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Acid modified graphite felt cathode electrode for low temperature H₂/Br₂ redox flow battery

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Abstract

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In this study, the performance of a modified PAN based graphite felt, an alternative electrode for cathode, was investigated for hydrogen/bromine flow battery. In these experiments, carbon paper was used as porous transport layer in the anode and graphite felt (GF) was used as the catalytically active electrode in the cathode. Graphite felt electrode used for cathode is also used in industry as thermal insulation material. The cathode kinetics of this relatively low-cost material was increased by acidic modification and used in flow battery cathode electrodes. To create functional groups on the cathode electrode, acidic surface modification of the graphite felt was carried out with H₂SO₄ and HNO₃ acid pairs with a volumetric ratio of V_{H₂SO₄} / V_{HNO₃} = 3:1. XRD and SEM analyzes were used for physical characterization of the modified graphite felt electrodes. Single cell potentiostatic polarization and power curves of the hydrogen/bromine flow battery were obtained to elucidate the effect of cathode graphite felt surface modification. In this study, comparison tests were performed for pristine graphite felt and modified graphite felt. The maximum powers detected from the single cell flow battery formed by pristine graphite felt and modified graphite felt cathode electrodes are 0.32 W/cm² (0.65V) and 0.40 W/cm² (0.65V), respectively. In flow battery tests, this 25% power increase in similar voltage values may be attributed to the improvement of the weak electrochemical properties of the graphite felt electrode by acidic modification.

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1. Introduction

Energy storage technologies are vital for the practical use of renewable energy. Among the renewable energy resources, wind and solar powers are widely used energy sources and they are considered as intermittent systems [1]. In order to increase the energy efficiency, these renewable energy sources must be coupled with a suitable energy storage system. One such promising technology for the electrical energy storage is flow batteries. Flow batteries can store electrical energy with high efficiency and for a longer period. Among all flow batteries, H₂/Br₂ flow batteries are considered as a promising battery technology due to their rapid cathode kinetics. In a typical low temperature H₂/Br₂ flow battery system operating on discharge mode, hydrogen gas (anolyte) is fed to the anode side and protons are formed by hydrogen oxidation reaction in the catalytic region. Then, protons are transported through the solid polymer membrane to the cathode. In the cathode side,

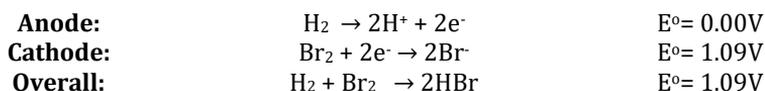
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liquid bromine solution (catholyte) is reduced to bromide ions at the cathode and form hydrobromic acid. The half-cell reactions for the H₂/Br₂ 2 flow battery system are (discharge mode):



One of the major advantages of this battery is that hydrogen and bromine are relatively inexpensive chemicals. Since the system contains bromine with its toxic and corrosive structure, overall flow battery design should be bromine and hydrobromic acid tolerant. Although the hydrogen-bromine flow battery has higher electrode kinetics compared to other popular flow battery systems, Br⁻, Br³⁻ or Br⁵⁻ ions in the cathode can pass through the anode and poison the platinum-containing catalyst in the anode (crossover), thus reducing the flow battery performance [2]. Bromine-based ions which pass through the membrane to the anode catalyst also hinder efficient operation of the battery at 0.6 V and below. Therefore, Preventing/reducing the passage of bromine based ions as a result of crossover through the conventional membrane (Nafion[®] 212) is an important problem to be solved for the hydrogen-bromine flow battery. In addition, expensive catalysts and electrodes that can be used on the cathode side increase the cost considerably. Cost-effective catalysts and porous transport layers may be used to reduce overall cost of the cell. For the Hydrogen/Bromine flow battery reactions precious metallic or bimetallic catalysts such as Pt/C and Pt-Ru/C or Rh_xS_y and Rh_xS_y/C may be used [3-6]. In addition, the bromine reduction reaction (BRR) can also be catalyzed by only carbon structures. Besides its role as porous transport layer (PTL), it is well documented in the literature that carbon paper, carbon cloth, carbon felt, and graphite felt also act as active catalyst for BRR. Graphite felt (GF) can be produced from polyacrylonitrile (PAN) by high temperature carbonization and graphitization process. Graphite felt is widely used as PTL in redox flow batteries due to its low cost (ca. \$70/m²), good electrical conductivity, high surface area with a porous structure (470-600 m²g⁻¹), and stable mechanical and chemical properties [7-9]. The performance of the hydrogen-bromine redox flow battery can be improved by applying surface modification processes to low-cost carbon-based electrodes.

