

A pluggable current collector for in-operando current measurements in all-vanadium redox flow batteries with flow field

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Abstract: Understanding current distribution in operating Vanadium redox flow batteries (VRFBs) is vital for improving battery design and performance as the non-uniform current density distribution is known as a major cause of the corrosion and side reactions in VRFBs. However, the existing method for current density measurement in the VRFB with flow field is complex and the rib conductive structure of graphite plate is changed which reduces the measurement accuracy and reliability. In this study, we propose a novel pluggable current collector for in-operando current distribution measurements which greatly simplifies the current density distribution measurement process in VRFBs with flow field. The new method relies on eight pluggable graphite units in a flow plate frame to replicate the actual serpentine flow field structure, thereby providing higher measurement reliability compared to the existing methods which are mostly invasive. Using the new method, current density distributions at different electrode compression ratios (*CR*) and inflow electrolyte rates are investigated. It is found that insufficient supplemental reactant in electrode border region is the main reason for the uneven current density distribution and the current density non-uniformity is intensified in the initial and final stages of cycling process. Increasing *CR* can improve the current density in the electrode core region. The overall current density uniformity in a VRFB with serpentine flow field can be enhanced by increasing the inflow electrolyte rate. The developed method is believed to facilitate the understanding of the coupled local reactions and transport processes and guide on the future design of VRFBs.

Keywords: Vanadium redox flow battery; Current distribution; In-operando measurements; Pluggable current collector; Serpentine flow field

1. Introduction

Redox flow batteries (RFBs) exhibit certain unique characteristics, such as low cost, flexible energy design, and long cycle life [1-4]. As such, the RFB therefore becomes a prospective energy storage technology for distributed power generation systems and for stabilizing local grid electricity supplies [5-7]. The RFB is an electrochemical system that stores energy in the circulating electrolyte. A typical single RFB cell consists of a positive electrode, a negative electrode, a proton exchange membrane, two graphite plates, and some fixture components. The membrane allows the diffusion of proton to maintain electroneutrality and preclude the two electrolyte solutions from cross-mixing. The positive and negative electrolytes are continuously pumped from external tanks to the cell, respectively. During the charge and discharge processes, electrochemical reactions occur on the electrode surface [8]. Preparation of RFB electrolytes could use either inorganic [9, 10] or organic active materials [11-14]. Among them, all-vanadium RFBs (VRFBs) are the most developed and widely used RFB system to date owing to its unique advantage in alleviating crossover since only one type of active element (vanadium) is used in this cell [15, 16]. In a typical VRFB, $\text{VO}^{2+}/\text{VO}_2^+$ and $\text{V}^{2+}/\text{V}^{3+}$ are separated as catholyte active species and anolyte species, respectively.

The uniformity of the current density distribution is mainly affected by the battery structure [17], electrode material [18, 19], and operating conditions [20]. The uneven current density distribution inside the electrode may cause excessive local overpotential and corrosion of electrode and graphite plate [21]. Such corrosion leads to carbon loss and resistance increment, resulting in lower energy efficiency and even battery failure [22, 23]. The graphite felt easily corrodes, and the carbon atoms of the electrode are oxidized to CO or CO_2 when the local voltage exceeds 1.7 V because the uneven reaction in the electrode. In the study of Xu

1 et al. [24, 25], the uniformity of species concentration distribution in VRFBs with and without the flow field
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3 was discussed. The study results showed that changing the flow field structure could improve electrolyte
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5 transportation. They also indicated that improving the uniformity of electrolyte distribution inside the battery
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7 can avoid local electrode corrosion and improve the VRFB service life. The measurement of current density
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9 distribution is the basis of the specie uniformity improvement and battery design optimization; accordingly,
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11 such measurement is necessary.
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17 Many online measurement devices for distributed data distributions have been designed to reveal the
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19 distribution characteristics that combine species transportation and electrochemical reactions in a half cell as
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21 a proof-of-principle study. The experimental results of current density distribution show that the distribution
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23 of current density is not uniform even in a laboratory test cell (with an active reaction area of $3 \times 3 \text{ cm}^2$ [26,
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25 27] or $10 \times 10 \text{ cm}^2$ [28-30]). The current density distribution measurement mainly includes indirect and direct
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27 methods. In the indirect method, the potential distribution in the electrode is first measured by using micro
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29 carbon fiber electrodes [28], segmented graphite plates [29, 30], or tiny platinum electrodes (dia. 100 μm)
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31 [31, 32]. Thereafter, the concentrations of active charged species, state of charge, or current distribution can
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33 be calculated according to an empirical formula. The accuracy of the calculated current density distribution
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35 is limited because the precision of the empirical formula cannot be absolutely guaranteed. Becker et al. [28]
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37 employed the indirect method to measure the local potential distribution inside the VRFB without the flow
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39 field by arranging eight micro carbon fiber electrodes (40 μm thick and 5 mm wide with lamination foil) on
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41 the interface of the positive carbon felt and membrane. Localized felt resistances were thereafter used as
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43 internal shunt resistances to calculate the current density distribution. They found that the current density
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45 exhibited a gradient along the main flow direction. However, in this work, the eight inserted carbon fiber
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47 electrodes blocked part of the membrane, thereby affecting the across transportation of protons during the
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VRFB operation. Moreover, the current density distribution immediately responds to operating conditions, making it difficult to track the current density signal using the empirical formula.

In the direct method, the current density is measured using the segmented graphite plate, and the current density of each block is recorded. The manufacture methods of segmented graphite plate for VRFBs with and without the flow field are differ. Using the direct method in the VRFB without the flow field, Hsieh et al. [33] investigated the effect of the electrolyte flow rate on the current density distribution in the VRFB with two types of collectors: segmented copper current collector and combined segmented graphite plate blocks with current collectors. The results showed that the current density near the outlet significantly decreased when the discharge capacity approached zero. They also pointed out that the accuracy of the measurement result cannot be ensured because the collector segmentation alone cannot guarantee that the contact resistance between each copper current collector and the graphite plate is the same. Gerber et al. [34] adopted a printed circuit board (PCB) with a segmented current collector in a 40 cm² VRFB without flow field to analyze the locally resolved current density distribution of the graphite felt electrode. Their results showed that the local current density in VRFB mainly depends on the transport of the electrolyte solution and the electrolyte flow in the porous electrode can be visualized. For the VRFB with the flow field, the segmentation procedure of the graphite plate with flow field is relatively complex, exigent, and difficult. The fabrication process is as follows: first, the partition grooves on the top surface of the graphite plate are milled then filled with low-viscosity epoxy resin; second, the backside (i.e., the region with no partition grooves) is milled out to electrically isolate several segments; finally, the channels on the top face of the plate are milled [35]. Clement et al. [26, 27] adopted the foregoing segmentation method and measured the current density distribution in a VRFB with the flow field. The experimental results showed that as the flow rate increased, the current distribution became more even. However, the rib area reduced because of the introduction of

