A New Structure Bipolar Plate for Vanadium Flow Battery

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Abstract: A pattern bipolar plate (BP) is designed to decrease the electrical contact resistance between the BP and carbon felt electrode (CFE) by increasing the BP's specific surface area through hot pressing the spherical crown pattern on the surface of the BP, and the carbon felt is pressed into the pattern by the stack tightening force. The contact area growth rate is 18.3% of a single cell which has 48cm^2 active area. The areal specific resistance (ASR) of conventional BP and pattern BP is 1309 mΩ·cm^2 and 946 mΩ·cm^2 at 20% electrode compression ratio, the pattern plate is 27% lower than the conventional plate. In the single battery charge/discharge cycle test, battery assembled with the pattern BP shows a 1% higher EE than the conventional BP.

Keywords: Vanadium Flow Battery; Bipolar Plate; Contact Resistance

1. Introduction

The vanadium redox flow battery (VRFB) is one of the most promising energy storage system (ESS) with various advantages such as non-explosiveness, unlimited power capacity and a long lifetime [1]. The VRFB system is shown in Figure 1. The single cell is composed of two bipolar plates, two electrodes, two frames and a membrane. The charge and discharge of VRFBs occur by the potential difference of vanadium ions through reduction and oxidation (redox) reaction. The cathodic reaction of VRFBs is as follows:

$$VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O$$

The anodic reaction of VRFBs is as follows:

$$V^{2+} \leftrightarrow V^{3+} + e^-$$

The energy efficiency and voltage efficiency of batteries are mainly affected by the ohmic resistance, concentration polarization and electrochemical polarization. The ohmic resistance is the main influencing factor accounting for 50%~70% including the bulk resistance and contact resistance of electrolyte, membrane, electrode, bipolar plate and so on.

