A comparative study of carbon felt and activated carbon based electrodes for sodium polysulfide/bromine redox flow battery

Hantao Zhou a,b,∗, Huamin Zhang a,**, Ping Zhao a,b, Baolian Yi a

Fuel cell R&D Center, Dalian Institute of Chemical physics, Chinese Academy of Sciences, Dalian 116023, PR China
Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

Received 24 November 2005; received in revised form 31 March 2006; accepted 31 March 2006
Available online 24 May 2006

Abstract

Carbon felt (CF) and activated carbon (AC) based electrodes for sodium polysulfide/bromine redox flow battery (PSB) were prepared and compared with a laboratory scale PSB flow cell in terms of structure and application performances. The structural properties of the two types of electrodes were characterized by filamentary analog and BET analysis, respectively. Catalyst coating, discharge behavior analysis and thermogravimetric analysis-mass spectrometry (TG-MS) were carried out to make out the different dominant factor in the application performances of the two materials. Compared to AC based electrode (ACE), despite of the relatively low surface area, CF demonstrates almost the same application performances, much more gains in electrochemical activity towards negative half-cell reactions by catalyst coating, and more even discharge voltage curve and stable cycling performance. At current density of 40 mA cm \(^{-2}\), an average energy efficiency of up to 81% over 50 cycles (about 600 h) has been achieved with cobalt coated CF, but with ACE only 64.7% within 16 cycles, which decreases quickly due to the loss of surface area resulted from sulfur depositing. The difference in structure related to mass transport makes the application performances gap between the two types of materials in PSB.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Polysulfide/bromine battery; Carbon felt; Activated carbon; Structure-performance relationship; Energy efficiency

1. Introduction

Sodium polysulfide/bromine redox flow battery (PSB) utilizes aqueous sodium polysulfide and sodium bromide solution as anolyte and catholyte (shown in Fig. 1), respectively [1]. The reversible electrochemical reactions during the operation of PSB may be represented, in simple terms, by the equation

\[
3\text{NaBr} + (n - 1) \text{Na}_2\text{Sn} \leftrightarrow \text{NaBr}_3 + n\text{Na}_2\text{S}_{n-1}, \quad n = 2 - 4
\]

During discharge, the reaction of the negative electrode involves the oxidation of \(\text{S}^{2-}\) anions to sulfur, which dissolves in excess \(\text{Na}_2\text{S}\) solution to form \(\text{Na}_2\text{S}_n\). At the same time, at the positive electrode \(\text{Br}_2\) dissolved in excess NaBr solution is reduced to \(\text{Br}^-\) anions. Sodium ions pass through the cation exchange membrane in the cell to provide electrolytic current flow and to maintain electroneutrality. Like other redox flow batteries [2–4], the most attractive feature of PSB is the separation of output power rating and capacity. Moreover, the electrolytes of PSB are plentiful and easily available at very low cost. Therefore, this system is more economical for scaling-up of energy storage capacity. However, an important disadvantage of PSB is the problem of cross-contamination of the half-cell electrolytes, thus needs for electrolyte management system to keep the system work efficiently with long cycle life [5–8]. Although the on-going electrolyte maintenance adds the operating costs of such a system, it is still the cheapest and most promising energy storage technology suitable for applications from 10 to 100 MW with duration up to 12 h [9–12].

Like other batteries, electrode is the key component of PSB. The electrode materials for redox flow batteries can be classified to rough two-dimensional (2D) and three-dimensional (3D) type, which corresponds to different electrolyte flow mode (shown in Fig. 2). Carbon felt (CF) or metal foam is commonly
used as 3D electrode, while carbon cloth, black carbon and activated carbon (AC) can only be employed as 2D electrode. In PSB, CF [13–15], carbon cloth [16], black carbon [17] and AC [18] are the main electrode materials for the aqueous bromide/bromine couple, and AC [7,19,20], metal foam [15] and CF [21] for the negative half-cell. The AC based electrode (ACE) developed by Regenesys Technologies Ltd. [19] illustrated only 56% energy efficiency [7] and 50% voltage efficiency [20] at 60 mA cm$^{-2}$. Ni foam has been first employed in PSB as negative electrode and demonstrated 77.4% energy efficiency during 48 charge–discharge cycles [15]. We also have developed CF based catalytic electrode that showed over 80% energy efficiency for PSB [21]. Clearly, the 2D and 3D electrode materials differ much in PSB. The obvious distinction between the two types of materials should be their different structural characteristics. On one hand, the specific surface area of AC is about several orders of magnitude higher than that of CF or Ni foam. On the other hand, the surface area of AC is mainly provided by pores in nanometer grade, while latter in micron grade. The gap in physical structure should make large differences in their application performances.