1 partition grooves, thereby affecting the electron conduction inside the battery. This means that apart from the
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3 complex process of creating segmentation on the graphite plate with the flow field, the rib area on the graphite
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5 plate is inevitably reduced. Another important issue is the influence of electrode compression. The
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7 compressible carbon fiber is the most commonly used electrode material for VRFB. In the VRFB with flow
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9 field, the carbon fiber electrode will intrude into the flow channel because of the compression which has an
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11 important effect on electrolyte flow characteristics and current density distribution [36, 37]. However, few
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13 studies consider the electrode compression when measuring the current density distribution.
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20 To sum up, the direct method for on-line current density measurement is necessary, especially for the
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22 VRFB with flow field. However, the existing research on direct method for the VRFB with flow field has
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24 many defects: 1) the reported segmentation procedure of the graphite plate with flow field is complex; 2) the
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26 rib area is reduced and the conductive structure is changed; 3) the effect of electrode compression is ignored.
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28 Accordingly, it is necessary to design an innovative and high accurate current density measurement device
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30 for VRFB with the flow field without introducing any factor that would have a negative influence. In addition,
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32 the influence of electrode compression on current density should be investigated.
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39 In this study, to avoid the influence of battery structure change on the species transport inside the battery
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41 during measurement, a simple and innovative in-operando measuring device for the internal current density
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43 distribution of the VRFB with the flow field is developed. The designed current measurement device is a
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45 pluggable structure in which the graphite plate is inserted into the flow frame. By separating the channel part
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47 from the rib part, the pluggable current collector device can completely retain the structure and function of
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49 these components. The pluggable current collector with flow field can measure the local current density
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51 distribution. Based on the in-operando measurement device without changing the flow field structure, the
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53 direct current density measurement is highly reliable, low cost, and highly promotable. The influences of
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electrode compression and electrolyte inflow rate on the current distributions are also investigated in this study.

2. Experimental

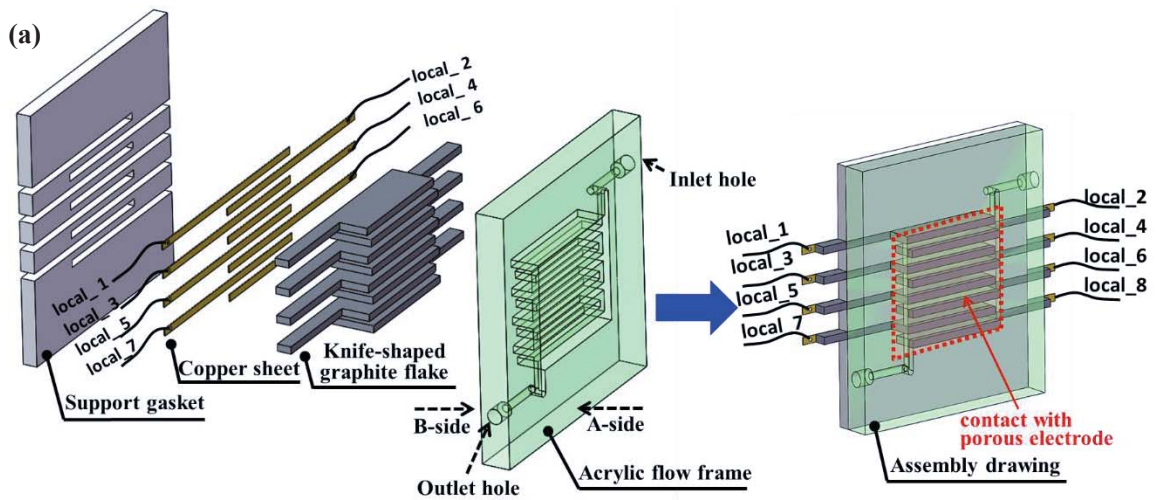
2.1. Pluggable current collector

The pluggable current collector with flow field is designed for measuring the current density distribution in a VRFB with a serpentine flow field. It mainly consists of knife-shaped graphite flakes and a flow frame with channel grooves. In this collector, in order to ensure the flow channel function and the collection of electrons, the structure and active area of the flow field are completely reserved. Figure 1(a) shows the schematic diagram of the pluggable current collector with serpentine flow field. The device includes an acrylic flow frame, several knife-shaped graphite flakes, copper sheets, and an insulating sealing gasket (support gasket). As shown in Fig. 1 (b), a serpentine flow channel is milled with seven U-type grooves ($36 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$) on the A-side of the acrylic flow frame ($70 \text{ mm} \times 70 \text{ mm} \times 8 \text{ mm}$). The channel grooves connect the inlet and outlet holes on the two broadsides of the acrylic flow frame. Eight straight cavities ($36 \text{ mm} \times 2 \text{ mm} \times 8 \text{ mm}$) are cut adjacent to the channel grooves for inserting the knife-shaped graphite flakes. As shown in Fig. 1 (c), the blade regions ($36 \text{ mm} \times 2 \text{ mm} \times 8 \text{ mm}$) of the knife-shaped graphite flake has the same size with the straight cavity. The blade region of the knife-shaped graphite flakes is inserted into the straight cavities of the acrylic flow frame from the B-side. The ribs of the serpentine flow field are thereafter formed on the A-side surface of the acrylic flow frame. The VRFB is thus electrically divided into eight local areas, and the ribs (graphite flake collector) are insulated from each other (as shown in Fig. 1(d)). The gap between the inserted knife-shaped graphite flake and straight cavity is plugged with sealant. The main function of the hilt region ($60 \text{ mm} \times 2 \text{ mm} \times 3 \text{ mm}$) is to fix the position of the knife-shaped graphite flake and increase the contact area with the copper sheet ($65 \text{ mm} \times 2 \text{ mm} \times 1.5 \text{ mm}$). Each

end of the copper sheet is connected to the external circuit for individual current measurements. The support gasket (70 mm × 70 mm × 4 mm) not only sets and fixes the hilt of the knife-shaped graphite and the copper sheet but also provides sealing and insulation.