The graphite felt used in this study is a low cost material generally used for thermal insulation at high temperature. On the other hand, poor electrochemical properties of the graphite felt limit the performance of the hydrogen-bromine flow battery system [10]. To enhance H₂/Br₂ flow battery system performance, one strategy may be to increase electrochemical catalytic activity. One way to achieve this goal is to increase functional oxygen groups within the electrode structure. Supply of functional oxygen groups over the surface of graphite felt leads to an increase in surface wettability and this results in an improved electrical conductivity. There are various effective techniques for surface modification in the literature such as thermal modification [11], acidic modification [12], electrochemical oxidation [10], nitrogen modification [13], metal modification [14], thermo-chemical modification oxygen plasma treatment and gamma-ray irradiation [15]. Among these methods, the acidic modification process increases the electrochemical activity by increasing the oxygen-containing functional groups on the graphite felt surface, as well as increasing the active reaction area due to acid corrosion. In a study by W. Zang et al. for vanadium redox flow batteries, it was observed that acid treatment applied to the graphite felt for VO²⁺/VO₂⁺ reaction increased the wettability of the graphite felt and decreased the resistance during charge transfer [16].

In this study, it was aimed to improve the kinetics of bromine reduction reaction in cathode by modifying the surface of low-cost graphite felt by acidic treatment. The effect of

modified graphite felt electrodes and carbon loading on H₂/Br₂ redox flow battery performance were investigated and compared with pristine graphite felt electrodes.

2. Materials and method

In this study, the electrode surface of graphite felt was modified with sulfuric acid and nitric acid. Then, anode and cathode catalysts were prepared. The catalysts were loaded over the electrodes in the specified proportions and pressed with a hot press by inserting a commercial membrane between them. Finally, steady state potentiostatic performance tests were performed with an electronic load in a single-cell (5 cm², interdigitated flow field) hydrogen bromine flow battery system.

2.1. Acidic modification

5 mm thick graphite felt (SGL[®] Carbon, Sigratherm GFA5) was cut to obtain an electro active area of about 5 cm² (2.2cm x 2.2cm). The graphite felt electrode was sonicated in anhydrous ethanol (%99, Sigma-Aldrich[®]) for 30 min. to remove impurities. Then, GF electrode was washed with de-ionized water. GF electrode was dried in an oven at 100°C for 5 h. Sulfuric acid (%98, Sigma-Aldrich[®]) and nitric acid (%69, Merck[®]) pairs were used for acidic oxidation. 2M sulfuric acid and 2M nitric acid were used in the acidic treatment process. The acid mixture was prepared so that the volumetric ratio was kept at about V_{H₂SO₄}/V_{HNO₃}= 3. GF electrode was oxidized in a sealed 100 mL Teflon-lined flask containing 40 mL of mixed acid solution at 80°C. The oxidized electrode was first washed with deionized water, and then sonicated with deionized water for 30 min. Electrode was dried in oven at 100°C for 5h.

2.2 MEA Preparation

Anode electrode was prepared by using commercial Pt/C catalyst (67 wt% from Tanaka Kikinzoku Kogyo) onto the porous transport layer (PTL) with a loading amount of 0.4 mg Pt/cm². On the cathode side, commercial carbon black (Vulcan XC-72, Cabot[®]) was used as catalyst. The electrode was prepared by loading the catalyst in an amount of 0.4 mg C/cm² onto PTL. In the anode and cathode catalyst loading process, the catalyst solution was prepared using catalyst (Pt/C or C), Nafion solution (15%, Ion Power[®]), deionized water and 2-propanol (Sigma-Aldrich[®]). The ratio of catalyst to Nafion solution was kept at around 7: 3 by weight. After the catalyst solution was homogenized using an ultrasonic bath, the catalyst ink was loaded onto the PTL by conventional brushing method. The membrane electrode assembly (MEA) structure is formed by placing a solid polymer membrane between the anode and cathode electrodes. Nafion-212 (DuPont[®]), a commercial solid polymer electrolyte membrane, was used without pretreatment for the proton exchange. Electrodes were prepared using porous carbon paper (SGL[®] Carbon, GDL 25BC) in the anode and graphite felt (SGL[®] Carbon, Sigratherm GFA5) in the cathode as the porous transport layer. MEA structure was prepared with a hot press at 135 °C and 5 bar for about 4 min.