In this paper, CF and AC based electrodes were compared to study the different application characteristics of the two types of materials. To our knowledge, there have been no reports in the literature directly comparing the application behavior of such electrode materials.

2. Experimental

2.1. Preparation of electrodes

2.1.1. Based on CF

The following two types of polyacrylonitrile (PAN)-based fiber felts were used: CF and graphite felt (GF) (Shanghai Xinxing Carbon Corp., China). Felts were tailored into 2 cm × 2.5 cm rectangular pieces of 0.5 cm in thickness and submitted to the following treatments: (i) boiling in 1 M NaOH for 1 h to make fibers hydrophilic; (ii) washing with deionized water until pH 7; (iii) being dried and preserved for use.

Catalytic 3D negative electrode was based on the GF. Pretreated felt was impregnated with cobalt nitrate aqueous solution and then dried at 80 °C. In order to reduce the metal cations, H2 (flow of 150 cm$^{3}$ min$^{-1}$) was fed to it and heated at a rate of 2 K min$^{-1}$, to a final temperature of 773 K. After maintaining the top temperature for 2 h, it was cooled to room temperature in a H2 atmosphere; immersed in Na2S solution and rinsed with deionized water. The catalyst loading was controlled through pore volume impregnation and weight method. The final loading was about 40 mg cm$^{-2}$.

2.1.2. Based on AC

The composition of ACE has been optimized in our previously work [22]. AC was prepared from coconut shells. It has a particle size in the range of 200–450 μm. Polyvinylidene fluoride (PVDF) powder with 1 μm diameter was chosen as the thermoplastic binder. Different from patent [19], carbon black and pore precursor were added. Carbon black (Vulcan XC-72) was used as the electrically conductive agent and NaBr was introduced to create more pores inside the electrode.

AC supported catalyst was prepared as following process: AC was soaked for 48 h in an aqueous solution of cobalt nitrite; then, followed the steps mentioned above for the catalytic 3D electrode. The catalyst loading was designed to be 50 mg cm$^{-2}$.

Firstly, AC particles, PVDF powder, carbon black powder and NaBr were well mixed according to the weight ratio of 15:3:2:2, then placed in a mould and compressed for 30 min at a temperature of 200 °C and a pressure of 4 MPa. Subsequently, the mould was cooled in water immediately. The resulting composite was cut into the size of 2 cm × 2.5 cm and first immersed in 20% ethanol, then boiled in deionized water until the salt was removed. The thickness of the obtained ACE was 0.5 cm.

2.2. Experimental apparatus and measurements

Fig. 3 presents a schematic representation of the laboratory scale PSB flow cell. It includes a single cell, two glass tanks and two magnetically driven pumps. The single cell was constructed from stainless steel end plates inserted with PTFE tie-ins and sealed by expanded PTFE gaskets of 0.2 mm in thickness. The electrolyte flow frames were machined from PTFE. The electrodes based on CF were pressed against current collectors made of graphite plates and reduced to 80% of their original thickness. For ACE, the gasket close to membrane was replaced.

Fig. 1. The principle of sodium polysulfide/bromine redox flow battery.

Fig. 2. Schematics of flow mode of 2D and 3D electrode applications for redox flow battery: (a) current collector; (b) ion exchange membrane; (c) electrode; (d) turbulence promoter.
with a fluoro rubber gasket of 1 mm in thickness to form a gap. In the gap, a stack of several polyethylene meshes was filled to support electrode and allow electrolyte to flow through the cell fluently. Therefore, the cavity thickness was 4 mm for 3D electrodes and 6 mm for 2D electrodes. A Nafion-117 membrane was used as separator. The single cell was constructed by screwing four bolts, and the interelectrode distance was controlled rigorously through a micrometer. Another flow cell with two saturated calomel reference electrodes was connected to it to record the potential of negative and positive half-cell electrodes and the cell open circuit voltage (OCV).