In the assembly, the flow field region (active area, 40 mm × 30 mm) of the acrylic flow frame is in contacts with the porous electrode. The local current of the porous electrode is collected by the graphite flake in contact. Moreover, the porous electrode is compressed to some extent to guarantee the good conductivity. To minimize measurement errors, it is important to ensure the uniform contact between the porous electrode and the pluggable current collector. The knife-shaped graphite flakes are marked as local_1–local_8 from the inlet to the outlet. Local_1, local_3, local_5, and local_7 are on the left; local_2, local_4, local_6, and local_8 are on the right. As shown in Fig. 1(d), the eight locations (local_1–local_8) are distributed in three typical regions: upper border region (local_1), core region (local_2–local_7), and bottom border region (local_8). The current density (i_{loc}) of the local porous electrode is the ratio of the measured current (i_t) to the area of the knife-shaped graphite flake (S),

$$i_{loc} = i_t / S \quad (1).$$



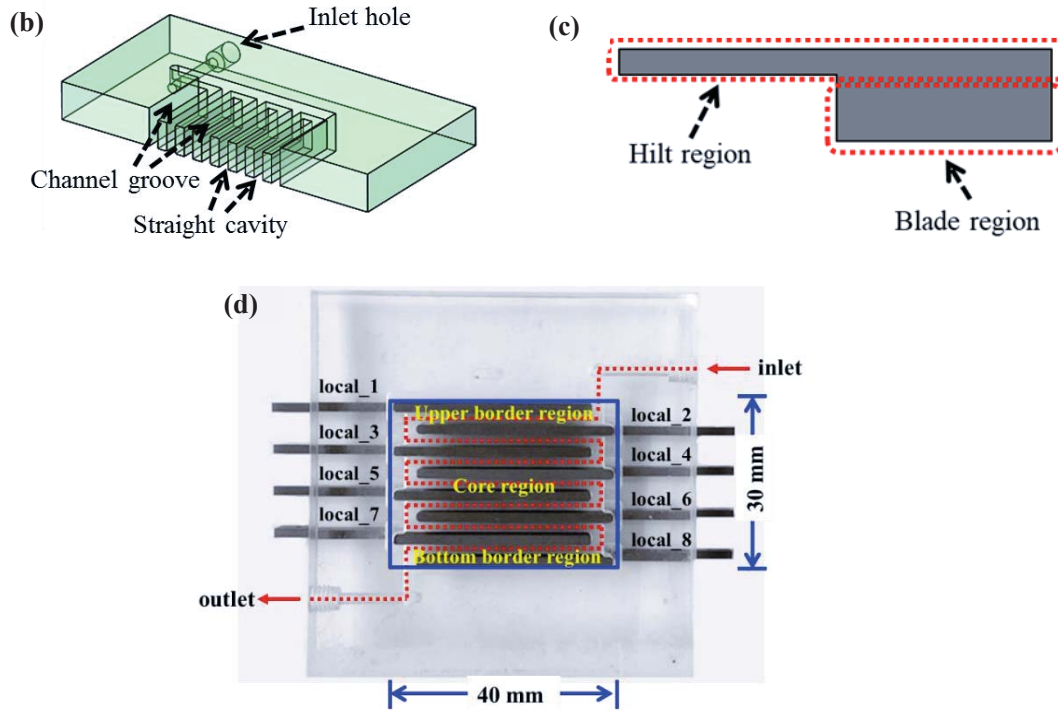


Fig. 1 Schematic of the pluggable current collector with serpentine flow field. (a) Composite and structure of pluggable current collector with serpentine flow field; (b) structure of the acrylic flow frame with channel grooves; (c) structure of knife-shaped graphite flake; (d) photograph of knife-shaped graphite sheets assembled into the acrylic frame.

2.2. Current distribution measurement

Figure 2 (a) shows the structure diagram of a single VRFB with a pluggable current collector for current density distribution measurement. In this work, the designed pluggable current collector is used on the positive side of the VRFB as a proof-of-principle study. A Nafion® 117 membrane separates the positive and negative electrodes, and Viton gaskets are used in the positive and negative electrodes. For preparing the membrane used in the VRFB, the membrane is soaked in a 2% H_2O_2 for 1 h at 80 °C and then rinsed with pure water for five times. The membrane is thereafter soaked in a 0.5-M H_2SO_4 for 1 hour at 80 °C and then rinsed with pure water for five times. After the pretreatments, the membrane is finally soaked in pure water. A 40-mm long and 30-mm wide graphite felt (SIGRATHERM® GFA5) with an original thickness of 6 ± 0.5 mm is used as the electrode. The GFA 5 felt, which can be easily compressed to different thicknesses with normal gaskets, is commonly used as the electrode material in VRFB studies [38, 39]. The felt was used

without any pretreatment. Both the positive and negative electrolytes are circulated by peristaltic pumps (Baoding Shenchen Precision Pump Co. Ltd., BT600N). Viton fittings (Masterflex® tube, FDA Viton 96412-14) are employed to connect the electrolyte reservoirs to the compartments with a 20-mL volume at each reservoir. The positive electrolyte contains $1.5\text{-mol}\cdot\text{L}^{-1}$ VO^{2+} and VO_2^+ ions in $3\text{ mol}\cdot\text{L}^{-1}$ sulfuric acid, whereas the negative electrolyte contains $1.5\text{-mol}\cdot\text{L}^{-1}$ V^{2+} and V^{3+} ions in $3\text{ mol}\cdot\text{L}^{-1}$ sulfuric acid. After assembling the device, the serpentine flow field on the positive side is identical to that on the negative side.

Figure 2 (b) shows the schematic diagram of the experimental system. On the positive side, each branch circuit of the copper sheet is connected to a bus line through a Hall current sensor (LTSR 6-NP, LEM Inc., Switzerland) for current measurement. A Princeton PARSTAT 4000 electrochemical workstation (Princeton Applied Research® Instrument) is utilized to test the charge/discharge performance of the VRFB. The cell voltage is controlled between 0.9 V and 1.6 V. The working electrode of the electrochemical workstation is connected to the bus line of the eight copper sheets on the positive side, and the counter electrode is connected to the negative copper plate of the battery to form a complete charging–discharging circuit. The eight Hall current sensors are mounted on the PCB, and the power supply module is used to provide a 5-V working voltage for the Hall current sensors. The signals, including the eight output signals of the Hall current sensors in the positive side of the VRFB and the temperature signal measured in the temperature chamber, are recorded by the Agilent data acquisition 34970A. The peristaltic pump draws out the electrolyte from the battery, and in order to reduce the influence of the friction heat it generates, the pump is applied to the outlet pipe of the VRFB. Figure 2(c) shows the experimental system, which mainly includes the test battery, electrochemical workstation, Hall current sensors, data acquisition instrument, and environment chamber. The electrolyte tanks and peristaltic pumps are placed in the temperature chamber to avoid the influence of ambient temperature variation. The measuring instruments are placed outside the temperature chamber.