2.3 Physical characterization

Surface morphology analyses of the samples were performed using scanning electron microscopy (SEM) with an acceleration voltage of 10kV (JEOL, JSM-7001F). The X-Ray diffraction (Rigaku, SmartLab) analysis of the samples was conducted using the Cu-K α 1 source with a screening angle of 2-90°, and scanning speed of 2° min⁻¹. X-ray photoelectron spectroscopy (XPS) (Specs-Flex XPS) was used to examine the functional groups over the surface of the electrodes.

2.4 Single cell performance tests of hydrogen-bromine redox flow battery

Hydrogen/Bromine redox flow battery polarization tests were performed using a single cell test system with an active area of 5 cm². Bipolar plates produced from graphite have interdigitated flow field design. Gold-plated electrolytic copper current collectors are used to record the potential and current. 200 micron thick Teflon gaskets are used at the anode and cathode to seal the cell. A torque wrench is used to compress the cell with a torque of 4 N.m per bolt. In the electrode preparation stage, SGL GDL 25BC and Sigratherm GFA5 graphite felt were used as porous transport layer at the anode and cathode respectively. For all anode electrodes, 0.4 mg/cm² (67% Pt/C) catalyst was loaded onto the SGL 25BC gas diffusion layer. In this study, no humidification was performed on the anode side. Hydrogen flow rate was set to 0.1L min⁻¹.

At the cathode, a mixture of 1 M HBr (500 mL) and 1 M (500 mL) Br₂ was circulated at a volumetric rate of 50 mL/min with a peristaltic pump (Watson Marlow E323). All experiments were conducted at room temperature (~25°C). Under the same conditions, 25BC/Nafion-212/Pristine GF, 25BC/Nafion-212/Modified GF, and 25BC/Nafion-212/Modified GF + Vulcan XC-72 MEAs were used in the cell and single cell hydrogen-bromine flow battery performance tests were performed. While the battery was operated in discharge mode, current values were recorded at the potentiostatic steady-state potentials at 0.05 V intervals starting from the open circuit voltage with an electronic load (Maynuo® M9714).

3. Result and Discussion

XRD patterns of pristine graphite felt and graphite felt after acidic modification are shown in Fig. 1. The most prominent peaks in all pristine and modified graphite felt samples are the peaks corresponding to planes (002) (JCPDS: No. 75-1261) and (100) at 26.4° and 44.6° respectively [17,18].

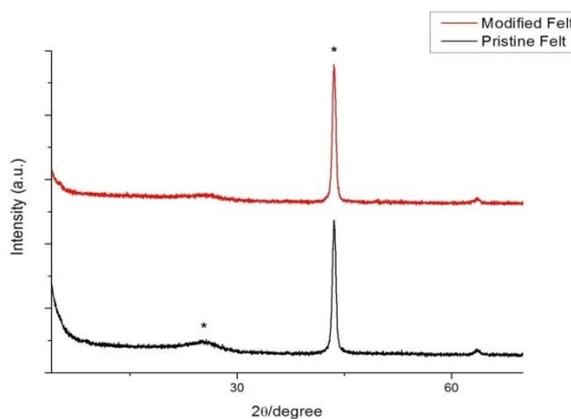


Fig. 1 XRD patterns of electrodes

The characteristic diffraction of the graphite felt in the (002) and (100) planes indicates that the graphite felt is partially oxidized. When the diffraction densities of pristine GF and modified GF were compared, it was found that the diffraction density decreased after oxidation due to acidic treatment. This reduction in diffraction intensity is generally attributed to defects formed in the structure after oxidation process. These structural defects may also be seen from the SEM micrographs given in Fig. 2. Diffraction peaks weaken as these defects in the structure cause partial irregularity of the reflection planes

in the crystal plane [17,19]. Type and content of the functional groups are validated by XPS analysis and this may explain and confirm the reduced diffraction intensity observed in XRD patterns. Pristine GF and modified GF surface morphologies are given in Figure 2. When SEM micrographs are analyzed, it is seen that acidic modification causes a change in the surface of graphite felt fibers. The fibers in the structure of the graphite felt are about 10 μm thick.