A custom-designed multi-channel battery testing system, BT2000 (Arbin Instruments Corp., USA) was connected to the PSB cell and acted as power supply and load. A computer installed with Arbin MITS Pro software (version 2.8) was used to control the Arbin instrument according to the charge–discharge schedules given by us and record the data related to the cell polarization characteristics and cycling efficiencies automatically. All the electrochemical experiments were carried out with the system.

It should be stated here that the cell state of charge (SOC) equals the fractional conversion of Br\(^-\) to Br\(_2\) according to reaction 2Br\(^-\) = Br\(_2\) + 2e\(^-\). The cell was charged and discharged at a constant current density of 40 mA cm\(^{-2}\). After charge capacity reaching 2.68 A h (about 50% state of charge of the cell), the cell was charged for 1 min at a constant current density in the range of 0–60 mA cm\(^{-2}\). After a 30 s rest interval, the cell was discharged for 1 min at the same current density as that used for charging. The above procedure was repeated at various current densities to obtain plots of current density versus cell overvoltage. The charge and discharge cycles were conducted between the upper charge capacity limit (1.07 A h, about 20% SOC) and lower discharge voltage limit (1.0 V). During cycling tests, the positive and negative electrode potentials with respect to SCE as well as the cell open circuit voltage were measured continuously. The cell coulombic efficiency is defined as the discharge capacity divided by the charge capacity, the energy efficiency as discharge energy divided by charge energy. Then the voltage efficiency can be calculated from dividing the energy efficiency by the coulombic efficiency.

2.3. Operation conditions

Unless specially mentioned, the operating conditions were as follows:
- The initial anolyte was 1.3 M Na\(_2\)S\(_4\) aqueous solution; catholyte was 4.0 M NaBr aqueous solution.
- Both of the volume of the two electrolytes was 50 cm\(^3\).
- The electrolyte flow rate was controlled by the diameter of electrolyte pipe and measured by a cylinder and a stopwatch; the flow rates of the two electrolytes were both about 30 cm\(^3\) min\(^{-1}\).
- The electrode area was 5 cm\(^2\) in all cases.
- All experiments were carried out at about 26 °C.

2.4. Characterization of electrode materials

2.4.1. Carbon felt

The surface morphologies of fiber felts were examined using a Super Depth Surface Profile Measurement Microscope VK8550 (Keyence, Japan). The physical details of them were summarized in Table 1. The porosity \(\varepsilon\) was calculated from the fiber density \(\rho_{\text{fiber}}\) and the apparent felt density \(\rho_{\text{felt}}\):

\[
\varepsilon = \frac{\rho_{\text{fiber}} - \rho_{\text{felt}}}{\rho_{\text{fiber}}}
\]

After being compressed to 80% of the original thickness, the porosity of CF and GF were reduced to 90.2 and 91.3%, respectively.

The structural properties of carbon felt have been well characterized by various methods in literature [23,24]. Because the reported data of mass transport coefficient in CF were all based on the specific surface area estimated by filamentary analog [13,25–29], so this method was chose to calculate the structural parameters of the CF materials. Assuming that felt consists of long, smooth and perfect non-porous cylindrical fibers, its mass specific surface area \(A_m\) was related to the diameter \(d_{\text{fiber}}\) and density of the fiber, according to:

\[
A_m = \frac{4}{\rho_{\text{fiber}} d_{\text{fiber}}}
\]

### Table 1

<table>
<thead>
<tr>
<th>Physical characteristics of the PAN-based fiber felts</th>
<th>CF</th>
<th>GF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber diameter(^b) (10(^{-6}) m)</td>
<td>18.7</td>
<td>17.6</td>
</tr>
<tr>
<td>Fiber density(^c) (g cm(^{-3}))</td>
<td>1.74</td>
<td>1.81</td>
</tr>
<tr>
<td>Felt density(^c) (g cm(^{-3}))</td>
<td>0.139</td>
<td>0.129</td>
</tr>
<tr>
<td>Porosity(^c) (%)</td>
<td>92.0</td>
<td>92.9</td>
</tr>
<tr>
<td>Specific surface area(^c) (cm(^2) cm(^{-3}))</td>
<td>1229</td>
<td>1256</td>
</tr>
<tr>
<td>Specific surface area(^c) (cm(^2) g(^{-1}))</td>
<td>171</td>
<td>162</td>
</tr>
<tr>
<td>Real-to-geometric area ratio(^d)</td>
<td>85.5</td>
<td>81.0</td>
</tr>
<tr>
<td>Volume resistivity(^d) ((\Omega) cm)</td>
<td>2.22</td>
<td>0.76</td>
</tr>
</tbody>
</table>

\(^{a}\) Measured.