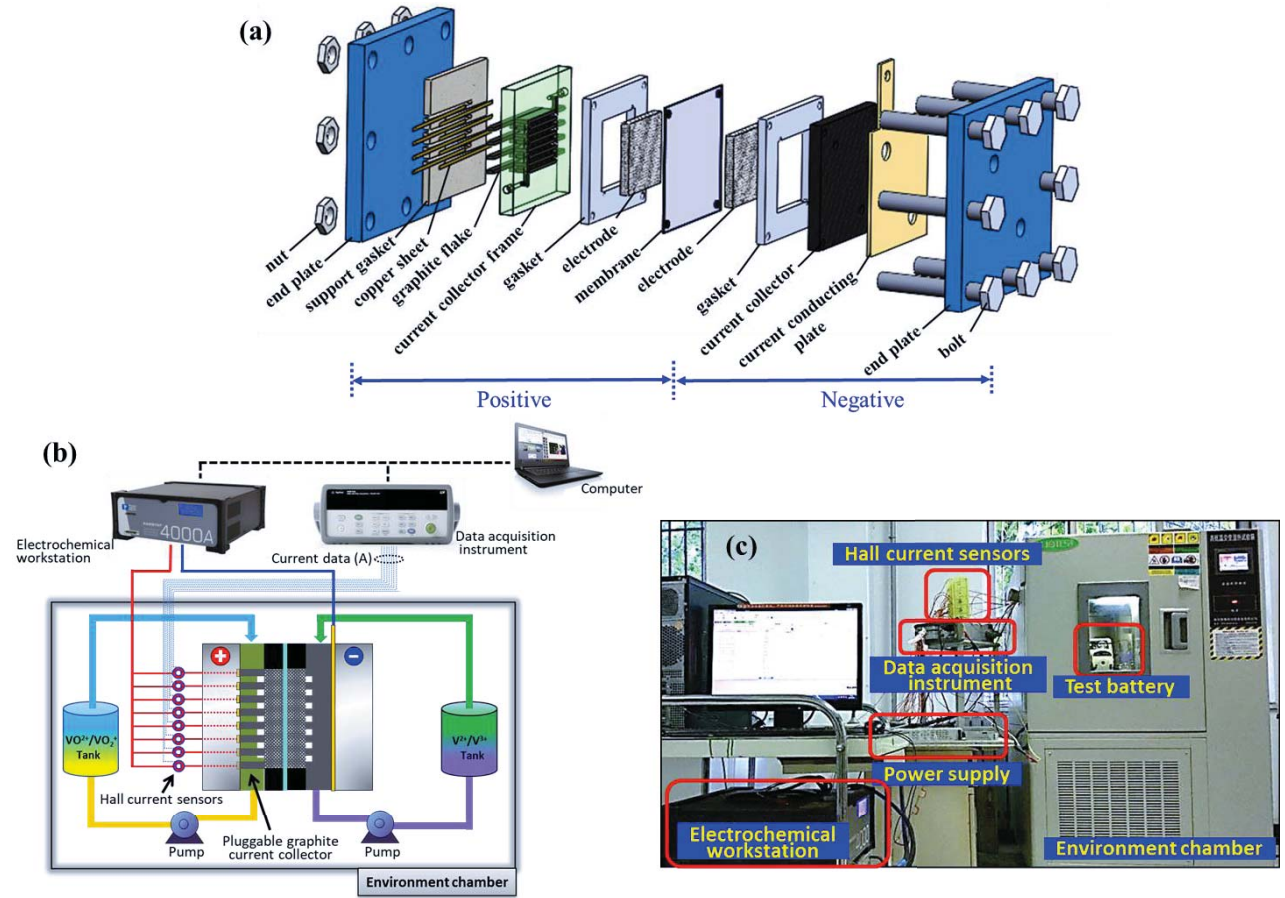


Fig. 2 Experimental system for measurement of current density distribution in a VRFB with serpentine flow field. (a) Structure for current density distribution measurement in a single VRFB; (b) diagram of the experimental system; (c) the experimental system.

In the test, the electrode compression ratio (CR) is controlled by the gasket thickness. Here, the gaskets with thicknesses of 5.15, 3.49, and 2.66 mm are used, and the corresponding CR s of the assembled electrodes are 14.2%, 41.8%, and 55.7%, respectively. The electrolyte inflow rate (Q_{in}) is set in the range from 10–40 $\text{mL} \cdot \text{min}^{-1}$. The charge and discharge current densities are both $20 \text{ mA} \cdot \text{cm}^{-2}$ and the temperature inside the chamber (T_{air}) is set to 25°C .

To evaluate the performance of the VRFB with the flow field at different electrode compressions and inflow flow rates, the coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE), which can be derived from the charge/discharge behaviors, are applied. The coulombic efficiency of a battery is defined as the ratio of the quantity of charges extracted from the battery during discharging ($\int i_{dischar}(t)dt$) to the quantity of charges entering the battery during charging ($\int i_{char}(t)dt$). The voltage efficiency is defined

as the ratio of discharge voltage to charge voltage. In order to simplify the data processing, the middle point values of discharge ($E_{char,middle}$) and charge voltages ($E_{dischar,middle}$) are used to calculate the voltage efficiency [40, 41]. The energy efficiency is calculated by using CE and VE . The computational equations are as follows.

$$CE = \frac{\int i_{dischar}(t)dt}{\int i_{char}(t)dt} \times 100\% \quad (2)$$

$$VE = \frac{E_{dischar,middle}}{E_{char,middle}} \times 100\% \quad (3)$$

$$EE = CE \times VE \quad (4).$$

The state of charge (SOC) can be deduced based on the measured open-circuit cell voltage (E_{oc}) [42, 43]:

$$E_{oc} = E_{oc,0} + \frac{RT}{nF} \ln \left(\frac{SOC}{1-SOC} \right)^2 \quad (5)$$

where $E_{oc,0}$ is the open-circuit cell voltage at $SOC=0.5$ and is equal to 1.4 V according to Haddadi-As [44].

The uniformity of electrode current density distribution (U) can be defined as

$$U = 1 - \frac{1}{I_{ave}} \sqrt{\frac{1}{8} \sum_{i=1}^8 (I_i - I_{ave})^2} \quad (6)$$

where I_i is the local current density; I_{ave} is the average of the local current densities measured on the eight graphite sheets.

3. Results and discussion

3.1 Current density distributions at different electrode compression ratios

In order to investigate the influence of electrode compression on battery performance, the charge/discharge curves and the corresponding VE , CE , and EE of the VRFB are obtained with $CR=14.2\%$, $CR=41.8\%$, and $CR=55.7\%$ at $Q_{in}=20 \text{ mL} \cdot \text{min}^{-1}$. Figure 3(a and b) shows the charge/discharge curves and the corresponding VE , CE , and EE values at the three CR values. The charge and discharge times increase as the electrode CR