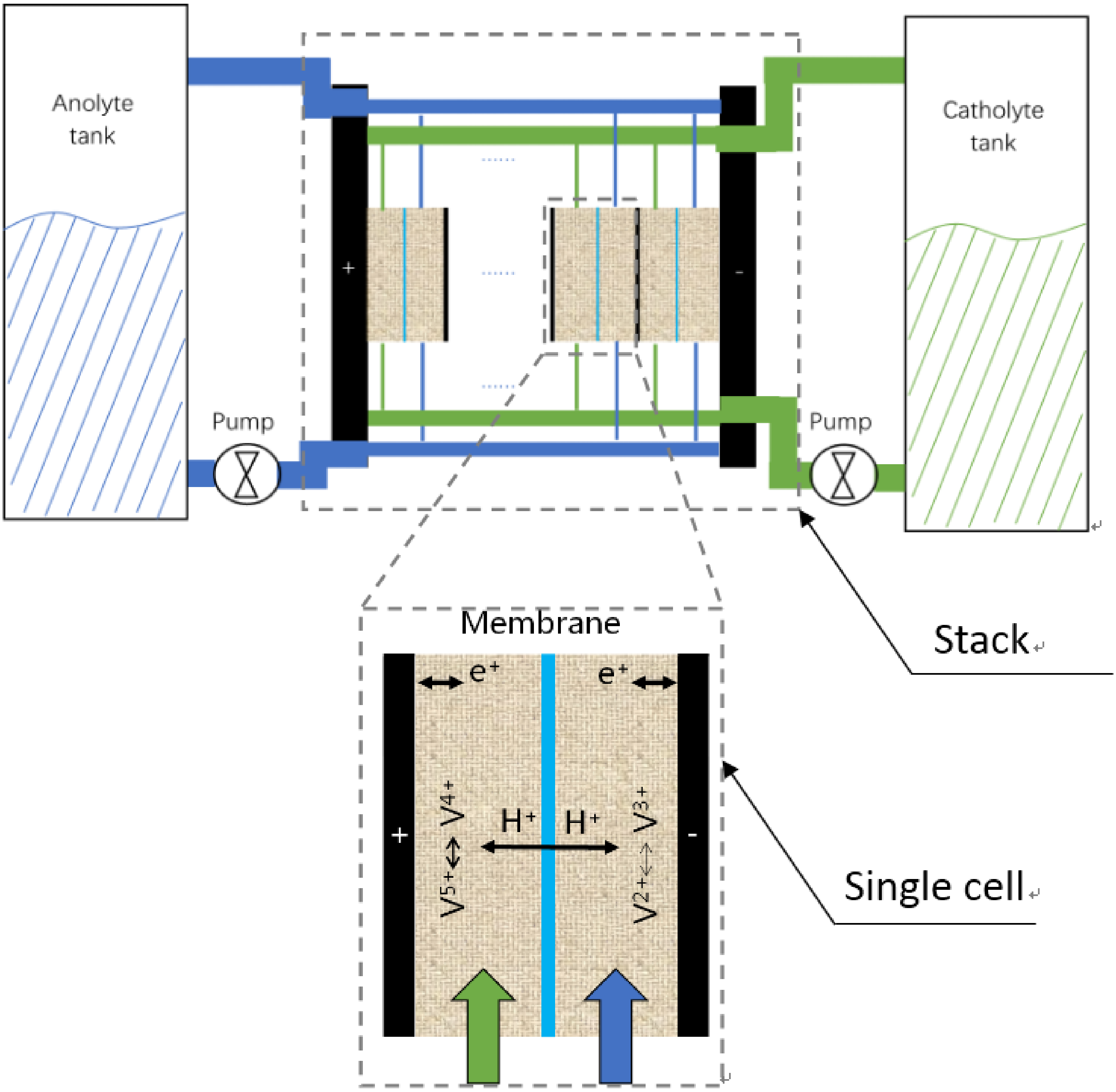


Fig.1. Schematic drawings of vanadium redox flow batter

The bipolar plates separate each single cell and provide electrical current paths to the adjacent cells in a VRFB stack. Therefore, bipolar plates should have high electrical conductivity and low permeability to vanadium sulfuric acid electrolytes [2,3]. At present, there are graphite BPs, metal BPs and composite BPs used in flow battery. Graphite BPs have high electrical conductivity and stable chemical properties, but the BPs are fabricated mainly through machining of thin graphite plates, which are vulnerable to breakage during machining and handling and to leakage due to high porosity[4]. Metal BPs have high electrical conductivity and stable chemical properties, but the BPs require coating process such as gold or titanium nitrate coating to prevent corrosion of metal in the acid environment of electrolyte, which incurs high cost and low productivity[5].Composite BPs have exellent corrosion resistance, high liquid resistance, high strength and low cost, which have greater advantages than graphite and metal BPs. However, the problem of relatively low electrical conductivity should be overcome compared to that of metal or graphite BPs due to its high electrical contact resistance.

In order to reduce the electrical contact resistance of composite BPs. Jun Woo Lim et al. developed a carbon fiber/polyethylene bipolar plate-carbon felt electrode assembly for vanadium redox flow batteries[1]. In their study, a carbon fiber/polyethylene composite BP-CFE (carbon felt electrode) assembly has been developed to decrease the contact resistance between the BP and CFE by embedding the CFE into the PE matrix of the carbon fiber composite BP through local thermoplastic welding process to decrease the electrical contact resistance. The developed BP-CFE assembly achieved 84% of energy efficiency, which is higher than that of the conventional BP of 82%.In Jaeheon Choe's study, a corrugated carbon/epoxy composite bipolar plate for VRFBs was designed to increase the efficiency of the electrolyte flow and decrease the area-specific resistance (ASR) of the BP[5]. In Dongyoung Lee's study, soft release films were inserted between the mold and the composite to prevent the formation of a resin-rich area and to expose carbon fibers on the surface of the bipolar plate. The developed method considerably decreased the ASR of the carbon composite bipolar plate without an expanded graphite coating[6]. Ki Hyun Kim et al. developed a carbon fabric/graphite hybrid composite BP composed of carbon composite with the expanded graphite coating layer for the VRFB to decrease the electrical contact resistance[7]. The energy efficiency of VRFB with the carbon/graphite hybrid composite BP was 86%, which was 6% higher than that of the conventional graphite BP.

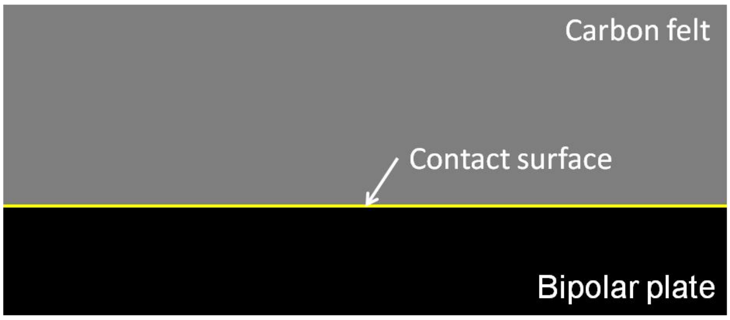
In this study, a pattern bipolar plate has been developed to decrease the electrical contact resistance between the BP and CFE by increasing the BP's specific surface area through pattern-roll-forming. To evaluate the performances of the pattern BP, the specific surface area and the areal specific resistance (ASR) were measured. Also the mechanical properties test was performed to verify the BP strength. Finally, the performances of the pattern BP were measured and compared with those of the conventional bipolar plate during the charge/discharge cycles of a single cell.