\(^{b}\) Provided by manufacturer.

\(^{c}\) Calculated.

\(^{d}\) Refers to a felt of 0.5 cm in thickness.
Then the volume specific surface area $A_v$ could be calculated through:

$$A_v = A_{m} \times \rho_{\text{felt}}$$

(4)

To multiply $A_v$ by electrode thickness we get the real-to-apparent area ratio $f$, which was introduced to estimate how much times of surface area could be gained from the geometric area.

The resistivities of the carbon felts were calculated from $I-V$ plots measured with the single cell without electrolytes and membrane.

2.4.2. Activated carbon

The BET surface area of AC, new ACE and used ACE (from negative half-cell) were obtained from nitrogen adsorption isotherms at 77 K on a Micrometrics ASAP 2010 sorptometer (Micrometeric Instrument Corp., USA). The used ACE sample was boiled in deionized water to remove the adsorbed sodium polysulfide before the test. A blank experiment was carried out with new ACE. The sample was impregnated in sodium polysulfide solution for 24 h and followed the same procedure for the used ACE. The pore volume, surface area and pore size distribution of meso- and macropores (2–300 nm diameter) were obtained by the BJH theory [30]. The pore size distribution of micropores was derived from the Horvath–Kawazoe formalism [31], while the micropore volume as well as surface area from t-plot method. The details were summarized in Table 2 (based on the mass of AC not electrode).

2.5. Thermogravimetric analysis-mass spectrometry (TG-MS)

The samples of CF and AC based electrodes before and after cycling application were analyzed by TG-MS experiments, which were carried out using a Pyris Diamond TG/DTA (PerkinElmer Instruments Inc.) coupled with a Pfeiffer ThermomStar MS (SII Seiko Instruments Inc.). Samples were placed in a ceramic sample holder, heated from 40 up to 700 °C at a constant rate of 10 °C min$^{-1}$ in an air atmosphere with a constant flow rate of 200 ml min$^{-1}$. The used ACE sample was pre-treated according to the same procedure for N$_2$ adsorption experiment.

3. Results and discussion

3.1. Structural properties of electrode materials

3.1.1. Carbon felt

CF or GF is suitable 3D electrode materials for redox flow batteries. Firstly, the high porosity and large pores formed by interlacing fibers allows the electrolyte flow through the felts fluently, thus the forced convection generated by electrolyte flow directly influences the interfacial liquid film thickness. This flow mode is most favorable for mass transport. Secondary, in a thick-
ness of 0.5 cm, the surface area of the felts is approximate two orders of magnitude of their apparent area (see Table 1). Therefore, larger working current can be expected with them.

Fig. 4 illustrates the morphologies of GF before and after being deposited with catalyst. Fig. 4(a) shows the single fiber has a clean and somewhat rough surface (the configuration of CF is similar to that of GF). Fig. 4(c and d) show the GF is an anisotropic medium consists of randomly dispersed fibers. Nitrogen adsorption method was failed to measure the surface area of the fiber felts, which confirms the absence of internal microporosity inside fibers and suggests the filamentary analog is a valid method to calculate the specific surface area of fiber felts. As shown in Fig. 4(b and d), the fiber surface has been coated with a layer of metal successfully. With the structural properties of the GF and the uniformly distributed catalyst on the fiber surface, the Co coated GF (Co-GF) was thought to be high performance negative electrode for PSB.

3.1.2. Activated carbon

Fig. 5 presents \( N_2 \) adsorption isotherms on AC, new ACE, blank sample and used ACE (from negative half-cell). It can be seen that the \( N_2 \) adsorption capacity decreases with the order of the four samples. As shown in Table 2, from AC to new ACE, the specific surface area is decreased by ca. 20%. It can be due to the blocking of a certain amount of space formed by AC particles and covering of some external surface of AC particles by polymer binder and conductive agent. The remaining electrolyte further decreases the \( N_2 \) adsorption capacity of the new ACE. However, the adsorption capacity is decreased largely from new ACE to used ACE. The specific surface area is reduced to 50% of that of new ACE (see Table 2), which may not only due to the residual electrolyte.

The pore size distributions of AC, new ACE and used ACE are shown in Fig. 6. Obviously, the pore volume of AC and new ACE is mainly provided by micropores with diameter less than 4 nm. This pore structure is surely not helpful for mass transfer inside AC, especially at high operating current density.