increases. According to our previous work [36] and the work of Park et al. [40], the electrode resistance decreases as *CR* increases, which is mainly attributed to the decreasing of the contact resistance between the porous carbon fiber electrode and the graphite plate. Therefore, a higher *CR* can result in a lower ohmic loss, which can prolong the charge and discharge time to reach the battery cutoff voltage. The *CE* value first increase from 86.4% to 93.4% as the *CR* value increases from 14.2% to 41.83% and then decreases with the further increase in electrode *CR*. Similar trend was also reported in the experimental studies of Wang et al. [36] and Park et al. [40]. For example, In the work of Wang et al. [36], the *CE* value increases from 79.0% to 90.1% as electrode *CR* increases from 0.3% to 41.8% and then decreases with further increment of *CR* at the current density 20 mA cm⁻². In the study of Park et al. [40], the *CE* value increases from 74.3% to 82.0% as electrode *CR* increases from 0% to 20% and then decreases with the further increase in electrode *CR* at the current density 20 mA cm⁻². Therefore, the present experimental results are reasonable. The *CE* value is influenced by the variation of charge/discharge time and the net convective crossover of the bulk electrolyte (i.e., vanadium permeation) [45]. The electrode compression influences the *CE* value from two aspects. On the one hand, the electrode compression reduces the ohmic loss and enhances the electron conduction, leading to electron transfer improvement and *CE* increase. On the other hand, during normal operation (i.e., within potential window of 0.9~1.6V, at current density of 20 mA·cm⁻²) of a VRFB, the *CE* is mainly limited by the vanadium ions crossover. Most cation exchange membranes such as Nafion, however, are proton-conducting in nature and thus do not inherently reject vanadium ions, given that vanadium ions and protons both bear positive charges [46, 47]. According to the research of Xi et al. [48], the diffusion coefficients of V²⁺, V³⁺, VO²⁺, VO₂⁺ in the Nafion 117 membrane are 3.13×10⁻¹² m² s⁻¹, 5.93×10⁻¹² m² s⁻¹, 5.0×10⁻¹² m² s⁻¹, 1.17×10⁻¹² m² s⁻¹, respectively. Therefore, the crossover of vanadium ions is inevitable in VRFB. The crossover amount of vanadium ions increases with the increase of charge/discharge times [49, 50]. Thus, longer

charge/discharge time caused by the electrode compression results in aggravation of the vanadium ions crossover, thereby reducing *CE*. The maximum *CE* value exists because of the two foregoing competing aspects. The *VE* value monotonically increases with the electrode *CR*. The *VE* value is influenced by the battery resistance. It monotonously increases as the battery resistance decreases with the increase in *CR*. With the combined effects of the *CE* and *VE* variation trends, *EE* first increases and then decreases with the increase in *CR*. The battery with *CR*=41.8% exhibits the highest *EE*.

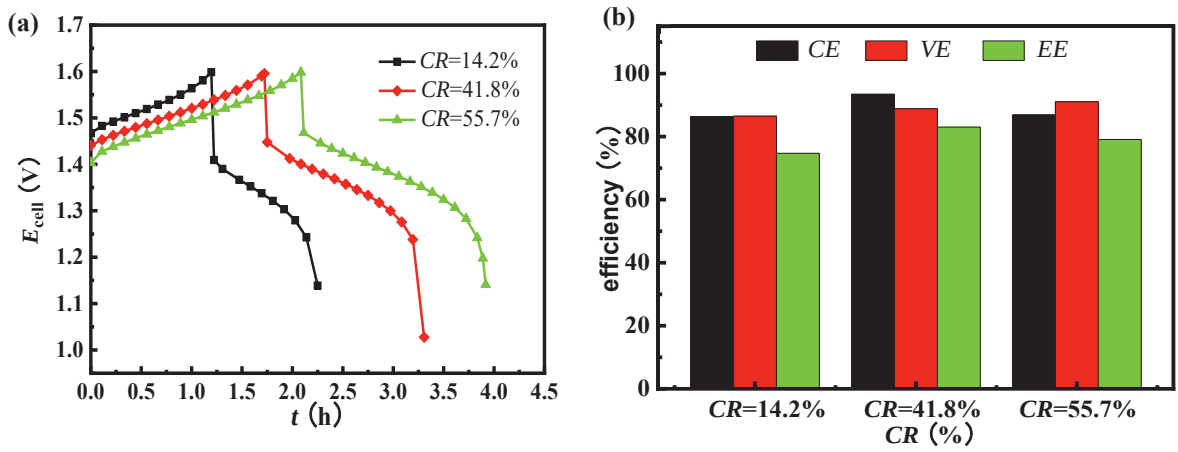


Fig. 3 Charge/discharge curves and the battery efficiency at different electrode *CR*s. (a) Charge and discharge curves and (b) *CE*, *VE*, and *EE*.

The current density distributions during the charge and discharge processes of batteries are obtained at three *CR*s (14.2%, 41.8%, and 55.7%) in order to investigate the influence of electrode compression on current density distribution. Figure 4(a–c) shows the current density distributions of eight locations (local_1–local_8) in a charge/discharge circle at the three *CR*s, the currents flow directions are opposite in the charge and discharge processes. The current density distribution exhibits a distinct uneven behavior. With the increase in electrode *CR*, the current density decreases in the border regions (local_1 and local_8) and increases in the core region (local_2–local_7).

