

**THE INVESTIGATION OF BATTERY PERFORMANCE
PARAMETERS AND THERMAL BEHAVIOUR IN
VANADIUM REDOX FLOW BATTERY**

BY

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A Thesis Presented to the
**COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS**

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

MECHANICAL ENGINEERING

DECEMBER 2024:

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

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I DEDICATE THIS WORK TO
MY BELOVED PARENTS,
AND
MY SIBLINGS |

ACKNOWLEDGMENTS

All the praises and thanks be to Allah, the Lord of the Alamin (mankind, jinns and all that exists), the most beneficent, the most merciful, for granting me this opportunity to complete my Masters at KFUPM.

My sincere thanks to King Fahd University of Petroleum and Minerals for providing me with the opportunity and financial assistance to pursue my MS degree.

My deep gratitude and thanks to my advisor, Dr. Obaidallah M. Munteshari, for his support, encouragement and guidance throughout my graduate studies. I am thankful to my Co-advisor, Dr. Mohammad Qamar, for the guidance and advice he has provided throughout my time as his student. I also appreciate and thank my advisor and co-advisor for providing me with the facility and all the materials and equipment required for my work. I am also thankful to my committee, Dr. Ali Al-Shehri for his guidance and cooperation.

I acknowledge the efforts and guidance of Dr. Mohammad Furquan and Dr. Zahid Manzoor Bhat to complete the project successfully. I would also like to thank them for their help and guidance during the execution of my experimental work.

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ABSTRACT

Full Name : [Mohammed Omer Farooq]
Thesis Title : [The Investigation of Battery Performance Parameters and Thermal Behaviour in Vanadium Redox Flow Battery]
Major Field : [Mechanical Engineering]
Date of Degree : [December 2024]

Vanadium Redox flow batteries are promising technologies that store energy generated through renewable means. The main idea of these flow batteries is to store energy in liquids, unlike solid-state batteries. The energy is stored in the form of electrochemical energy in the electrolyte stored in tanks. Their main advantage is the decoupling of the energy and power making it feasible for its scalability independently from each other. These batteries are used for stationary energy storage applications like grid storage. The advantage of Vanadium is its unique ability to exhibit four oxidation states making it viable to use as a single electroactive species in the electrolyte. This feature also reduced the risk of mixing up and cross-contamination for the electrolyte. The primary element of VRFB is the Vanadium Pentoxide (V_2O_5). The Vanadium in Vanadium Pentoxide is in the V^{+5} oxidation state. This V^{+5} oxidation state needs to be reduced to V^{+4} and V^{+3} to make the electrolyte suitable for galvanostatic cycling. The reducing agent used for this process is Oxalic acid. The Vanadium Pentoxide is dissolved in aqueous sulfuric acid solution and oxalic acid is added to it. This solution is stirred at 600 rpm for about 72 hours for the solution to dissolve and reduce properly. The cell is assembled with bipolar plates, electrodes, membrane, current collectors, and end-frames. The bipolar plates are made of graphite material having

a triple serpentine flow field. The area of the flow field is 25 cm^2 . The electrodes are made of graphite felt which needs to be activated to make it hydrophilic by heating it to 400°C for about 10 hours. The membrane used is the Nafion-212 membrane which is a cation exchange membrane which allows only the positive ion to diffuse through it. The temperature sensor from DiLiCo Engineering is introduced between the bipolar plate and the current collector to measure the temperature distribution on the plate. The sensor has 48 segments which record the temperature of the electrode individually. 40 ml of the prepared electrolyte is taken as anolyte and catholyte for galvanostatic cycling.

The study analyzes the real-time temperature distribution patterns on the anode (negative electrode) and cathode (positive electrode) of the vanadium redox flow battery in a full-cell configuration. The patterns are analyzed under various current densities ($60, 75$, and 90 mA cm^{-2}), electrolyte flow rates (50 and 100 mL min^{-1}), and different operating temperatures of the cell and tanks (25°C and 30°C) during the galvanostatic cycling. The real-time temperature variations are recorded at the negative and positive electrodes during the charge-discharge cycling and then represented in 2D temperature distribution contours. It is noted that the temperature of the negative electrode increases during charging and falls during discharge. Conversely, the temperature of the positive electrode decreases during charging and increases during discharging. A comprehensive analysis and discussion of the temperature distribution at the electrodes are presented. Furthermore, the distribution of applied current density during the galvanostatic cycling at both electrodes is carefully mapped. The study offers valuable insights into the temperature distribution behavior of vanadium redox flow batteries, which could be advantageous for future technological

advancements. Specifically, catholyte species precipitate during galvanostatic cycling at moderate temperatures, a problem for vanadium redox flow batteries.

ملخص البحث

الاسم الكامل: محمد عمر فاروق

عنوان الرسالة: دراسة معاملات أداء البطارية والسلوك الحراري في بطارية الفاناديوم ذات تدفق الأكسدة والاختزال

التخصص الرئيسي: ماجستير العلوم في الهندسة الميكانيكية

تاريخ الحصول على الدرجة العلمية: ديسمبر 2024

بطاريات الفاناديوم ذات تدفق الأكسدة والاختزال هي تقنية واعدة لتخزين الطاقة الكهربائية المتولدة من مصادر متجددة. الفكرة الرئيسية لهذه البطاريات هي تخزين الطاقة في السائل الحامل للأيونات (الكتروليت)، حيث يتم تخزين الطاقة في شكل طاقة كهروكيميائية في الإلكتروليت المخزن في خزانات مستقلة. ميزتها الرئيسية هي فصل كمية الطاقة المخزنة وقدرة (أو سرعة) التخزين مما يسهل عملية الزيادة والنقصان في كل منهما على حدة. يستخدم الفاناديوم في هذا النوع من البطاريات لقدرته الفريدة على إظهار أربع حالات أكسدة مما يجعله قابلاً للاستخدام كنوع واحد من المواد النشطة كهربائياً في الإلكتروليت. المادة الأساسية لهذا النوع من البطاريات هي خماسي أكسيد الفاناديوم (V_2O_5)، حيث يكون الفاناديوم في خماسي أكسيد الفاناديوم في حالة أكسدة V^{+5} ، يجب تقليل حالة أكسدة V^{+5} هذه إلى V^{+4} و V^{+3} لجعل الإلكتروليت مناسباً للشحن، والعامل المختزل المستخدم في هذه العملية هو حمض الأكساليك، يتم إذابة خماسي أكسيد الفاناديوم في محلول حمض الكبريتيك المائي ويضاف إليه حمض الأكساليك، يتم تحريك هذا المحلول بسرعة 600 دورة في الدقيقة لمدة 72 ساعة تقريباً حتى يذوب المحلول ويختزل بشكل كامل، يتم تجميع الخلية بألواح ثنائية القطب وأقطاب كهربائية وغشاء ومجمعات تيار وإطارات نهائية. الألواح ثنائية القطب مصنوعة من مادة الجرافيت ذات مجال تدفق ثلاثي المسارات. تبلغ مساحة مجال التدفق 25 سم². الأقطاب الكهربائية مصنوعة من لباد الجرافيت الذي يحتاج إلى التنشيط لجعله متقبلاً للماء عن طريق تسخينه إلى 400 درجة مئوية لمدة 10 ساعات تقريباً. الغشاء المستخدم هو غشاء Nafion-212 وهو غشاء تبادل كاتيوني يسمح فقط للأيون الموجب بالانتشار من خلاله. يتم إدخال مستشعر درجة الحرارة من DiLiCo Engineering بين اللوحة ثنائية القطب ومجمع التيار لقياس توزيع درجة الحرارة على اللوحة. يحتوي المستشعر على 48 قطعة تسجل درجة حرارة القطب بشكل فردي. يتم أخذ 40 مل من الإلكتروليت المحضر على شكل أنوليت وكاثوليت.