It can be expected that the reactants in these tiny pores will become depleted during operating thus lead to the increasing of concentration polarization. The pore volume is also decreased by 50% from new ACE to used ACE, but is still mainly provided by micropores.

Anyhow, the high specific surface area of AC seems to be a very attractive feature for electrochemical reactions.

3.2. Polarization test

Fig. 7 shows the polarization behaviors of GF, CF, ACE, Co-ACE and Co-GF in the PSB flow cell. The curves of pure felts are different with those of pure ACE, on which the cell overvoltage is in proportion to the current density. This indicates different polarization mechanism between those electrodes. It is known that the cell overvoltage may be caused by three factors: electrode electrochemical activity, internal resistance and mass transport. For the experimental results obtained previously [21], various carbon materials showed little difference in the elec-
trochemical activity against positive half-cell reactions, so the differences resulted from electrochemical activity in polarization characteristic are thought to be mainly originated from the negative electrode of PSB. From the point of view of surface area, the ACE has surface area (5 cm² ACE of 0.5 cm thick has ca. 1366 m² surface area) almost more than 30,000 times of that of the GF or CF that we can believe the ACE may exhibit extremely high electrochemical activity. However, ACE demonstrates nearly the same performance as that of CF, even a slightly low at higher current density (see Fig. 7). So it can be concluded that electrochemical activity is not the major factor causing the bad application performance of ACE. In addition, the resistance of ACE is smaller than 0.5 Ω cm [22], which is lower than those of felts. Clearly, concentration polarization differentiates ACE from CF.

According to the results obtained previously [21], the electrode overpotential shows no clear dependence on the resistance of CF. Furthermore, the forced convection should be the main mass transport mode for CF at the flow conditions of the PSB flow cell. Therefore, for carbon fiber felt materials, the electrochemical activity plays the main role in the polarization behavior of CF. The fiber surface chemical property such as carbon–oxygen functional groups may decide the activity against negative reactions [32,33] and shift the equilibrium (S2²⁻ ↔ 2S²⁻) toward electroactive species S2²⁻ [34,35].

The addition of catalyst to negative electrode can clearly make out the different polarization behavior between the two types of materials. At 40 mA cm⁻², by catalyst coating, the cell charge overvoltage with GF is decreased from 353 to 75 mV, while with ACE from 191 to 145 mV. The catalyst enhanced the electrochemical activity of the GF much more than it did on ACE. Obviously, the catalyst utilization in ACE is considerably low, which can be assigned to the poor mass transfer inside it.

### 3.3. Discharge behavior analysis

Analyzing constant current discharge behavior is also able to distinguish the different application characteristics of the two materials. Generally, three zones can be observed on a current versus electrode potential curve of an electrode: conversion controlled (or charge transfer controlled), mass transport controlled and secondary reaction zone, with the increasing overpotential [36]. So, during the constant current discharging of PSB, three regions should also be observed. At the beginning, the cell may be conversion controlled. Thus, the cell voltage will decrease with the decreasing of electroactive species in bulk electrolyte (leads to the shift of half-cell potential, can be estimated by Nernst equation). Within several hours, the cell internal resistance does not vary significantly (can be seen in the next cycling experiments). Therefore, the discharge curve should be parallel to the open circuit voltage curve. However, with the discharge proceeding, the electroactive species will become less and less, the cell may turn to be mass transport controlled. Within this region, the cell voltage will decrease more quickly, thus the deviating of discharge curve from OCV. Of course, it is desired that this turning point would come as later as possible. When the outlet concentration is decreased to be zero, then the cell will come into the secondary reaction region.

When the cell is mass transport controlled, if ideal plug-flow conditions and negligible axial dispersion are assumed, the mass balance may be expressed by [27]:

\[
\frac{C_{in} - C_{out}}{C_{in}} = 1 - \exp\left[-\frac{k_mA}{Q}\right]
\]  

(5)

where \(C_{in}\) and \(C_{out}\) are the inlet and outlet concentration (mol dm⁻³), respectively, \(k_m\) the mass transport coefficient (dm s⁻¹), \(A\) the electrode surface area (dm²) and \(Q\) is the flow rate (dm³ s⁻¹).