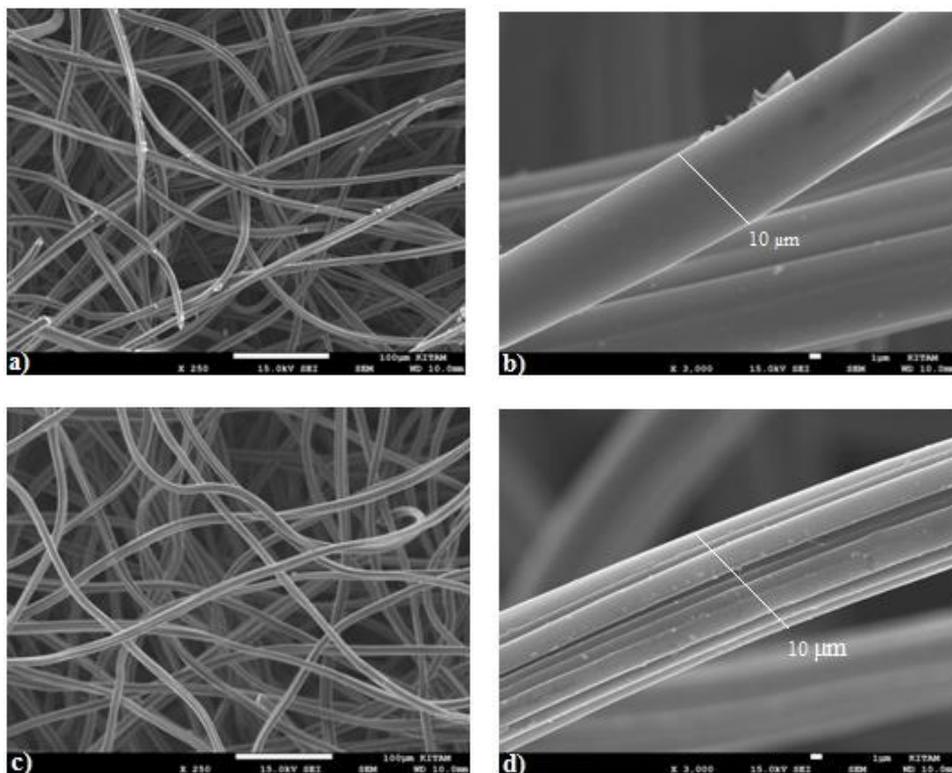


Fig. 2 SEM micrographs of cathode electrodes for a-b) Pristine graphite felt, and c-d) Modified graphite felt

When the SEM micrograph is examined, it is seen that there are micro changes due to oxidation on the graphite felt surface. Acidic modification caused roughness on the surface of graphite felt fibers. Surface oxygen groups and roughness can be controlled by altering the concentration of the acid pair to values higher than 2M used in this study. These defects caused by modification especially created small cavities on the fiber structure and increased the surface area of the graphite felt.

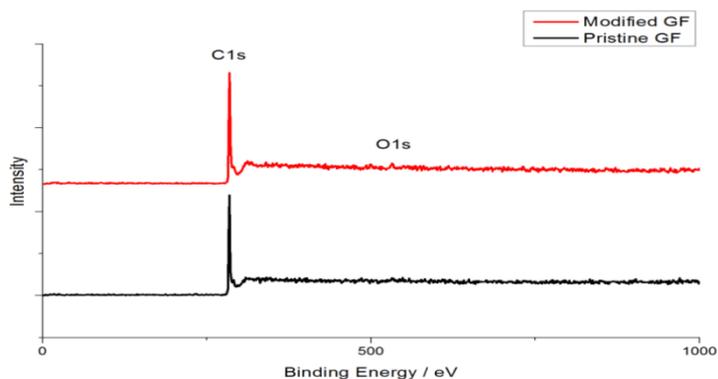


Fig.3 XPS surveys of pristine and modified graphite felts

XPS survey spectra given in Fig. 3, indicates C1s and O1s binding energy values were centered at 284.7 eV and 532.0 eV respectively. Considering XPS results, no significant impurities were found on the graphite felt surface. In addition, oxygen containing functional groups were detected with the XPS analysis. XPS data were used to fit a curve by peak deconvolution method to get C1s and O1s spectra of the pristine and modified graphite felt samples. C1s and O1s spectrums of the graphite felt samples are given in Fig. 4. Spectra are calibrated according to the binding energy of the carbon at 284.7 eV. The functional group contents on the surface of the samples are listed in Table 1. Table 1 confirmed the increase of oxygen-containing functional groups on the electrode surface after modification.