يهدف هذا البحث إلى دراسة أنماط توزيع درجة الحرارة وتغيرها مع الوقت على القطب السالب والقطب الموجب للبطارية. يتم تحليل الأنماط تحت كثافات تيار كهربائي مختلفة (60 و 75 و 90 مللي أمبير لكل سم²) ومعدلات تدفق الإلكترونات (50 و 100 مل في الدقيقة) ودرجات حرارة تشغيل مختلفة للخلية والخزانات (25 درجة مئوية و 30 درجة مئوية). يتم تسجيل الاختلافات في درجة الحرارة في الوقت الحقيقي عند الأقطاب السالبة والموجبة أثناء دورة الشحن والتفريغ ثم يتم تمثيلها في خطوط توزيع درجة الحرارة ثنائية الأبعاد. يلاحظ أن درجة حرارة القطب السالب تزداد أثناء الشحن وتنخفض أثناء التفريغ. وعلى العكس من ذلك، تنخفض درجة حرارة القطب الموجب أثناء الشحن وتزداد أثناء التفريغ. يتم تقديم تحليل شامل ومناقشة لتوزيع درجة الحرارة عند الأقطاب. علاوة على ذلك، يتم رسم خريطة توزيع كثافة التيار أثناء الشحن والتفريغ عند كلا القطبين بعناية. تقدم الدراسة رؤى قيمة حول سلوك توزيع درجات الحرارة لبطاريات تدفق الفاناديوم المؤكسدة، والتي قد تساعد لفهم عمليات الترسيب في هذا النوع من البطاريات وإيجاد حلول هندسية للتغلب على التباين في درجات الحرارة وتزايدها.

CHAPTER 1

INTRODUCTION

1.1 Background of energy storage.

With rapid globalization, industrialization, and advancements in science and technology, the need for energy is growing at a rapid pace. Also, a transition to meet the energy requirements from conventional means of burning fossil fuels to harvest energy through renewable means such as solar, wind etc. has led to an increase in demand and challenge in Energy storage systems [1]. Wind and solar energy are intermittent renewable sources; they only produce electricity when the sun or wind shines. To maintain a steady power supply, energy storage devices store extra energy during periods of high output and release it during periods of low production [2]. ESS controls supply and demand variations to assist in stabilising the grid. Blackouts can be avoided by using them to supply power instantly during disruptions or outages. Energy costs may increase during periods of high demand. Energy storage lowers costs and eases the strain on the grid by enabling utilities and consumers to store energy during off-peak hours and use it during high-demand [3]. ESS and renewable energy sources might take the role of diesel generators in isolated or off-grid locations, offering dependable and clean electricity. ESS are essential in lowering carbon emissions because they facilitate the transition from fossil fuel-based power generation to renewable sources [4].

1.2 Types of Energy storage systems.

There are various types of Energy storage devices based on their methods of storing energy. Mechanical energy storage consists of pumped hydro storage, compressed air energy storage, and flywheels which store energy in the form of kinetic and potential energy; Electrochemical energy storage has batteries and supercapacitors which store energy in the form of electrochemical energy; Thermal energy storage which stores energy in the form of sensible heat storage, latent heat storage, and thermochemical storage which stores energy in the form of heat; Electrical energy storage which has capacitors, superconducting magnetic energy storage which stores energy in the form of electrostatic and magnetic energy; Chemical energy storage consisting of hydrogen storage, and synthetic fuels which store energy in the form of chemical energy [5–7]. Of all the energy storage systems, under Electrochemical energy storage, redox flow battery is one of them[8].

1.3 Flow batteries.

Redox flow batteries (RFBs), also known as flow batteries, are a kind of electrochemical energy storage device in which the energy is stored in external tanks filled with liquid electrolytes [9]. To transform chemical energy into electrical energy and vice versa, these electrolytes pass through an electrochemical cell. Flow batteries allow flexibility in scaling up energy storage capacity by simply expanding the size of the electrolyte tanks, in contrast to traditional batteries that store energy within solid electrodes [10]. The main components of redox flow battery systems are electrolyte tanks, electrochemical cells, pump pipes etc.

1.4 Concepts and early development.

In the early 1980s, Maria Skyllas-Kazacos and her team at the University of New South Wales in Australia developed the first Vanadium Redox Flow Battery . Vanadium was selected due to its unique ability to exist in four stable oxidation states, which allowed the same element to serve as both the positive and negative electrolyte. Vanadium was selected due to its unique ability to exist in four stable oxidation states, which allowed the same element to serve as both the positive and negative electrolyte. This design minimized cross-contamination issues and increased the battery's stability and lifespan [11].

1.5 Advancements and early commercialization.

Gradually, VRFB technology improved as research concentrated on improving the cell design, membrane composition, and electrolyte concentration. After early prototypes were made, the US and Japan investigated VRFB for grid applications in the 1990s [12]. However, its early usage was constrained by the price of vanadium and the absence of long-lasting materials for long-term cycling. The emergence of renewable energy sources and the demand for extensive, long-duration energy storage in the early 2000s sparked a resurgence of interest in VRFB. Many companies started creating VRFB systems for grid and industrial uses. Improved ion exchange membranes, electrolyte stability, cost reduction, and VRFB lifetime and performance were the main areas of research [13].

1.6 Modern developments and growth in deployment.

These days, VRFB technology is thought to be a viable option for storing renewable energy, especially in areas that need long-duration storage (4–12+ hours). Better membrane materials, electrode designs, and more concentrated vanadium electrolytes are examples of

recent developments that have increased the efficiency of VRFBs. VRFBs are being used for grid applications, renewable energy storage, and microgrids as the demand for energy storage rises, particularly in areas with a high concentration of renewable energy sources[14,15].