In addition, the following mass charge balance equation should always be true unless secondary reaction is taking place:

\[
C_{in} - C_{out} = \frac{I}{zFQ}
\]  

(6)

where \(I\) is the operating current (A), \(z\) the number of electrons (2) and \(F\) is the Faraday constant (96485 C mol⁻¹).

Combining Eqs. (5) and (6) we obtain the relationship for the calculation of the first critical inlet concentration \(C_{1st}\) (mol dm⁻³):

\[
C_{1st} = \frac{I/zFQ}{1 - \exp[-k_mA/Q]}
\]  

(7)

At the second turning point the outlet concentration is zero. The second critical inlet concentration, \(C_{2nd}\), can be given by:

\[
C_{2nd} = \frac{I}{zFQ}
\]  

(8)

Fig. 8 shows the \(k_m\) according to the six correlations in the literature [13,25–27], which are listed in Table 3. The values based on [Fe(CN)₆³⁻]/[Fe(CN)₆⁴⁻] and Hg²⁺/Hg⁰ are higher than those based on Br₂/Br⁻ almost two orders of magnitude. However, as shown in Fig. 9, the values of \(C_{1st}\) based on Br₂/Br⁻ are not more than two times of those based on [Fe(CN)₆³⁻]/[Fe(CN)₆⁴⁻] or Hg²⁺/Hg⁰. Furthermore, all the values of \(C_{1st}\) are very close to \(C_{2nd}\). So it can be expected that the mass transport controlled region will last a very short time. This is confirmed by the discharge curve of CF (shown in Fig. 10, unstable large discharge current of \(\geq 100\) A cm⁻²).
Table 3
Correlations between the mass transfer coefficient and the electrolyte velocity

<table>
<thead>
<tr>
<th>Authors</th>
<th>Redox couple</th>
<th>$A_v$ (cm$^{-1}$)</th>
<th>$k_m$ (cm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Kinoshita and Leach [13]</td>
<td>Br$_2$/Br$^-$</td>
<td>110</td>
<td>$1.3 \times 10^{-3}u^{0.72}$</td>
</tr>
<tr>
<td>(b) Kinoshita and Leach [13]</td>
<td>Br$_2$/Br$^-$</td>
<td>88</td>
<td>$1.2 \times 10^{-3}u^{0.61}$</td>
</tr>
<tr>
<td>(c) Bek and Zamyatin [25]</td>
<td>Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$</td>
<td>160</td>
<td>$1.9 \times 10^{-2}u^{0.352}$</td>
</tr>
<tr>
<td>(d) Schmal et al. [26]</td>
<td>Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$</td>
<td>113</td>
<td>$1.6 \times 10^{-2}u^{0.40}$</td>
</tr>
<tr>
<td>(e) Delanghe et al. [27]</td>
<td>Hg$^{2+}$/Hg$^0$</td>
<td>185</td>
<td>$1.7 \times 10^{-2}u^{0.40}$</td>
</tr>
<tr>
<td>(f) Delanghe et al. [27]</td>
<td>Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$</td>
<td>185</td>
<td>$2.2 \times 10^{-2}u^{0.36}$</td>
</tr>
</tbody>
</table>

Where $u$ is the electrolyte velocity in the empty cross-section (cm s$^{-1}$).

0 V lower voltage limit), which is parallel to the OCV almost throughout the discharge process, except for close to the end where there is insufficient bromine in catholyte thus the cell voltage decreases sharply in a very short time [15]. At the flow rate used in the text (0.625 cm s$^{-1}$), the $C_{1st}$ is $3.86 \times 10^{-3}$ M (concentration of Br$_2$, calculated with the correlation (b) in Table 3, the highest value among them) and the $C_{2nd}$ is $2.07 \times 10^{-3}$ M. The difference between $C_{1st}$ and $C_{2nd}$ is less than the consumption per pass (equal to $C_{2nd}$) corresponds to time of 4 s. At the 1.0 V, the $C_{out}$ was calculated to be $2.00 \times 10^{-3}$ M (almost 100% discharge depth) by Nernst equation with the recorded positive half-cell potential of 0.966 V, so the $C_{in}$ was $4.07 \times 10^{-3}$ M, which is higher than the $C_{1st}$. Therefore, the cell was still conversion controlled at 1.0 V.

