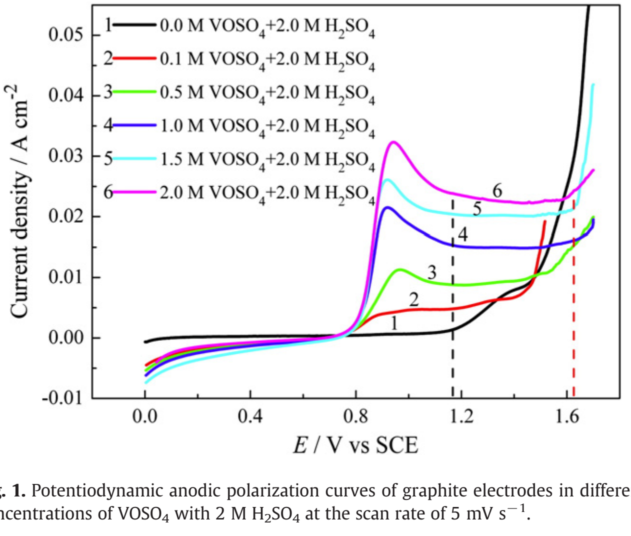

Fig. 1. Potentiodynamic anodic polarization curves of graphite electrodes in different concentrations of $VOSO_4$ with 2 M H_2SO_4 at the scan rate of 5 mV s^{-1}.

3.2. Effect of polarization potentials on the composition of gases evolved from the graphite electrode in 2 M H_2SO_4 + 2 M $VOSO_4$

Fig. 2a–f shows mass spectra for the gases evolved from the graphite electrodes under potentiostatic anodic polarization at different potentials from 1.5 to 2.0 V, in which the upper-left insets are *i–t* curves for each polarization process, together with the corresponding Faradaic charge. When the polarization potential on the graphite electrode is 1.5 V (Fig. 2a), there are few electrochemical oxidation products of carbon, such as CO and CO_2 which are detected by mass spectroscopy, and, similarly, there is no O_2 evolving from the electrode at the same time. This suggests that 74.7 C of Faradaic charge during the anodic polarization process at 1.5 V is predominantly attributed to electrochemical oxidation of VO^{2+} to VO_2^+. When the polarization potential exceeds 1.6 V (Fig. 2b and c), CO_2 and CO can be detected by mass spectroscopy, and the amounts of CO_2 and CO evolved from the electrode increase with the polarization potential. This has given rise to a significant increase in the anodic current because of CO_2 and CO evolution besides oxidation of VO^{2+} to VO_2^+. Furthermore, the amount of CO_2 evolved is greater than that of CO, which means that electrochemical evolution of CO_2 on the graphite electrode occurs more preferably than CO at room temperature, in accordance with thermodynamics. The O_2 can be detected at potentials more than 1.8 V (Fig. 2d–f). The amount of O_2 evolved from the electrode is even greater than that of CO_2 when the polarization potential reaches 2.0 V (Fig. 2f). This implies that the evolution rate of O_2 is the highest among the three kinds of evolved gases, CO, CO_2 and O_2, when the polarization potential is positive enough.

3.3. Effect of polarization potentials on the composition of gases evolved in 2 M H_2SO_4

Fig. 3a–d shows mass spectra for the gases evolved from the graphite electrodes under different anodic polarization potentials from 1.3 to 1.9 V. When the anodic potential is 1.3 V (Fig. 3a), several gases are evolved from the anode according to the mass spectrum. CO_2 and CO can be detected simultaneously at the anodic potential of 1.4 V (Fig. 3b), which is lower than that in 2 M H_2SO_4 + 2 M $VOSO_4$. This suggests that it is more favorable for the evolution of CO_2 and CO on the graphite electrode in 2 M H_2SO_4, which can lead to more extensive corrosion of graphite electrode. This is in agreement with the conclusion of potentiodynamic anodic polarization curves in this study. It is also detected that the amount of CO_2 is larger than that of CO (Fig. 3c and d), which is similar to the performance in 2 M H_2SO_4 + 2 M $VOSO_4$. However, there is no difference for the behavior of O_2 evolution in 2 M H_2SO_4 compared to that in 2 M H_2SO_4 + 2 M $VOSO_4$.

The SEM images of graphite electrodes polarized at 1.9 V for 1 h in 2 M H_2SO_4 + 2 M $VOSO_4$ and 2 M H_2SO_4 are shown in Fig. 4a and b, respectively. They illustrate that the corrosion grooves developed on the electrode surface from evolution of CO_2 and CO are much deeper in 2 M H_2SO_4. This indicates that the corrosion rate of graphite electrode in 2 M H_2SO_4 is higher than that in 2 M H_2SO_4 + 2 M $VOSO_4$. The rates of weight loss of the graphite electrode in 2 M H_2SO_4 + 2 M $VOSO_4$ and 2 M H_2SO_4 are evaluated as 0.013 g cm^{-2} h^{-1} and 0.061 g cm^{-2} h^{-1}, respectively.

4. Conclusions

The electrochemical corrosion of the graphite electrode anodically polarized in 2 M H_2SO_4 + 2 M $VOSO_4$ and 2 M H_2SO_4 was investigated by on-line mass spectrometry. The results show that CO_2 and