1.7 Vanadium redox flow battery.

The Vanadium Redox Flow Battery (VRFB) is an innovative energy storage technology renowned for its scalability, long life span, and suitability for grid-scale applications [16]. This electrochemical energy storage system employs vanadium-based electrolytes to store and release electrical energy. VRFBs are recognized for their ability to store large amounts of energy, making them a promising solution for renewable energy integration, grid stabilization, and peak shaving [17]. The precursors for Vanadium redox flow batteries are Vanadium Pentoxide (V_2O_5) which is a relatively inexpensive vanadium compound, readily available, Vanadium Sulfate ($VOSO_4$) which is highly soluble in the electrolyte but has higher cost compared to V_2O_5 , Ammonium Metavanadate (NH_4VO_3) which is more expensive and less readily available for large-scale applications, Vanadium Trioxide (V_2O_3) has limited availability and less commonly used, and Vanadium Chloride (VCl_3) which is more expensive and less commonly used industrially [18].

1.8 Working principle of VRFB.

The fundamental principle on which redox flow batteries work is the oxidation and reduction of ions in an electrolyte [19]. The exchange of ions takes place through a proton exchange membrane which separates the two half-cells of the battery. The two liquids circulate in their respective channel and the current flows through the external circuit. In

the redox flow battery systems. Vanadium is used as an electrolyte as it can exhibit four different oxidation states in a solution [20]. This makes the Vanadium redox flow battery with a single electroactive element instead of two. The key redox pairs are V^{+4}/V^{+5} at the positive electrode and V^{+2}/V^{+3} at the negative electrode [21]. During the charge at the positive electrode the Vanadium which is at the V^{+4} oxidation state gets oxidized to the V^{+5} oxidation state and during discharge, it reduces from the V^{+5} oxidation state to the V^{+4} oxidation state. Similarly, at the negative electrode during charge, the Vanadium which is at V^{+3} oxidation reduces to a V^{+2} oxidation state and during discharge, it oxidizes from V^{+2} to V^{+3} oxidation state [18].

1.9 Advantages of VRFB.

One key advantage of VRFBs is their decoupled energy and power capacity. By adjusting the size of the electrolyte storage tanks, these batteries can be scaled up or down independently to suit specific energy storage needs [16]. This feature makes VRFBs well-suited for stationary applications, such as storing excess energy generated by renewable sources like solar or wind power for later use during peak demand periods.

Moreover, vanadium flow batteries facilitate a more environmentally friendly source of energy, the technology itself is sustainable. Vanadium flow batteries' reusable electrolyte eliminates the need to mine new vanadium to replace batteries. The very first successful demonstration of Vanadium Redox flow battery was presented by Maria Skyllas-Kazacos in the year 1980s. It employed vanadium in a solution of sulfuric acid. The electrode used in this battery is graphite felt. The oxidation states of the Vanadium in the solution is +2, +3, +4, +5.

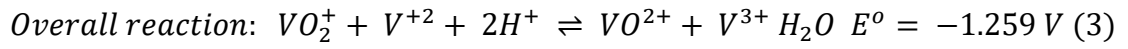
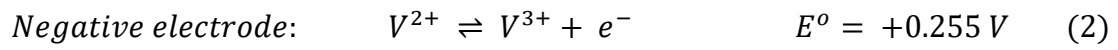
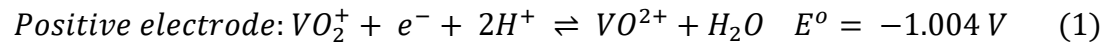
1.10 Challenges for VRFB.

However, despite their advantages, VRFBs currently face challenges related to cost and energy density. Vanadium has a high demand from the steel industry and restricted worldwide supply, the active ingredient in VRFBs, is costly and volatile in price. A substantial amount (30–50%) of the overall system cost is attributed to the price of vanadium. Nafion and other ion-selective membranes are costly and add to the total cost[9]. The energy density of VRFBs is lower than that of other battery technologies, such as lithium-ion. This makes them less appropriate for applications with limited space because they necessitate larger tanks and more room. Also it makes them less competitive in mobile and compact systems and restricts their use to stationary applications . Additional thermal management techniques are necessary since the vanadium electrolyte is prone to freezing at low temperatures (below -10°C) or precipitating at high temperatures (over 50°C). One important area of current study is stabilising vanadium electrolytes for a larger temperature range [22]. Over time, ion-selective membranes may deteriorate, decreasing their effectiveness and raising maintenance expenses. System performance is decreased by electrolyte crossover, which occurs when vanadium ions cross the membrane and cause imbalances in the electrolyte composition [23]. VRFBs exhibit lower energy efficiency (typically 70–85%) compared to other battery types due to overpotentials in redox reactions and resistive losses in the system. Achieving an optimal balance between flow rates and efficiency is crucial for minimizing energy losses [24].

Ongoing research and development efforts aim to address these limitations, seeking to improve the energy density of the electrolyte solutions and reduce overall system costs to enhance the competitiveness of VRFBs in the energy storage market [16].

The mechanism of the vanadium redox flow battery is illustrated in the following reaction.

The half-cell reactions at the cathode and anode are:



CHAPTER 2

LITERATURE REVIEW

Various factors affect the performance of the redox flow battery. They are the concentration of the electrolyte, electrolyte flow rate, overpotential heat, operating temperature of the cell etc [25]. These factors need to be monitored meticulously to enhance the performance thereby increasing the efficiency and reliability of the cell.

2.1 Overpotential heat.

Overpotential heat: Basically, the overpotential heat are of three kinds. Activation overpotential, Ohmic overpotential and Concentration overpotential. Ohmic potential is a result of the movement of charged species in the cell. It is determined by the summation of all the electrical resistances offered by the components of the VRFB that participate in the electrochemical reactions and their flow[26]. The contribution of the ohmic overpotential in VRFB is due to the movement of electrons through the carbon felt electrode, bipolar plate, and current collector from each side and in the external circuit. It is also contributed by the proton or the ion movement through the electrode and proton exchange membrane.

The ohmic overpotential can be given by the equation:

$$\eta_{\text{ohmic}} = j \left(\frac{w_e}{\sigma_e} + \frac{w_m}{\sigma_m} + \frac{w_{gp}}{\sigma_{gp}} + \frac{w_{cc}}{\sigma_{cc}} + \frac{w_e}{k_{\text{eff}}} \right) \quad (1)$$

where j is the current density; w_e is the thickness of the carbon felt electrode; σ_e is the conductivity of the carbon felt; w_m is the thickness of membrane; σ_m is the conductivity of the membrane; w_{gp} is the thickness of graphite plate; σ_{gp} is the conductivity of graphite plate; w_{cc} is the thickness of current collector plate; σ_{cc} is conductivity of current collector

plate; k_{eff} is the effective ionic conductivity of vanadium electrolyte. Electrode conductivity depends on the geometry and the material of the electrode.

When the current density is extremely high, a concentration overpotential develops because of the substantial change in electrolyte concentration at the bulk and at the electrode surface. High reactant species fluxes are necessary to maintain high currents; the surface concentration may be significantly lower than the bulk concentration [27].