Table 1. XPS curve fit data for the surface functional groups

Sample	C1s			O1s	
	C=C	C-C	C-O	C=O	C-OH
Pristine GF	33.70	16.31	14.93	18.54	16.52
Modified GF	31.21	18.78	18.20	31.81	

As it can be seen from Fig. 4, C1s peak positions and binding energies were attributed to C-C (287.7 eV), C=C (283.75 eV, 285.1 eV) functional groups [20]. Considering oxygen containing carbon bonds, C-O (532.0 eV, 533.4 eV, 533.4 eV), C=O (530.0 eV, 531.2 eV, 531.4 eV, 531.7 eV), -OH (532.7 eV) functional groups are detected for O1s peak [21-23].

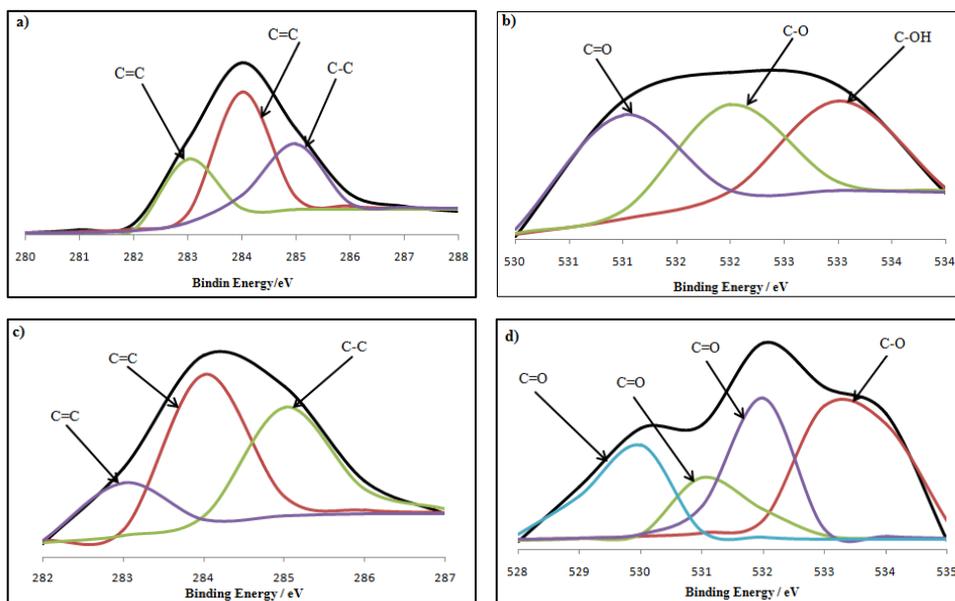


Fig. 4 XPS curve-fit for C1s and O1s spectra of cathode electrodes, pristine GF (a and b), modified GF (c and d)

The hydrogen/bromine redox flow battery performances of pristine GF and modified GF were performed by an electronic load using a single cell with an active area of 5 cm² and bipolar plates having interdigitated flow channel architecture. Polarization and power curve data of the flow battery system for different cathode electrodes are presented in Figure 5. Table 2 lists the maximum current and power density for the tested electrodes. As Fig. 5 and Table 2 are examined, the increase in cell performance due to acidic modification is clearly observed. It may be suggested to use more concentrated acid pair solution to modify the surface electrodes to get even better performance results. On the other hand, a slight increase in hydrogen/bromine redox flow battery performance was detected when a typical carbon black (Vulcan XC72) was loaded (0.4 mg C/cm²) into the cathode electrode, especially when the fuel cell is operated at higher current densities. Optimal cathode carbon black loading values over the surface of the modified graphite felt will be reported in a future study.

The maximum power densities obtained from Pristine GF, modified GF and modified GF + Vulcan XC-72 cathode electrodes are 0.32 W cm², 0.38 W cm², and 0.40 W cm², for the potentials of 0.65 V, 0.75 V, and 0.65 V respectively.

As the flow battery is operated at lower potentials (< 0.6 V), considerable performance loss is observed. This phenomenon may result from the crossover of species such as Br⁻ Br³⁻ [8]. This performance loss may be prevented with a proper electrolyte to minimize crossover and as well as with a better anode catalyst (bromine tolerant HOR catalyst).