2. Experimental

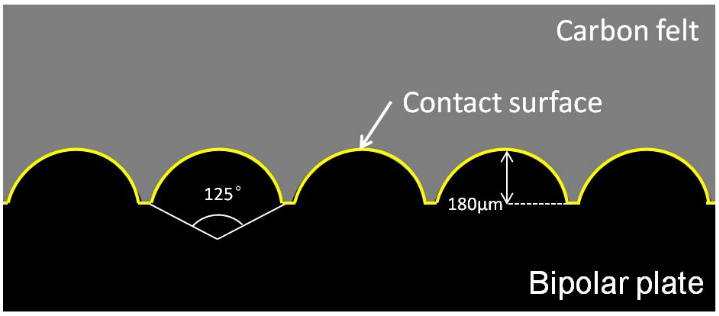
2.1 Design concept of pattern bipolar plate

The main factors affecting the contact resistance between BP and CFE are surface conductivity, contact area and contact pressure. In this paper, the contact resistance is reduced by increasing the contact area between BP and CFE. The conventional structure of BP and CFE is shown in Figure 2.a. The contact surface between the BP and CFE is smooth and the contact area can be easily calculated. In this paper, In order to increase the contact area, the specific surface area of the bipolar plate is increased by hot pressing the spherical crown pattern on the surface of the BP, and the carbon felt is pressed into the pattern by the stack tightening force which is shown in Figure 2.b.

The protrusion of the pattern bipolar plate is designed as a spherical crown with a radius of 330μm and a height of 180μm. The surface area of the spherical crown is 3.73×10^{-3}cm^2 and the corresponding region of the conventional BP is 2.72×10^{-3}cm^2, the growth rate is 37%.



(a)



(b)

Fig.2. Schematic diagrams of contact areas between the CFE and the BP; (a) smooth contact surface between CFE and the conventional BP, (b) pattern contact surface between CFE and the pattern BP.

2.2 Pattern bipolar plate preparation

The process of material mixing system is shown in Fig.3. First, conductive materials, such as carbon black, graphite and polypropylene and composite additives, such as lubricants, dispersants, coupling agents are weighted in a certain proportion. After high-speed mixing, a functional mixture is obtained which is then placed in the extrusion system by transmission band.

The bipolar plate extrusion system is shown in Fig.4. After mixing, the bipolar plate material is transported to the dryer machine through the feeder machine, and then the raw material is extruded into seven heating tubes by screws to be heated. The melted material is extruded through extruded mould. A pattern roller is arranged in front of the extruder head to press pattern on the extruded bipolar plate.