Towards the conclusion of charge/discharge, when the bulk concentration is very low, the surface concentration may become extremely low and create a condition where the reaction rate is constrained by the diffusive flux and the charge transfer mechanism is governed by mass-transfer.

2.2 Electrolyte flow rate.

Electrolyte flow rate plays an important role in the performance of the cell. In study thin graphite sheets were used to separate the flow channel and the carbon felt electrode thereby allowing the electrolyte to flow through the electrode by making grooves in it. This makes the pressure drop significantly higher in a cell compared to other VRFB. In literature [28] [29] where thin flow frames of thickness three or less used lead to high pressure loss compared to grooved flow channels. For large cells, the larger pressure drop becomes a crucial design factor even though it may not be significant for small cells. In another study where 8 mm thick flow frames along with 2 gaskets 1 mm thick each were studied. For flow rates up to $300 \text{ ml} \cdot \text{min}^{-1}$, the pressure loss changes slightly nonlinearly with flow rate and remains considerably below 20 kPa [30]. In contrast, the instance claimed by [28] that their thin-frame, thin graphite sheet cell saw a cell pressure drop of 200 mbar (20 kPa) with a flow rate of 100 ml per minute. This comparison highlights the improvements in pressure

drop that can be realized utilizing thick flow frames, despite the possibility of minor differences in measurement locations, cell design, and electrode permeability. In another study [31] to improve the system efficiency and by keeping the capacity high, an optimal strategy of electrolyte flow rate is proposed. The result showed that by increasing the electrolyte flow rate at constant current density the capacity of the cell increases, but the system efficiency decreases. In an optimal strategy during charging process, the battery is first operated at low flow rate and then increased to higher flow rate when a certain voltage is reached. During the discharge process the same strategy is used as in charging process. The results showed that there is an increase in performance of the battery by 8% compared to the operating conditions with high flow rate.

2.3 Electrolyte and its concentration and composition.

The electrolyte, one of the most crucial parts of the vanadium redox flow battery (VRFB), has a big influence on the capital cost, performance, and characteristics of the cell. The electrolyte composition will affect the VRFB's practical uses, operating temperature range, and energy density. There have been several ideas put out to raise the operational temperature range and energy density. The stability of the electrolyte may be changed, which can impact cell performance, operating temperature range, energy density, electrochemical kinetics, and cost efficiency. Electrolyte contaminants can also be introduced into the vanadium solution in trace amounts. In a study [32] it is discussed that the composition of 2 M V^{+5} in 2-3 M H_2SO_4 fully charged positive electrolyte tends to gradually precipitate when stored at higher temperature. This causes the blockage and flow restrictions in the plates and electrode. For the vanadium ions in sulfuric acid solution, the solubility or dissolution of vanadium ions V^{+5} can be increased by decreasing the

temperature or increase in sulfuric acid, whereas for the vanadium ions V^{+4} , V^{+3} , V^{+2} it can be improved by elevating the temperature and decreasing the sulfuric acid[33].

In another study where impurities in vanadium redox flow batteries and additives for stabilising the electrolyte was discussed [34]. This study showed that the solubility of the vanadium ions has been increased with increase in temperature. Additionally, several additives or stabilising agents are discussed for vanadium V^{+5} , V^{+4} ions in terms of solubility and maintaining and operating at high temperature. It describes the additive and its quantity to be used for a particular molarity of vanadium ions, the temperature for its addition and its effect on the electrolyte condition & performance and the extension to which it has been effective. Out of these additives for reducing and maintaining the electrolyte at high temperatures glycerol, L-ascorbic acid, Citric acid, Phosphorus acid, Ammonium Sulphate, Thiourea, Succinic acid and Glycine are available to us.

At operating temperatures of 40 °C and above, electrolyte additives can function as precipitation inhibitors to lessen electrolyte precipitation [35]. A capacity reduction in the VRFB may result from the high concentration vanadium electrolyte's tendency to precipitate at higher temperatures. Research on sodium pyrophosphate dibasic (SPD) as a precipitation inhibitor has been reported. Improvements in precipitation time were seen when the SPD concentration increased to 0.1 M. In addition, it was found that the precipitation time decreased by using 3 M H_2SO_4 as the solvent in the vanadium electrolyte. When 0.1 M SPD was introduced, the charge/discharge studies with SPD at 40 °C revealed marginal increases in the discharge capacity .

2.4 Operating temperature.

The operating temperature also plays an important role in the performance of the cell and maintaining the stability of the electrolyte [36]. By adjusting these operating parameters during the charge and discharge processes, the study [37] fully analyses the temperature distributions and the variations of irreversible-reversible and joule heating sources inside the porous electrodes to highlight the thermal behaviour of the vanadium redox flow battery. According to the results, both operating parameters can improve battery performance, and throughout both operations, the negative electrode experiences higher values of irreversible and reversible heat sources than the positive electrode. The joule heating source rises as the working temperature rises but falls as the molar concentration of the electrolyte rises. Additionally, during the charge and discharge processes, there isn't a significant variation in temperature between the interiors of the two electrodes.

With a rise in temperature, the reversibility of redox couple was found to be better. It was found that the redox couple's chemical reversibility in the negative electrolyte V^{+3}/V^{+2} was superior to that of the redox couple in the positive electrolyte V^{+4}/V^{+5} [38].

In a study considering the operating temperature and flow rate of electrolyte on the charging/discharging capacities were examined [39]. The experiment was performed under three different cell temperatures, two electrolyte flow rates and three current densities. When comparing the polarization curves at 60 mA.cm^{-2} , SF_{50} 6.6, 13.2 at various cell temperatures, it can be shown that the discharge capacity is significantly influenced by the cell temperature, especially when operating at 10°C . When the cell temperature is reduced from 25°C to $+10^\circ\text{C}$ for the high flow rate, there is an approximate 15% loss in discharge capacity and a nearly 50% drop when the temperature is reduced to 10°C . The discharge

capacity falls in each of the three scenarios for the low flow rate. For the low flow rate instance at 10°C, the loss of discharge capacity is greater than 60%, demonstrating the marginally positive impact of higher circulation rate on discharge capacity. Furthermore, for the current density of 40 mA.cm⁻² and 80 mA.cm⁻², where SF₅₀ corresponds to 19.8 and 9.9 respectively, the charging and discharging capacities has been increased for 40 mA.cm⁻² current density and decreased for 80 mA.cm⁻² current density. There has been relatively little charging and discharging for the high current case at temperatures below 10°C, even though the decline is only modest (about 15-20%) between cell temperatures of 25°C and 10°C. Mass transfer polarization occurs right away in this situation, most likely because of the reactant species low mass diffusivity.