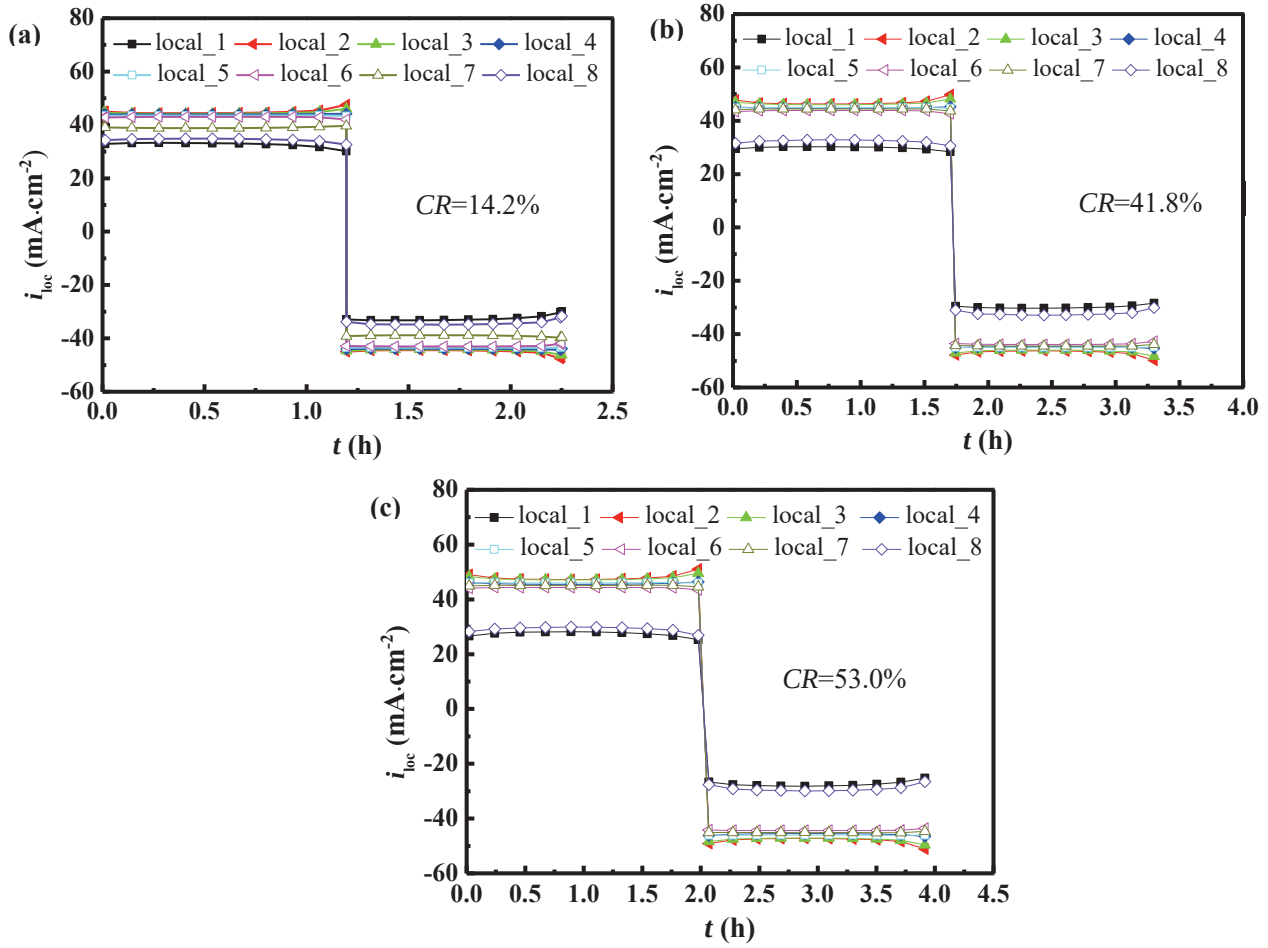


Fig. 4 Current density distribution during charge and discharge processes at different electrode CRs: (a) 14.2%, (b) 41.8%, and (c) 55.7%.

In order to specifically compare the local current density distributions at different electrode CRs, the current density variations in the three typical regions (upper border region: local_1; core region: local_2, local_4, and local_7; bottom border region: local_8) versus SOC in the charge process are shown in Fig. 5 (a); for simplicity, the current density data of local_3, local_5, and local_6 are not provided. At each CR, the current densities in the border regions (local_1 and local_8) are smaller than those in the core region (local_2, local_4, and local_7). In the core region, the current density gradually decreases along the flow direction (from local_2 to local_7). The uneven current density distribution is induced by the variations in the electrolyte mass flow rate entering the porous electrode. The upper border and core region of the porous electrode are adjacent to the flow channel. The flow resistance in the upstream flow channel (adjacent to the upper border region) is lower than that in the midstream flow channel (adjacent to the core region) because

1 the length of the flow channel at the upper border region is shorter than that at the core region. Therefore,
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3 insufficient quantities of electrolytes flow into the upper border region, and considerable quantities of
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5 electrolytes flow into the core region, leading to a smaller current density in the upper border region than that
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7 in the core region. The current density gradually decreases from local_2 to local_7 because of the reactant
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9 consumption along the electrolyte flow direction in the core region. In the bottom border region connected
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11 to the outlet, the flow resistance of the electrode is higher than that in the adjacent downstream flow channel.
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13 As a result, the quantity of electrolyte entering the porous electrode is relatively insufficient in this bottom
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15 border region; thus, the current density in this region is also smaller than that in the core region.
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19 As the value of electrode CR increases, the current densities gradually decrease in the border region
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21 (local_1 and local_8) and increases in the core region (local_2, local_4, and local_7). The electrode porosity
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23 decreases and the electrolyte flow resistance increases with the increase in CR . This means that small
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25 electrolyte quantities penetrate into the upper (local_1) and bottom (local_8) border regions, resulting in the
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27 reduction of current densities in the border regions. In the core region, although the flow resistance is
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29 enhanced as electrode CR increases, the electrode further intrudes into flow channel, resulting in higher
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31 electrolyte flow rates in the flow channel and the adjacent porous electrode. The effect of electrode intrusion
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33 on the flow rate increase is more prominent in the core region of the electrode. The positive effect of this
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35 intrusion on the flow rate increase is greater than the negative effect of electrode compression on the flow
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37 rate reduction. As more quantities of electrolytes flow into the core region of the electrode, the current density
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39 increases with CR increase in the core region.
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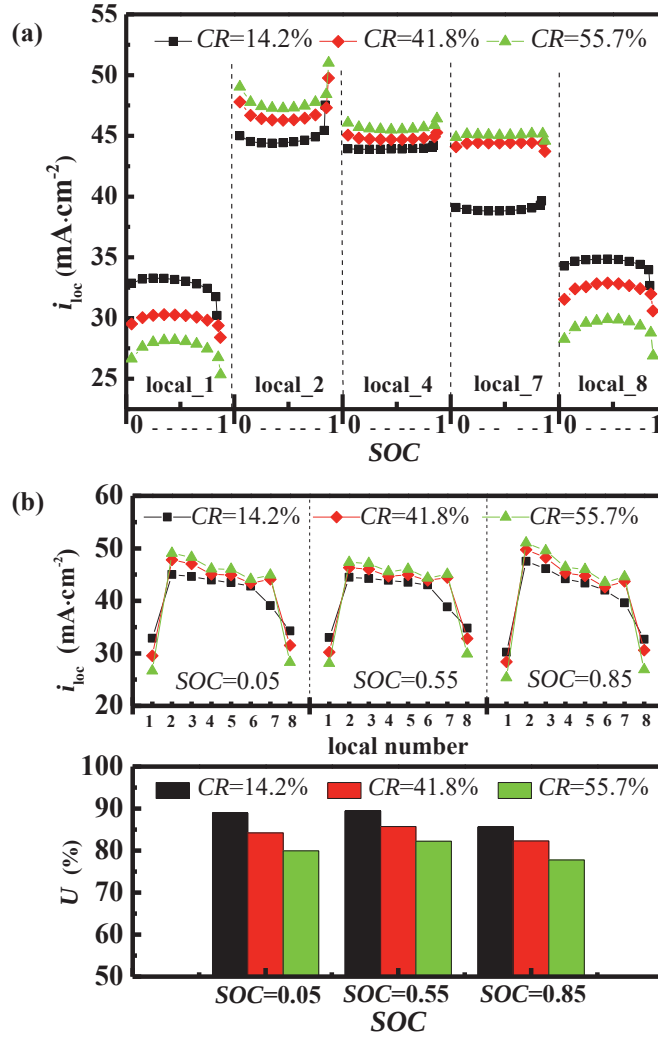


Fig. 5 Comparison of local current density distributions at under different electrode CRs during charge process. (a) Variation of the local current density distribution; (b) uniformity of current density distribution.