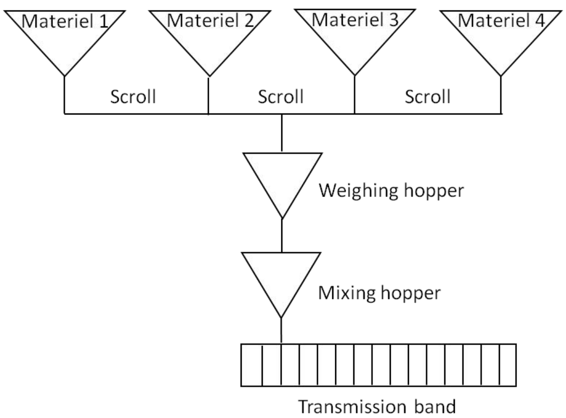


Fig.3. Bipolar plate material mixing system

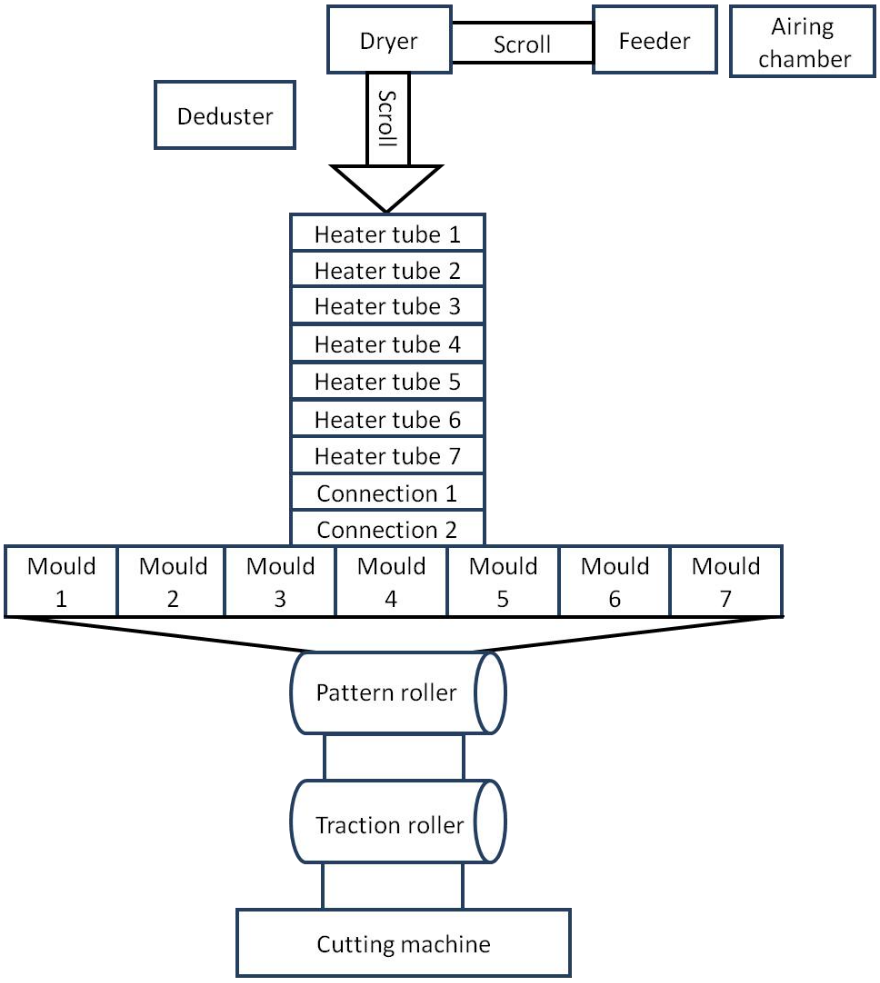


Fig.4. Bipolar plate extrusion system

The main technological parameters of extrusion and rolling are shown in Table 1~2. The heating temperature of the heater tube is 180-190℃ and the temperature of extruded mould is 180-230℃ which is shown in Table 1. The pattern roller is installed in the distance from the extruder head 25 cm -35 cm which has a 120℃ temperature on the surface which is shown in Table 2. The clear pattern is pressed on the bipolar plate by constantly adjusting the gap between the upper and lower rolls.

Table1 The temperature of heater tubes and extruded moulds.

Machine	Section	Temperature (℃)
Heater tube	1	180
Heater tube	2	180
Heater tube	3	187
Heater tube	4	187
Heater tube	5	187
Heater tube	6	187
Heater tube	7	187
Extruded mould	1	225
Extruded mould	2	225
Extruded mould	3	180
Extruded mould	4	180
Extruded mould	5	180
Extruded mould	6	225
Extruded mould	7	225

Table 2 The main technological parameters of extrusion and rolling.

Distance between extruded mould and pattern roller(cm)	Extrusion rate (m/s)	Roller temperature (℃)
25-35	0.08	120

2.3 Apparent test

The spherical bulges on the surface of bipolar plate are clearly visible which is shown in Fig.5 and the bulges distribution is uniform which has no fragmentary or shedding. There are no apparent problems such as cracks, chromatic aberration, or ripple of the bipolar plate. It shows that the rolling process is stable, and the pattern can be successfully pressed on the bipolar plate.

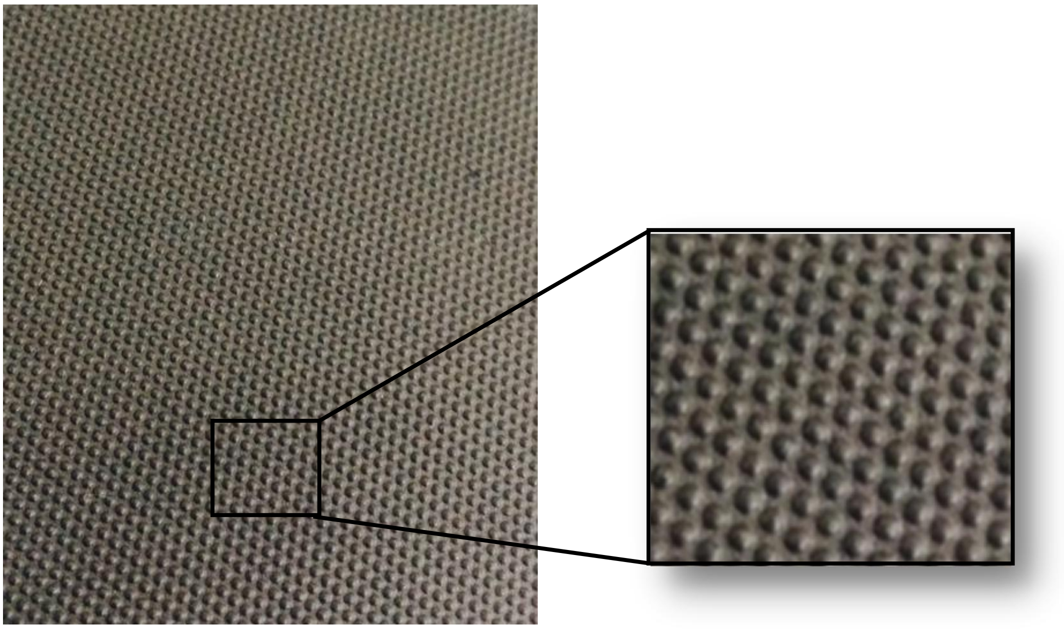


Fig.5. The pattern bipolar plate

Before doing the inspection of the tread plate, prepare the sample plate as shown in Fig.6. The sample is placed on the carrier platform which is vertical to the stage, and one side can be supported by a conductive support block. The sample and support block are fixed on the carrier platform with conductive tape.