2.5 Current density.

In another study, the effect of current density and flow rate on the performance of the battery was examined [40]. Two different cases were analysed, one by changing the current density in a cycle and keeping the flow rate constant. The other by changing both the current densities and the flow rate in a cycle. In case(i) two different approaches were examined, one with small current density (60 mA.cm⁻²) during charging process and large current density (90 mA.cm⁻²) during discharging process and vice versa for a constant electrolyte flow rate of 90 mL.min⁻¹. In case(ii) high flow rate and current density is applied during charging process and low flow rate and current density is applied during discharge process. The results for both the cases obtained are as follows. The lower current density during charging process takes more time to charge than the higher current density and discharges early than the higher current density and vice versa. According to the experimental findings, case(ii) requires 8136 seconds more time than case(i) does after 10

cycles of the same working conditions, or 813.6 seconds longer per cycle. case(ii) voltage value is low during the charge stage and high during the discharge stage. The study demonstrates that after several cycles, the case(ii) can release more energy storage capacity.

In another study, to explore the VRFB temperature responses under various operating and surrounding environmental circumstances, a lumped model with the auxiliary pump effect was created [41]. Investigations were also conducted into how the electrolyte flow rate and temperature affect the electrical properties and efficiency of the battery. Numerical simulations are carried out using a one-kilowatt VRFB system. When the thermal hydraulic model was compared to experimental data, there was generally good agreement. According to the results of the simulation, hydraulic design and flow rates have an impact on pump power. Under typical operating conditions for the stack design and chosen electrolyte volume, the temperature in the stack and tanks raised by approximately 10°C. For the suggested battery arrangement, an ideal flow rate of roughly 90 cm³.s⁻¹ was found to enhance battery efficiency.

2.6 Flow field design.

In a study, a new or novel cell structure is proposed to eliminate some of the components to improve safety, extend the cell life, and to promote ease in the assembly of the cell with fewer components [42]. Instead of conventional graphite flow field plates, rigid impermeable polyvinyl chloride (PVC) sheets were introduced which has flow channels embedded in them. This new design made the cell lighter in weight, easy to assemble, eliminates unnecessary components, and avoid any leakage of electrolyte from the cell. Several tests, such as cycling and polarization measurements for different currents and flow rates over a wide range, Electrochemical Impedance Spectroscopy (EIS) for analysis of

internal resistance, were performed and compared with the traditional one. The performance of the new design cell is superior to the conventional cell in terms of average coulombic and energy efficiency, which results in reduced degradation capacity during cycling under the same operating circumstances. The high feed rate of electrolyte solutions onto both sides of a battery cell resulted in an immediate boost in the battery's output capacity, according to polarization measurements of this novel design. Based on the same outer cell dimensions for both designs, the new design generates more power due to a greater output current and a bigger electrochemical surface area [42].

The pressure drop, power density, and area-specific resistance are all significantly impacted by the flow field. Comparing the cell with flow field to the cell without, it was discovered that the area-specific resistance of the former was 13% lower [43]. By lowering the ohmic losses, this can raise the cell's voltage efficiency. Additionally, flow field negatively impacts peak power density. At high electrolyte flow rates, it was found that the flow cell with flow field delivered a power density that was over 2.5 mW cm^{-2} greater than the cell without flow field [43]. The serpentine, parallel, spiral, interdigitated, and conventional patterns are examples of popular flow field designs[44]. Various flow fields have varying effects on power density and pressure drop. Because of its lengthy flow route, the serpentine flow field design was found to have the most pressure decrease. Only a small amount of electrolyte can flow in the channels due to the pressure differential between the neighbouring channels, which causes the electrolyte to bypass the flow route by passing beneath the rib (through the carbon electrode). As a result, the cell's through-plane distribution is enhanced, raising the peak power density. According to reports, the electrolyte flow in the interdigitated flow field primarily occurs through the electrode. In

this instance, the electrolyte flow channel was comparatively shorter and showed a minimal pressure loss [44]. According to reports, the parallel and spiral flow fields had the lowest electrochemical efficiency across all flow sectors. Here, the total amount of pressure decline was said to be minimal. As a result, the pressure between the channels must be consistent.

2.7 Methods of preparation of electrolyte.

In a study of electrolyte preparation, the performance of electrolyte prepared from different types or grades of raw vanadium pentoxide material was investigated [45]. Chemical reduction method is used to reduce the electrolyte and the reducing agent used is oxalic acid ($C_2H_2O_4$) and the solvent used is concentrated sulfuric acid. The different grades of V_2O_5 are 98%, 99%, 99.5% purity and purchased from different manufacturers. The impurities present are K, Na, Mg, Fe, Al, Ca, Mn, Cr. As the purity of the electrolyte decreases, the conductivity of the electrolyte is decreasing whereas the viscosity of the electrolyte is increasing. Cyclic Voltammetry was also performed, and based on these tests the high purity electrolyte has significantly better performance than the low purity ones. The performance of this electrolytes like columbic efficiency, voltage efficiency, energy efficiency, voltage, discharge capacities. Electro chemical testing revealed that lesser grade V_2O_5 raw materials were used to create electrolytes, which had weaker electrochemical activity and reversibility and greater solution resistance.

In a study, the feasibility, sustainability, and effectiveness assessment of three different procedures for preparation of vanadium acid-based electrolyte was done [46]. The different methods for preparation were dissolution of precursors (electrolyte A), chemical reduction using oxalic acid (electrolyte B), electrochemical reduction using home-made H-shaped

electrolysis cell. The properties like energy efficiency, charge-discharge capacity, cycle duration and stability of the electrolyte was analysed. The manufacture of electrolytes A and B ensured complete control over the preparation process, enabling them to reach the specified target in terms of total vanadium and chloride concentration. These electrolytes provided extremely excellent electrochemical performance.

2.8 Effects of various parameters on temperature distribution.

In a study of temperature distribution, the various parameters affecting the temperature distribution is studied. A three-dimensional model for VRFB is simulated and thermal analysis is done [47]. Ohmic heat gets vital in heat generation if applied current density is large enough. As current density increases, electrochemical reaction heat rises proportional, activation heat rises at parabolic rate, ohmic heat rises at parabolic rate. Variation in flow rate and current density substantially alter the charge/discharge characteristics, temperature rise and distribution of temperature [48]. As temperature increases, the magnitude of overpotential decreases. For lower temperatures, the decreased reaction rate constants lead to an increase in the magnitude of the overpotential in order to maintain fixed applied currents.

2.9 Research Motivation.

From the background and literature review, it has been observed that the parameters affecting the vanadium redox flow battery system are electrolyte flow rate, operating temperature, current density and overpotential heat. So, a meticulous study needs to be done to find optimum solutions to enhance the performance of the cell and analyse the temperature distribution pattern to eliminate the heat released due to electrochemical

reaction, ohmic resistance heat which gets accumulated over time and results in a decrease in the performance and lifespan of the cell, electrolyte, electrode, and membrane.