In order to evaluate the current uniformity in the VRFB at different CRs, the current density distributions and corresponding calculated uniformities are obtained at SOC of 0.05, 0.55, and 0.85. Figure 6(b) shows the current density and uniformity versus CR (14.2%, 41.8%, and 55.7%) at the three SOC. During the charging process, at a fixed CR, the uniformity of the current density distribution slightly improves as SOC changes from 0.05 to 0.55, and then decreases as SOC further increase to 0.85. This indicates that the current density uniformity is low at the initial and final stages (SOCs approximately 0.05 and 0.85, respectively); in the middle of the charging stage (when SOC is approximately 0.55), the current density uniformity is high. This is attributed to the significant active and concentrated polarizations at the initial and

final charging stages. At different CR s, the uniformity of the current density distribution decreases from 89% to 80% as the electrode CR increases from 14.2% to 55.7% at $SOC=0.05$. In the core region, the uniformity of current density distribution significantly improves with CR increases. As discussed, the reactant transportation is enhanced in the core region of the electrode, resulting in an improved uniformity of electrochemical reactions. The uniformity of current density distribution in the middle region of the electrode is thus improved with CR increase. In summary, the uniformity of current density is mainly influenced by the electrolyte transportation in the border region of the electrode. The uniformity can thus be improved by refining the electrolyte supplement in the porous electrode in the border region.

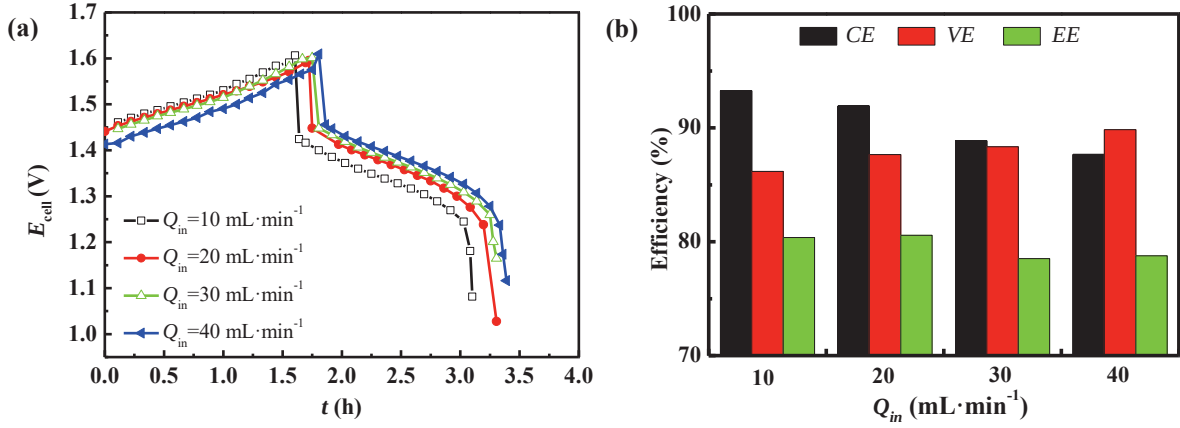


Fig. 6 Comparison of charge–discharge curves and CE , VE , and EE of the battery with different electrolyte inflow rates. (a) Charge and discharge curves; (b) CE , VE , and EE .

3.2 Current density distributions at different electrolyte inflow rates

In order to investigate the effects of electrolyte inflow rate on the charge and discharge performances, the current density distribution of the battery with $CR=41.8\%$ is employed at electrolyte inflow rates of 10, 20, 30, and 40 $\text{mL}\cdot\text{min}^{-1}$. Figure 6 shows the comparison between the charge–discharge performances and corresponding CE , VE , and EE at the four electrolyte inflow rates. The battery charge and discharge times gradually increase with the increase of electrolyte inflow rate. The mass transport is enhanced since the electrolyte inflow rate increases[38, 51]. Thus, a higher Q_{in} with enhanced mass transport results in reduced mass transport limitations and lower polarization and lower polarization, which can prolong the charge and

discharge time to reach the battery cutoff voltage [52]. With the increase in electrolyte inflow rate, CE decreases, VE practically remains unchanged, and EE decreases. The transmembrane diffusion of vanadium ions becomes more severe as battery charging and discharging times increases, thus resulting in a lower CE . The VE remains practically unchanged because of the insignificant change in battery resistance as the electrolyte inflow rate increases. With the combined effects of CE and VE , EE monotonously decreases by 1.6% when the Q_{in} is increased from 10 to 40 mL·min⁻¹.