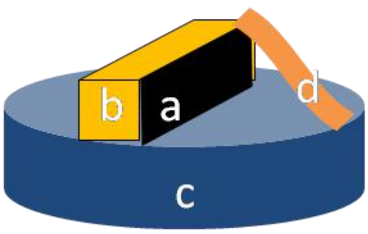


Fig.6. Sample preparation(a: Test sample,b: Conductive support block,c: carrier platform,d: Conductive tape)

Then put the prepared sample into the SEM machine for observation at the condition shown in Table 3.

Table 3 SEM condition.

Vacuum degree (pa)	Acceleration voltage (kV)
4.8×10^{-5}	5

2.4 Measurement of electrical properties

The areal specific resistance(ASR) of the pattern plate under different electrode compression ratio was measured, using the experimental setup shown in Fig.7. The size of the pattern bipolar plate specimens was Φ50mm×10mm. The pattern BP specimen was placed between the CFEs and they were inserted between the two gold-coated copper electrodes that were connected to a power supply and a multi meter. The ASR was calculated with the measured voltages under the electrode compression ratio of 20%,35%,50%. The environmental temperature was controlled to be 25℃ under atmospheric pressure to prevent the thermal effect on the electrical resistance of the carbon fiber. The total resistance R(total) of the BP and the system resistance R(system) are defined by Eqs. (1) and (2), respectively. Then the areal specific resistance ASR(bipolar plate) of the BP defined by Eq. (3), is calculated by subtracting the system resistance from the total resistance as follows.

$$R_{(total)} = 2R_{Au(Cu)-CFE} + 2R_{CFE} + 2R_{CFE-BP} + R_{BP} \quad (1)$$

$$R_{(system)} = 2R_{Au(Cu)-CFE} + 2R_{CFE} \quad (2)$$

$$ASR_{(bipolar\ plate)} = 2R_{CFE-BP} + R_{BP} \quad (3)$$

where

$R_{(total)}$: Total resistance of the pattern bipolar plate

$R_{(system)}$: System resistance of the measurement setup

$ASR_{(bipolar\ plate)}$: Areal specific resistance of the pattern bipolar plate

$R_{Au(Cu)-CFE}$: Interfacial contact resistance between the electrode and the carbon felt

R_{CFE}: Bulk resistance of the carbon felt

R_{CFE-BP}: Interfacial contact resistance between the carbon felt and the bipolar plate

R_{BP}: Bulk resistance of the pattern bipolar plate

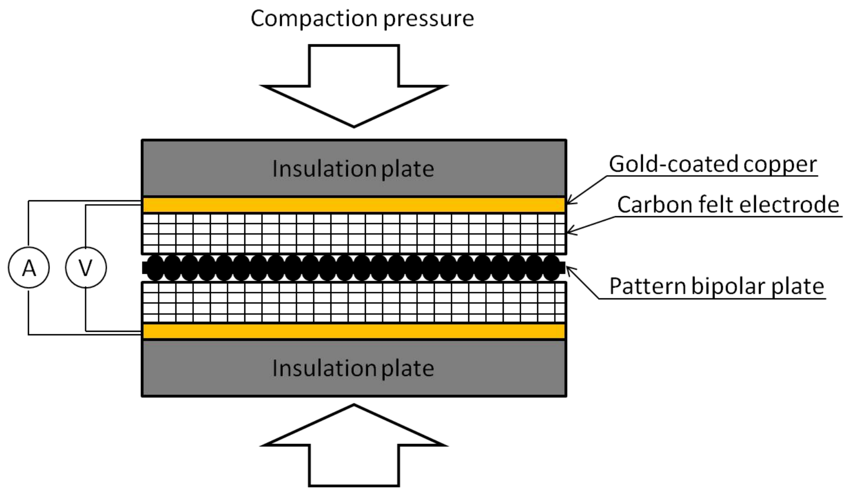


Fig.7. Experimental steup for areal specific resistance measurement

2.5 Mechanical strength measurements

The pattern plate was cut to 100mm×10mm rectangular spline to test the bending strength according to Fig. 8, and compared with the conventional bipolar plate. The strength of the bipolar plate is calculated by Eqs. (4).