The novelty of this work is the preparation of the electrolyte using the chemical reduction method as mentioned in the literature review. Oxalic acid as a reducing agent has been reported in the literature but it has not been used and analysed for the reduction and performance of the battery. In this work, we use oxalic acid in a certain quantity or concentration for the composition of the main elements used in this cell. Also, the average temperature distribution is recorded for the cell during charge and discharge at both electrodes. The contours of temperature and current distribution in the electrodes are plotted to analyse the distribution for a triple serpentine flow field.

CHAPTER 3

RESEARCH OBJECTIVES

The main aim of this work is to study the performance behaviour of the Vanadium redox flow battery.

The specific objectives are:

- To investigate the performance of the RFB's cell under different operation conditions including:
 - current densities,
 - electrolyte flow rate,
 - operating temperature.
- To investigate the real-time temperature distribution at the cathode and anode during charge and discharge.
- To investigate the temperature distribution in the electrode at the cathode and anode associated with redox reaction in RFB's cell upon charging and discharging.

CHAPTER 4

RESEARCH METHODOLOGY

4.1 Materials and Electrolyte Preparation.

The materials used are Vanadium Pentoxide (V_2O_5), Solvent Sulfuric acid (H_2SO_4) and the reducing agent Oxalic acid ($C_2H_2O_4$).

Chemical reduction is the most often used and matured method for the preparation of electrolytes. Firstly, the raw material for this process is V_2O_5 . The V_2O_5 (V^{+5}) solution is prepared by using sulfuric acid and deionized water. 0.8 M V_2O_5 is mixed with 2.5 M sulfuric acid and deionized water is added to make 160 ml of solution. This solution is heated and stirred at a particular temperature and particular rpm respectively overnight to form a clear solution of V_2O_5 . 0.8 M of Oxalic acid as a reducing agent is added to the solution. The solution is heated and stirred at a particular temperature and particular rpm respectively for a certain time. The V^{+5} solution reduces and turns to V^{+3}/V^{+4}) and is poured into both the compartments of the VRFB, and the cell is analysed for charge and discharge. For a solution of 160 millilitres, 23.2 grams of Vanadium Pentoxide, 22.24 millilitres of sulfuric acid and 16.1 grams of Oxalic acid were used.

Chemical	Molar Mass
Vanadium Pentoxide (V_2O_5)	181.88 g/mol
Sulfuric acid (H_2SO_4)	98.079 g/mol
Oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$)	126.07 g/mol

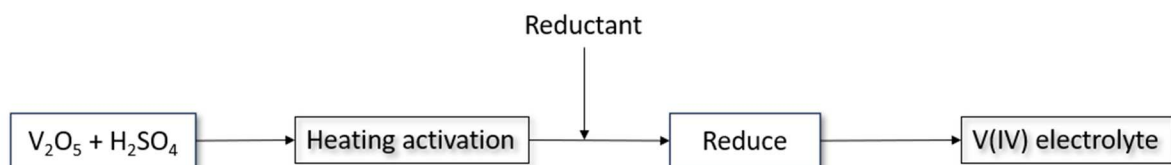


Fig. 1. The chemical reduction process of preparing vanadium electrolyte.

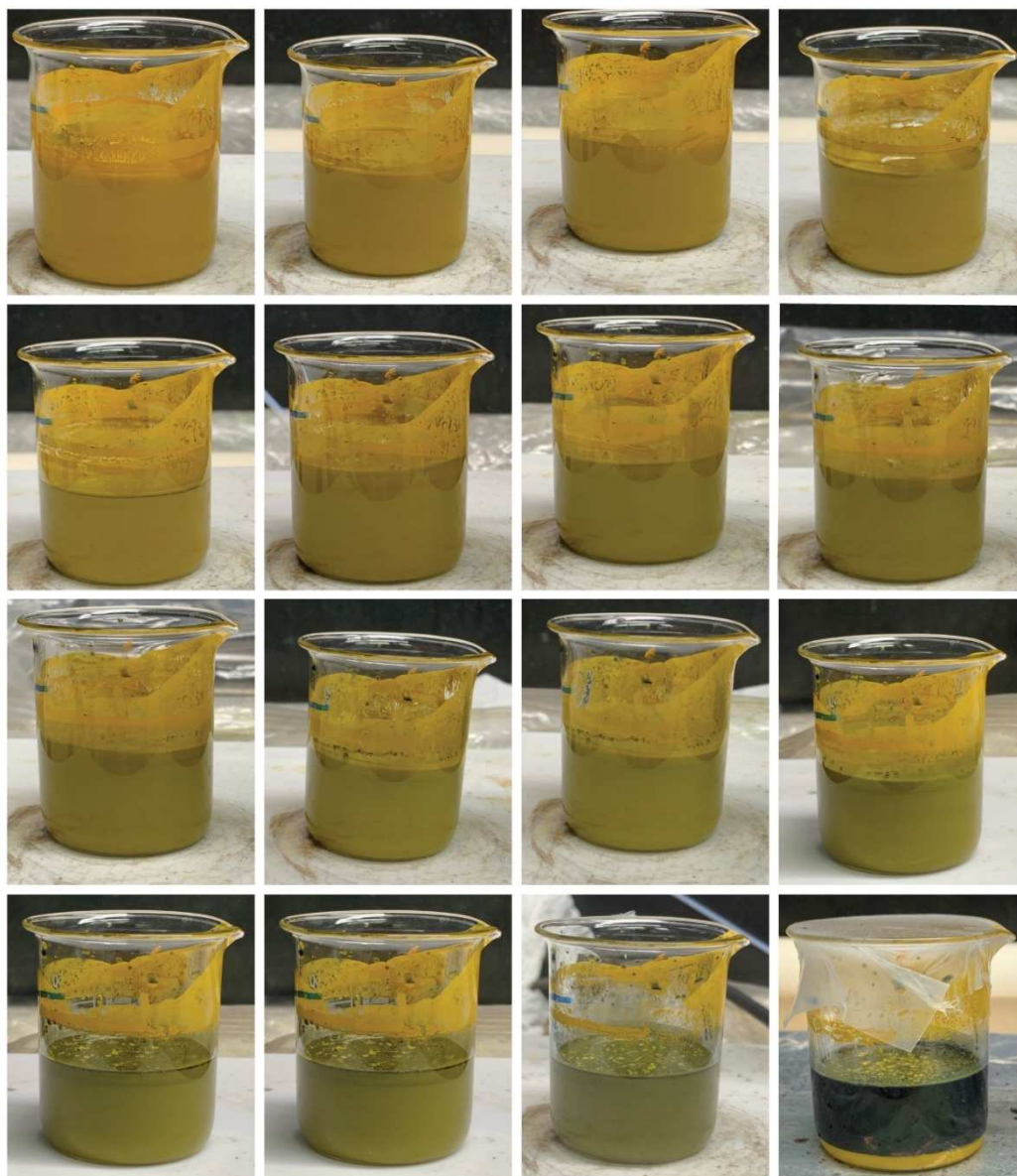


Fig. 2. Process of Preparation of electrolyte.