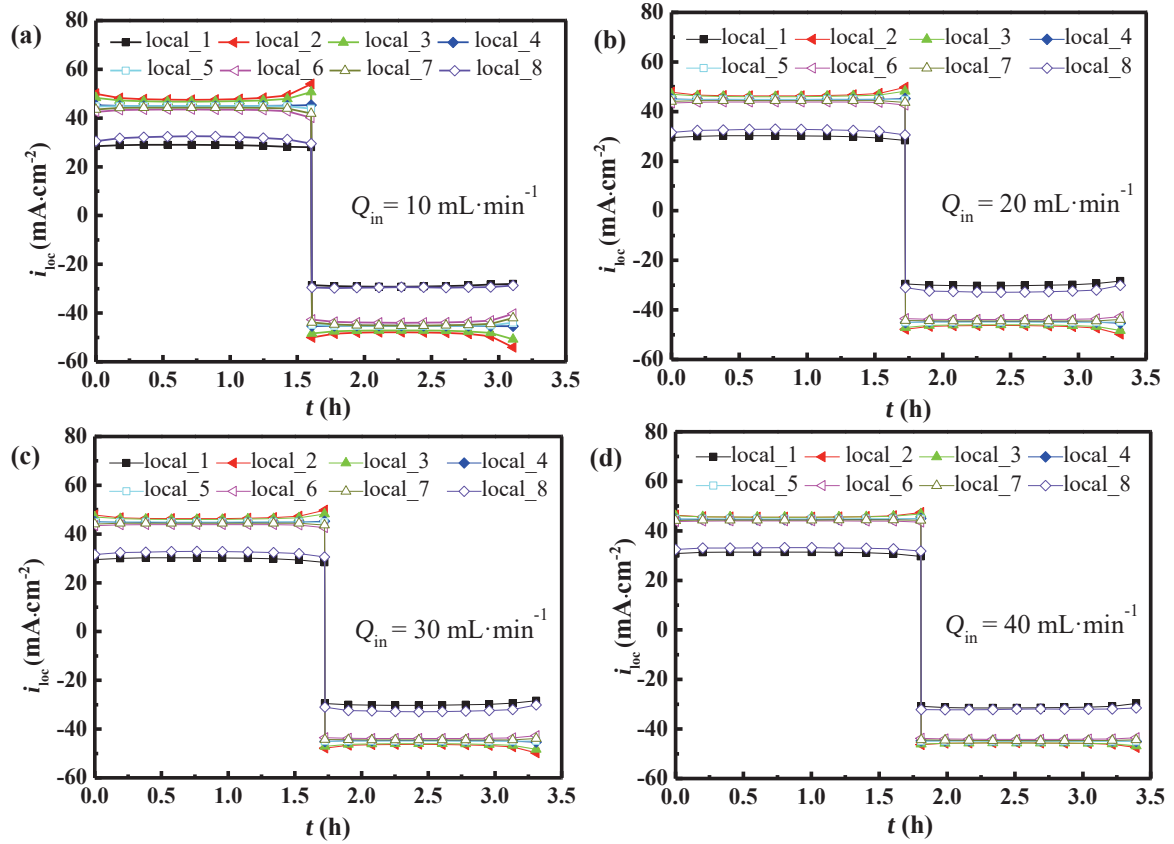


Fig. 7 Comparison of current density distributions at different electrolyte flow rates: (a) $Q_{in} = 10 \text{ mL} \cdot \text{min}^{-1}$, (b) $Q_{in} = 20 \text{ mL} \cdot \text{min}^{-1}$, (c) $Q_{in} = 30 \text{ mL} \cdot \text{min}^{-1}$, and (d) $Q_{in} = 40 \text{ mL} \cdot \text{min}^{-1}$.

The current density distributions during the charge and discharge processes of batteries are obtained at four Q_{in} values (10, 20, 30, and 40 mL·min⁻¹) in order to investigate the influence of electrolyte inflow rate on current density distribution. Figure 7 (a–d) shows the current density distributions of eight locations (local_1–local_8) in the charge–discharge cycles at the four Q_{in} values. At different flow rates, the current density distributions in the middle stage of charge and discharge processes are not affected by the inflow rate.

During the initial and final stages, the inhomogeneity of the current density distribution increases with the increase in the inflow rate because of the decrease in concentration polarization.

To specifically compare the local current density distributions at different inflow rates, Fig. 8 (a) presents the variation of current density versus *SOC* in the three typical regions (upper border region: local_1; core region: local_2, local_4, and local_7; bottom border region: local_8). At different electrolyte inflow rates, the current density in the border region (local_1 and local_8) increases, whereas that in the near-border region (local_2) decreases; the current density is insensitive to the electrolyte inflow rate in most parts of the core region. The current density distribution variation is influenced by the change in electrolyte inflow rate and charge conversion restriction.

In order to evaluate the current uniformity in the VRFB at different electrolyte inflow rates, the current density distributions and the corresponding calculated uniformities are obtained at *SOCs* of 0.05, 0.55, and 0.85. Figure 8 (b) shows the current density and the uniformity versus Q_{in} (10, 20, 30, and 40 mL·min⁻¹) at the three *SOCs*. At a fixed inflow rate, the uniformity of the current density distribution is higher in the middle stage (*SOC*=0.55) than those in the initial (*SOC*=0.05) and final (*SOC*=0.85) stages of the charging process. At different inflow rates, the uniformity of the overall current density distribution improves as the inflow rate increases. Moreover, the uniformity of the current density distribution exhibits the maximum increase at the final stage of the charging process (*SOC*=0.85) as the electrolyte inflow rate increases. For example, when Q_{in} increases from 10 to 40 mL·min⁻¹, the uniformity increases by 6.4% at *SOC*=0.85; this is larger than that at *SOC*=0.05 with a 4.5% increase. The polarization of the electrochemical reaction is intense at the initial and final stages of the charging process. Increasing the reactants transportation in the porous electrode, particularly in the border region, can therefore effectively improve the uniformity of the current density distribution.

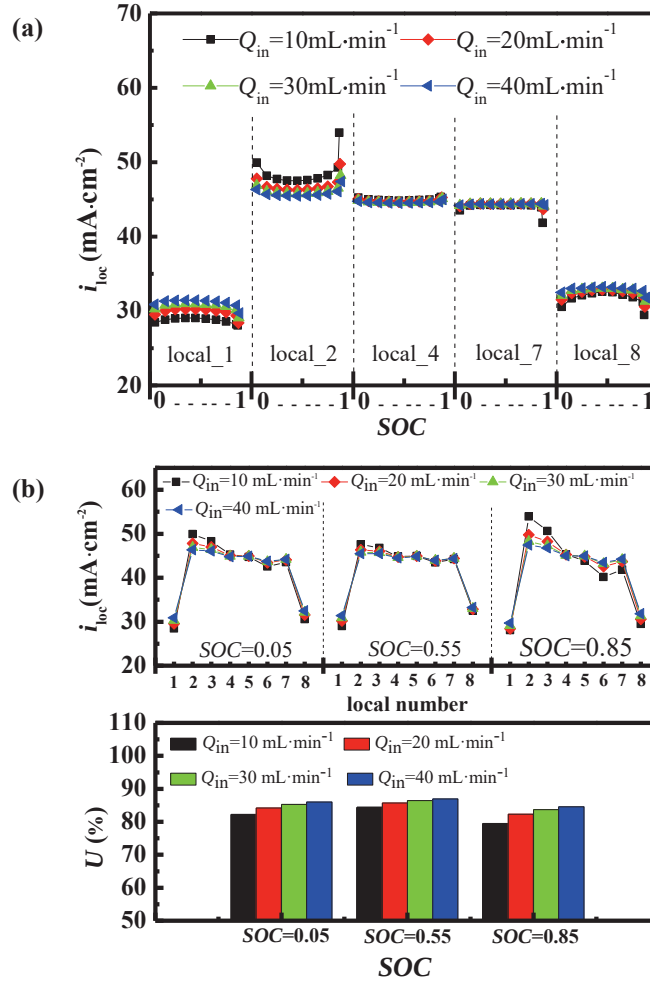


Fig. 8 Comparison between local current density distribution at different Q_{in} during charging process. (a) Variation of the local current density distribution; (b) uniformity of current density distribution.

4. Conclusions

A pluggable current collector with the flow field is designed to realize the in-operando measurement of current density distribution without changing the VRFB structure. The simple and innovative in-operando measuring device mainly consists of knife-shaped graphite flakes and a flow frame with channel grooves. By separating the channel part from the rib part, the pluggable current collector device can completely retain the structure and function of the channel and rib components. An uneven distribution of current density is observed during the battery cycle. The current density in the core region is higher than that in the border region of the porous electrode. Moreover, the uniformity of the current density in the middle stage is higher than those in the initial and final stages. The energy efficiency first increases and then decreases with the

1 increase in electrode compression ratio; with the increase of inflow rate, the energy efficiency monotonously
2
3 decreases. With the increase in the electrode compression ratio, the current density increases in the core
4
5 region and decreases in the border region of the porous electrode. The overall current density uniformity
6
7 decreases, but the uniformity in the core region increases. With the increase in the inflow rate, the current
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9 density increases in the border region and decreases in the near border region; the current density variation
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11 in the core region is not sensitive to the inflow rate. The overall current density uniformity increases with the
12
13 inflow rate. The developed pluggable current collector will contribute to on-line measurement and provide
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15 theoretical support for the flow field design of VRFB.
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