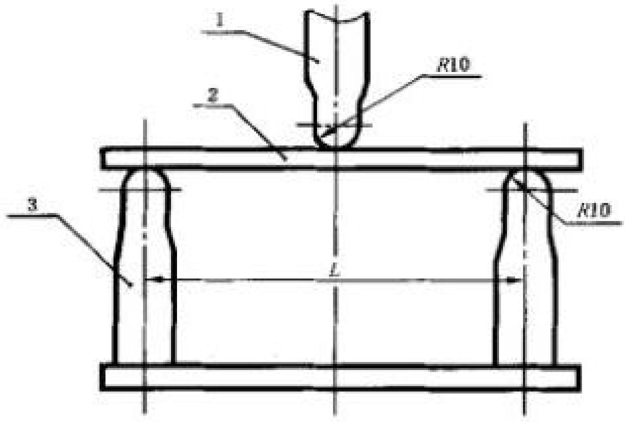


Fig.8. Material testing machine

(1. pressure head, 2. sample, 3. support)

$$\sigma = \frac{3P \times L}{2b \times \delta^2} \tag{4}$$

where

σ: Bending strength/MPa

P: Fracture load/N

L: Distance between two feet of the support/mm

b: The width of the sample/mm

δ: The thickness of the sample/mm

2.6 Charge/discharge test

To investigate the performance of the pattern bipolar plate, charge/discharge tests were performed using a single cell test equipment. Ion exchange membrane is Nafion212. The surface area of the electrode is 48cm^2 and the compression ratio should be controlled to 20% after assembly. The single cell test conditions are as follows. The temperature of constant temperature water bath pot is set at 37℃ that would keep the battery temperature between 35℃ to 39℃. The electrolyte is 80ml sulfuric acid solution of vanadium which has a vanadium concentration at about 1.65-1.66mol/L and flow rate is 70 ml / min. Charge and discharge at constant current density 80mA/cm^2.

3. Results and discussion

3.1 Apparent test

As shown in Fig.9. the apparent appearance of the pattern can be clearly observed and the height of patterns can be measured. Seven points are randomly selected to be measured which is shown in Fig.10. The height of the seven points is 150 to 200 μm. Considering the measurement error, the height is relatively uniform and the average is 180 μm which is shown in Table 4. The radius of the projections can be calculated to be 330.9 μm. According to Eq. (1), the surface area of the projections (sphere cap) can be calculated to 0.003743cm^2.

$$S = 2\pi rh \tag{5}$$

The surface area of the pattern plate is 8.77 cm^2 larger than the conventional 48 cm^2 bipolar plate. In an ideal state, the area of the electrode area is 8.77 cm2 larger than the conventional plate which is shown in Table 5.