The electrodes used in the experiment are carbon felt from Sigracell as shown in Fig. 3. The thickness of the electrodes is 4.6 mm. These carbon-felt electrodes are heated in a muffle furnace at 400°C for about 10 hours. The heating of the electrodes is typically done to enhance the electrochemical performance of the cell. The surface structure of the electrode is changed by high-temperature treatment, which increases its surface area and adds more active sites for the vanadium ion redox processes. This enhances the charge/discharge efficiency of the battery by improving the kinetics of the processes. By thermal treatment, the surface functional groups get modified by introducing oxygen-containing groups which improves the wettability of the electrode, ensuring better contact with the electrolyte. Heat can lower the material's surface resistance by eliminating impurities or improving the electrode material's microstructure. This improves the battery's overall performance by reducing internal resistance. It increases the electrode material's mechanical strength and stability, making it more resilient to long-term use under the cyclic stress of VRFB systems.



Fig. 3. Muffle furnace and carbon felt electrodes for VRFB.

The membrane used for the experiment is the perfluoro sulfonic acid proton exchange membrane (T-N-212) also known as Nafion 212 as shown in Fig. 4. The membrane needs to be activated by cleaning and removing impurities, hydrating the membrane and preparing it for efficient ion exchange. To activate it, the membrane is immersed in 3% H_2O_2 solution and heated to 80°C for 1 hour. This removes the dirt and other organic contaminants from the membrane. The membrane is washed multiple times with deionized water before immersing it in 0.5 M H_2SO_4 and heating it to 80°C for 1 hour. This replaces sodium or other ions with protons (H^+), enhancing the ion exchange capacity. After this process, the membrane is kept immersed in deionized water until the membrane is used for the cell's fabrication.

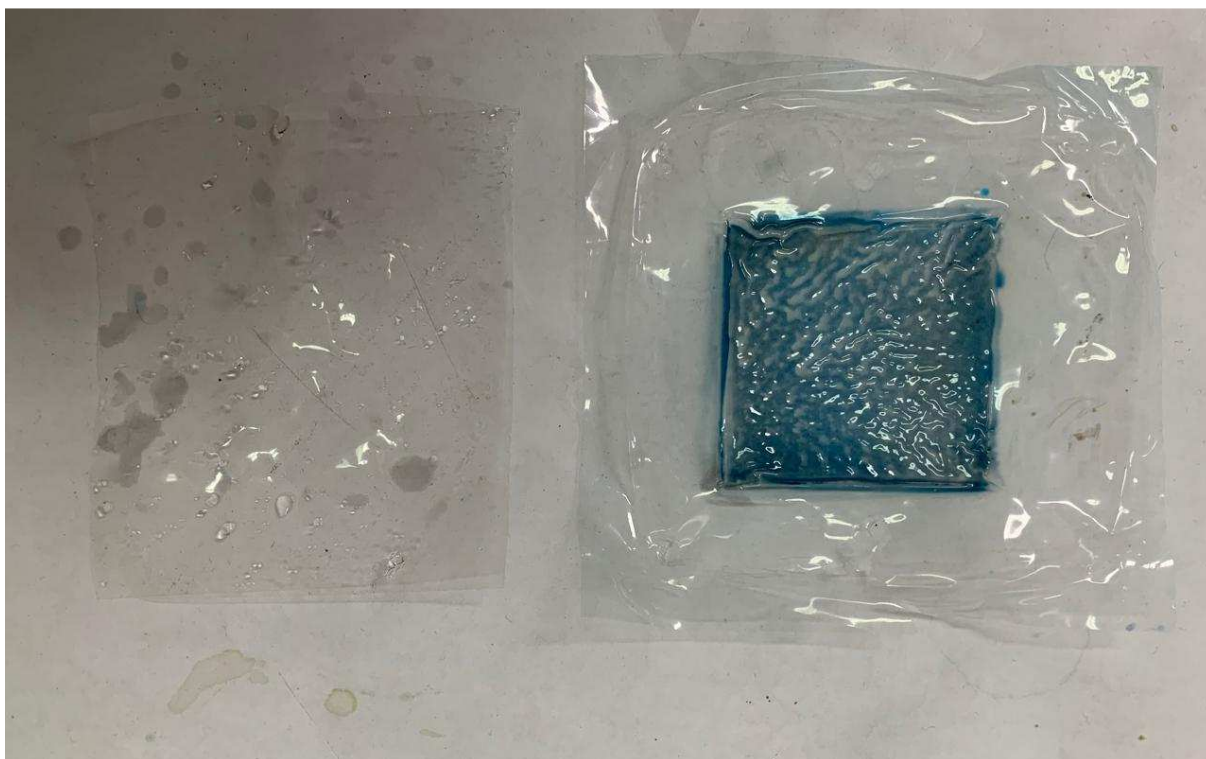


Fig. 4. Nafion membrane before and after use for VRFB.

The bipolar plate used in the experiment is made of carbon. The bipolar plate has a triple serpentine flow field for the circulation of electrolytes as shown in Fig. 5. The cross-sectional area of the flow field is 0.0315 x 0.04 inches. By ensuring consistent electrolyte flow across the electrode surface, the triple serpentine design minimises dead zones and enhances reactive species mass transport. Compared to single or double serpentine designs, this layout reduces pressure loss, which makes it energy-efficient for large-scale operations. The complex pathway also improves reaction kinetics by enhancing convective mixing and decreasing concentration polarization. Long-term operational reliability in energy systems depends on thermal stability, which is ensured by its sturdy architecture, which facilitates efficient heat dispersion.