Considering the low current density region, it is observed that the performance of pristine GF is low. Losses in this region can be attributed to catalytic activation. Relatively higher performance of the modified GF in the low current density region may result from the increased kinetics of bromine reduction after acidic modification and consequently to an increase in catalytic activity.

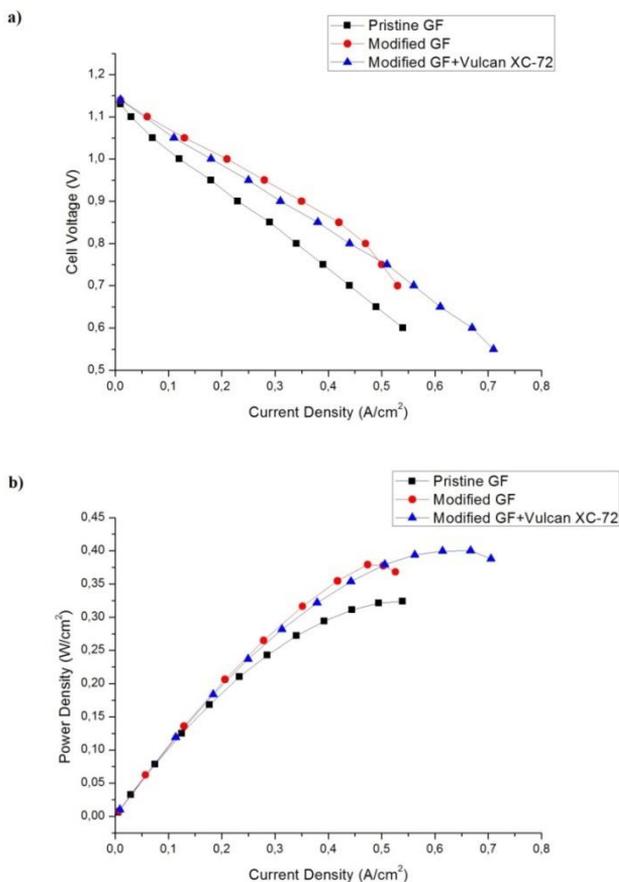


Fig. 5 Single cell H₂/Br₂ redox flow battery performance for different cathode electrodes at 25 °C a) polarization curve and b) power curve

Table 2. Current and maximum power densities for the prepared cathode electrodes

Anode	Cathode	Cell Voltage (V)	Current Density (A/cm ²)	Power Density (W/cm ²)
SGL 25BC	Pristine GF	0.65	0.49	0.32
SGL 25BC	Modified GF	0.75	0.50	0.38
SGL 25BC	Modified GF+Vulcan XC-72	0.65	0.61	0.40

4. Conclusion

In this study, it was aimed to increase the performance and decrease the cost of the hydrogen-bromine flow cell system. For this purpose, low-cost modification processes were applied to the graphite felt electrode used in the cathode. The surface of the graphite felt used as an electrode in the cathode can be modified by methods such as thermal, electrochemical or acidic treatment. Acidic treatment, which is fast and low cost, provided the desired improvement in this work. Compared with the modified and carbon loaded

cathode electrodes, pristine graphite felt performance was observed to be lower. Selected graphite felt is generally used for insulation purposes (e.g. high temperature oven applications) and this felt has a relatively lower surface area. As a result of the surface modification of cathode graphite felt with acidic treatment, flow battery performance increased with the increase in electrochemicals for bromine reduction reaction. The use of graphite felt electrode as a bromine cathode electrode in the hydrogen-bromine flow battery system significantly reduces the cost of the battery. XPS results indicate the presence of oxygen-containing functional groups on the electrode surface and confirm the increase of these groups after acidic modification. The electrochemical activity of the electrode has been significantly improved by increasing the defects created on the graphite felt electrode surface and the active functional groups containing oxygen. The electroactive reaction area provided by the functional groups enhanced the hydrogen/bromine flow battery performance by accelerating the electrode kinetics of the reduction reaction at the cathode. In addition, functional groups on the surface reduced resistance on the cathode electrode formed during charge transfer, and accordingly, single cell flow battery performance was improved. In order to further improve the electrochemicals of cathode electrode, it is recommended to determine the appropriate carbon types (e.g. carbon blacks, ordered mesoporous carbons, CNTs, etc.) and the optimum carbon loading amounts for graphite felt electrodes modified with concentrated acid pairs.

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