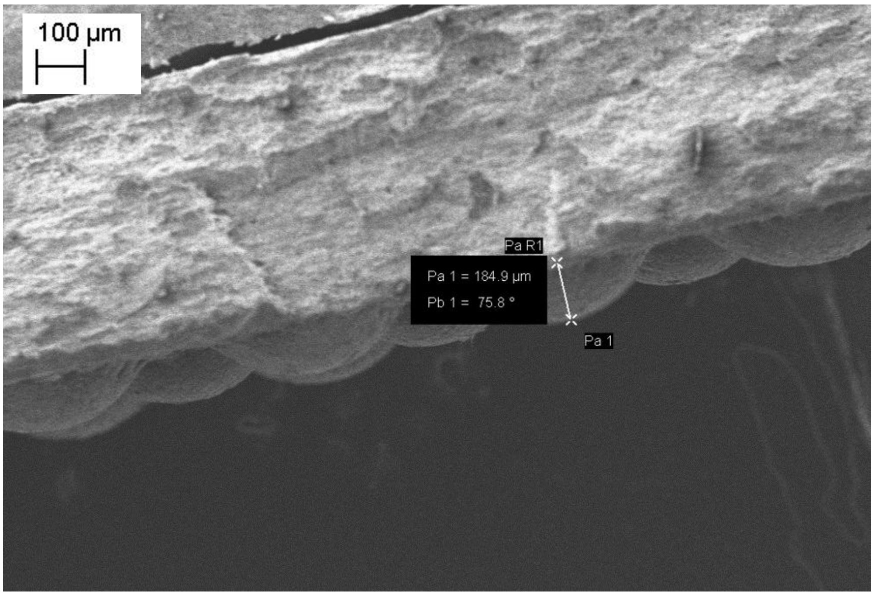


Fig.9. Electron microscope images of patterns

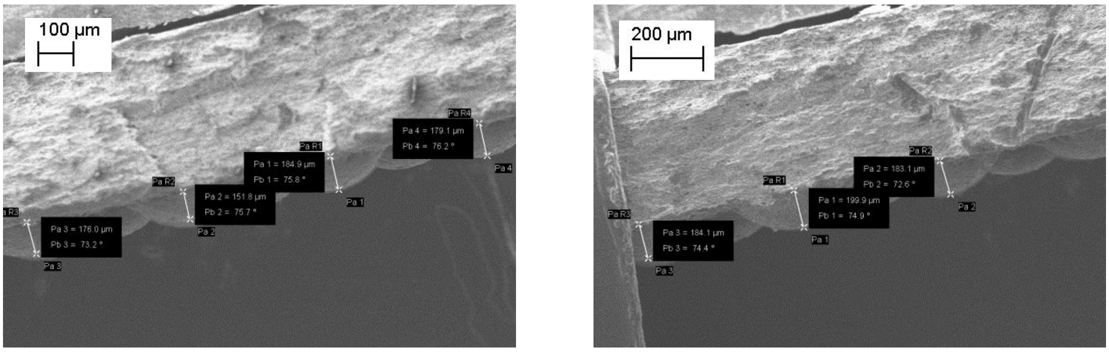


Fig.10. Measure the height of patterns

Table 4 The height of seven patterns.

Raised number	height(μm)
1	184.9
2	151.8
3	176
4	179.1
5	199.9
6	183.1
7	184.1
Average	179.8

Table 5 Pattern plate surface area of 48 cm^2 single cell.

Bipolar plate	Single projection surface area(cm^2)	Projection number in electrode area	Projection surface area(cm^2)	Total surface area（cm^2）	Increase surface area(cm^2)	Increase rate
Pattern plate	3.74×10^{-3}	8625	32.3	56.8	8.8	18.3%
Conventional plate	2.72×10^{-3}	0	23.5	48	-	-

3.2 Measurement of electrical properties

As shown in Fig.11, the ASRs of pattern bipolar plate in different electrode compression ratio were lower than those of conventional bipolar plate. ASR of two different bipolar plate both reduced in different degrees with the increase of electrode compression ratio. The ASR of conventional bipolar plate and pattern bipolar plate is 1309 $m\Omega\cdot cm^2$ and 946 $m\Omega\cdot cm^2$,and the pattern plate is 27% lower than the conventional plate. When the compression ratio increased to 50%, the ASR of two bipolar plates decreased to 444 $m\Omega\cdot cm^2$ and 371 $m\Omega\cdot cm^2$, and the pattern plate was 16% lower than the conventional plate. It can be seen that with the increase of the compression ratio, the ASR of the two kinds of plates is constantly approaching, because the reduction effect of the contact resistance between the bipolar plate and electrode caused by the increase of the specific surface area of the bipolar plate is not obvious when the compression ratio is continuously increased.

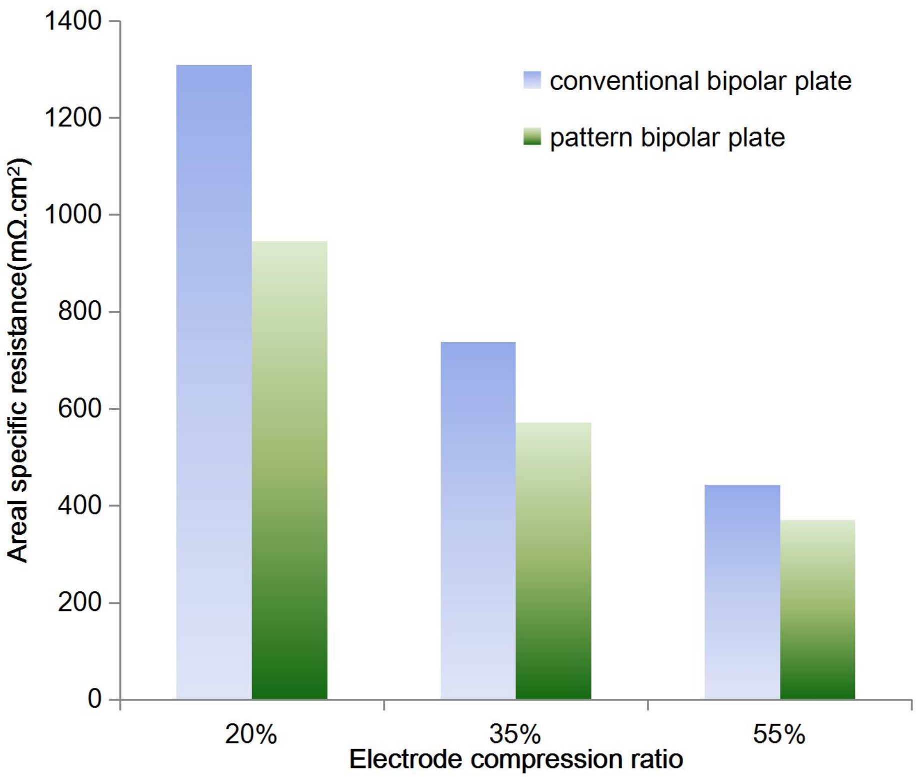


Fig.11. ASRs of conventional/pattern bipolar plate under different electrode compression ratio

3.3 Mechanical strength measurements

The bending strength of the pattern bipolar plate is 41.5MPa, which is 8% lower than that of the conventional bipolar plate 45.3MPa, as shown in Table 6. This is because the bend-resist ability of the gaps among patterns on the surface of the pattern bipolar plate is weak where fracture occurs during the strength test.