However, the cell using ACE comes to mass transport controlled region so early, as can be seen from the discharge curve of ACE in Fig. 10, the cell turned to be mass transport controlled at SOC approximate 8%, corresponds to 0.16 M Br$_2$, much higher than the $C_{1st}$ of CF. As shown in Fig. 11, there are three concentration gradients in ACE: from the bulk electrolyte to the electrode outside surface; from the electrode outside surface to the inside surface; from the external surface to the internal surface in a single AC particle. For the solid structure, the pores formed by AC particles would not act as good passages for mass transport, during which the diffusion should be the dominant contributing factor. Therefore, the internal surface contributes little to the effective electrode surface area. Moreover, the impact of the insulating binder distribution and the coating of the AC on the electrode external surface can further reduce the available surface area. If PVDF is covering the surface of the AC this will leave a roughened surface which has little surface area whereby the electrode will behave like a simple parallel plate reactor.

3.4. Cycling experiments

Fig. 12 shows the cycling efficiencies of ACE and Co-ACE. Over 16 cycles, the average energy efficiency of only 64.7% was obtained with pure ACE, while for Co-ACE was 66.1%.
Same as the polarization test results, catalyst cannot improve the electrode performance too much. Moreover, with the increasing cycle number, the cell efficiencies decrease quickly. For ACE, the energy efficiency is decreased from 67.4 to 60.8% as well as voltage efficiency from 74.1 to 66.2%. Co-ACE exhibits the same tendency that the energy efficiency decreases associated with the decreasing of voltage efficiency, which suggests the deteriorating of electrode performance. However, the cell using CF based electrodes succeeded in maintaining constant energy efficiency, as can be seen in Fig. 13, 64.3% energy efficiency was obtained over 50 cycles, which is close to that of ACE. When the cell using the Co-GF and GF as negative and positive electrode, respectively, over 50 cycles (about 600 h), average coulombic, voltage and energy efficiency were achieved by 96.1, 84.3, 81.0% (shown in Fig. 14), respectively, which is really a great advancement upon activated carbon based electrodes [7,20]. Fig. 15 shows a well-defined voltage profile of the cell throughout the cycling test.

Researchers [37–39] found there was element sulfur produced during sulfide oxidation process. One can expect that the sulfur produced inside ACE especially in micropores can’t be redissolved because of the shortage of electrolyte resulted from poor mass transport. Then, the accumulated sulfur will either block the pores or cover the surface, thus lead to the electrode performance deterioration. The results of N2 adsorption experiments have confirmed this mechanism, as discussed before. Actually, we did found some element sulfur crystals on the external surface of used ACE, which proves that the performance degradation of ACE owes to the sulfur depositing. However, no obvious sulfur was found on CF.

TG-MS experiments were carried out to further investigate the sulfur depositing on the two materials. The TG weight loss curves as well as MS (m/z = 64, SO2) are shown in Fig. 16. The TG curves of new CF and used CF exhibit only one weight loss phase. The first weight loss phase around 100°C of new ACE and used ACE is due to the release of the absorbed moisture. The phase around 450°C of the four samples is assigned to the oxidation and combustion of the carbon. By MS, SO2 (m/z = 64) was only detected with used ACE. It should be noted here that
Fig. 16. The TG as well as MS curves with: (line 1) new CF; (line 2) used CF; (line 3) new ACE; and (line 4) used ACE. Used samples are from negative half-cell. The MS curve of (2) (3) (4) offset by $1.0 \times 10^{-13}$, $2.0 \times 10^{-13}$ and $3.0 \times 10^{-13}$ A, respectively, based on that of (1).

the SO$_2$ might not only originate from the residual electrolyte, which is not solely responsible for the decrease of surface area as well as pore volume. This also indicates that sulfur depositing did not occur on CF.

4. Conclusions

The poor mass transport in ACE limits the utilization of its high surface area. Especially during cycling test, the sulfur accumulating inside ACE leads to the fast efficiency deterioration. However, for the structure benefit mass transport, 3D CF shows the same polarization performance but more even discharge voltage. At 40 mA cm$^{-2}$, using Co-GF as negative electrode and GF as positive electrode, the PSB cell has successfully achieved stable energy efficiency greater than 80% over 50 cycles. Based on this study, CF seems to be superior to AC in the applications for PSB electrodes, because of the higher energy efficiency which can be easily enhanced by catalyst coating and better cycling stability for the absence of sulfur passivating.

Acknowledgements

This work was supported by the CAS Innovation Program (No. DICP-K2002D3) and the Nation 863 Program of China (No. 2005AA516020).

References