Table 6 Bending strength measurements.

Pattern BP (MPa)	Conventional BP (MPa)
41.5	45.3

3.4 Charge/discharge test

From the single cell charge/discharge test, the pattern bipolar plate achieved 79.4% of energy efficiency, which is higher than that of the conventional bipolar plate of 78.5% as shown in Fig. 12. This is because the ohmic loss was reduced by the lower cell resistance due to the reduced total resistance compared to that of the conventional bipolar plate. Also, it was found that there was no degradation on the pattern bipolar plate after 500 cycles of the test. Therefore, the pattern bipolar plate is suitable for the VRFBs application, and it can replace the conventional bipolar plate.

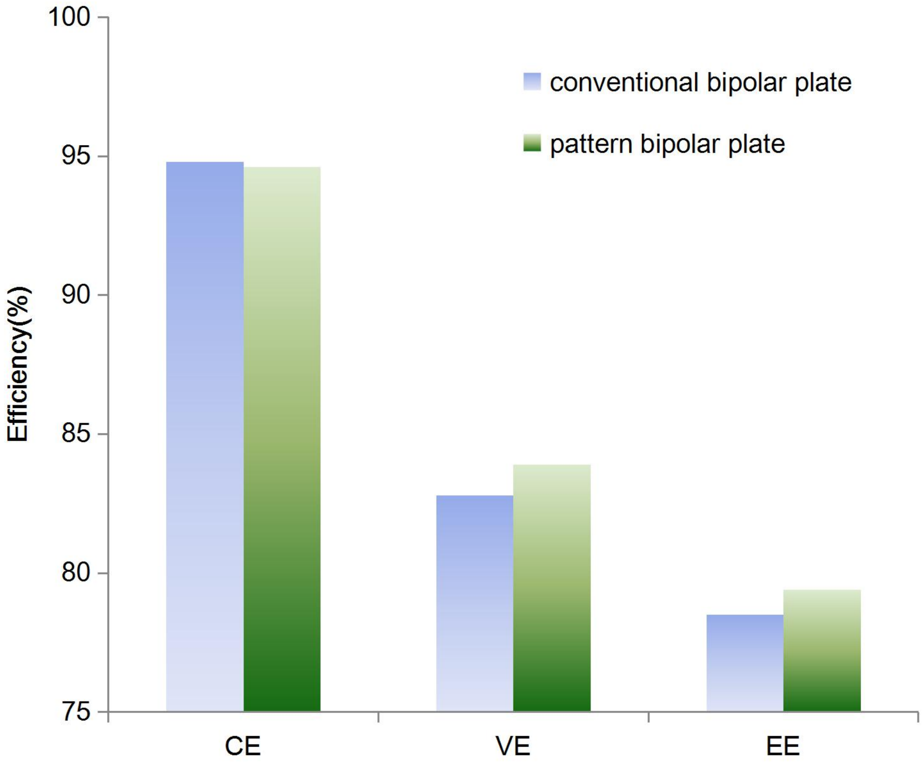


Fig.12. Charge/discharge efficiencies of the pattern bipolar plate and the conventional bipolar plate

4. Conclusion

In this work, pattern bipolar plate was rolled to decrease the areal specific resistance (ASR) of vanadium redox flow battery (VRFB). The apparent, mechanical strength and the electrical resistance were measured. Also, the single cell charge/discharge tests were conducted for performance assessment.

For single cell size, The surface area of the pattern plate is 8.77 cm^2 larger than the conventional 48 cm^2 bipolar plate. The areal specific resistance (ASR) of conventional BP and pattern BP is 1309 $m\Omega\cdot cm^2$ and 946 $m\Omega\cdot cm^2$ at 20% electrode compression ratio, the pattern plate is 27% lower than the conventional plate. Experimental results showed that pattern bipolar plate with 55% compression ratio showed the lowest areal specific resistance (ASR). The bending strength of the pattern bipolar plate is 41.5MPa, which is 8% lower than that of the conventional bipolar plate 45.3MPa.

From the single cell charge/discharge test, the developed pattern bipolar plate achieved 79.4% of energy efficiency, which is higher than that of the conventional BP of 78.5%. Furthermore, there was no degradation in the developed BP-CFE assembly after 500 cycles of the test.

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