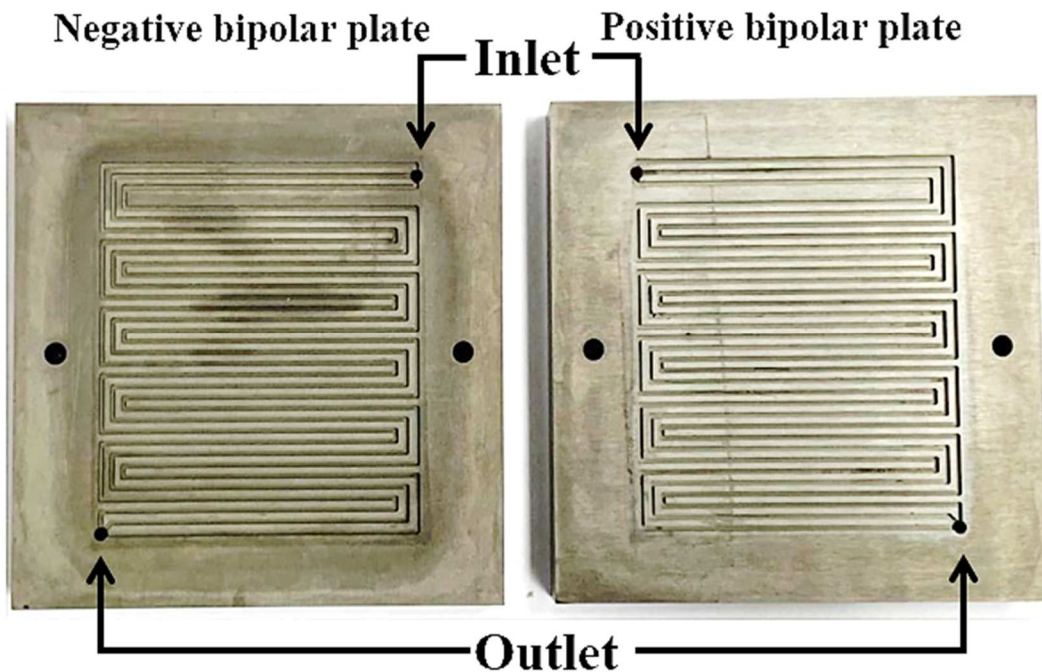


Fig. 5. The direction of electrolyte flow through the bipolar plate.

To maintain a constant temperature for the cell or to isolate it from the surrounding temperature, a glass wool duct is used. It is an excellent thermal insulator, which prevents heat exchange between the outside and inside of the material. The glass wool is made into fine particles to fill the spaces and gaps, and a wall is placed around the cell as shown in Fig. 6.

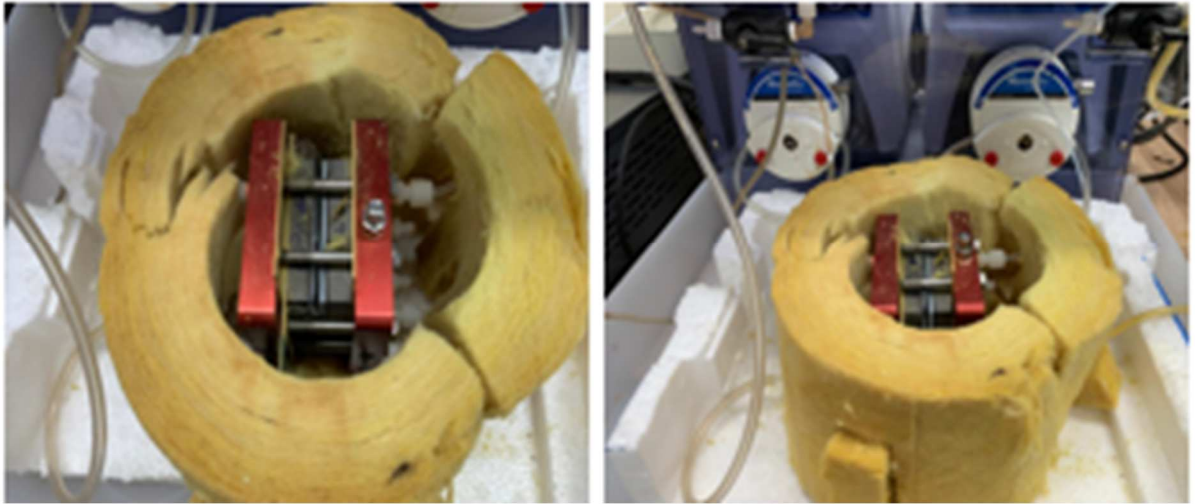


Fig. 6. Thermal isolation of the cell using glass wool.

4.2 Fabrication of cell.

The fabrication or assembling of the cell is another important aspect to make it function properly and leak proof.

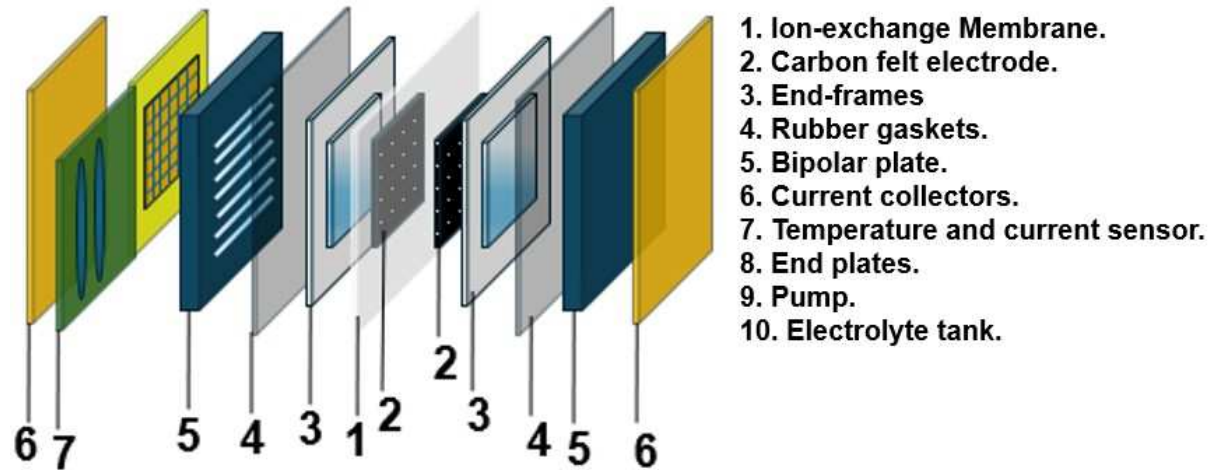


Fig. 7. Schematic diagram of the cell.

The main component of the cell consists of end-frame, current collector, carbon plates, graphite felt, mid-frame and nafion membrane.

The flow channel is grooved into the carbon plates which can have serpentine flow, interdigitated flow etc., which allows the electrolyte to flow in these channels. The graphite felt act as an electrode and has a high conductivity, favourable permeability. Nafion membrane is used to allow the transfer of ions from anolyte and catholyte and through the external circuit electrons flow and generate the electricity. The electrolytes are stored in positive and negative tanks known as catholyte and anolyte respectively.

4.3 Pre-charge or formation of electrolyte.

The pre-charge or formation of electrolyte refers to the initial process of electrochemically converting the vanadium ions into the desired state for galvanostatic cycling. The Vanadium Pentoxide in its raw electrolyte state has V+5 ions which is chemically reduced with oxalic acid to a mixture of V+4 and V+3 state. To create the balance required for the redox reactions during charge/discharge cycles, a portion of this vanadium is electrochemically converted into other redox-active species, such as V+4, V+3, and V+2, during the pre-charge stage. Once the vanadium is in its respective oxidation state at the anode and cathode the cell is then ready for galvanostatic cycling. Usually, to obtain this, an external voltage is applied to the cell across the battery electrodes which initiates the redox reactions at both the electrodes. The process is continued until the appropriate proportions of vanadium in the required oxidation states are achieved. The pre-charge process is monitored until the desired state-of-charge (SOC) is reached, often measured via cell voltage.

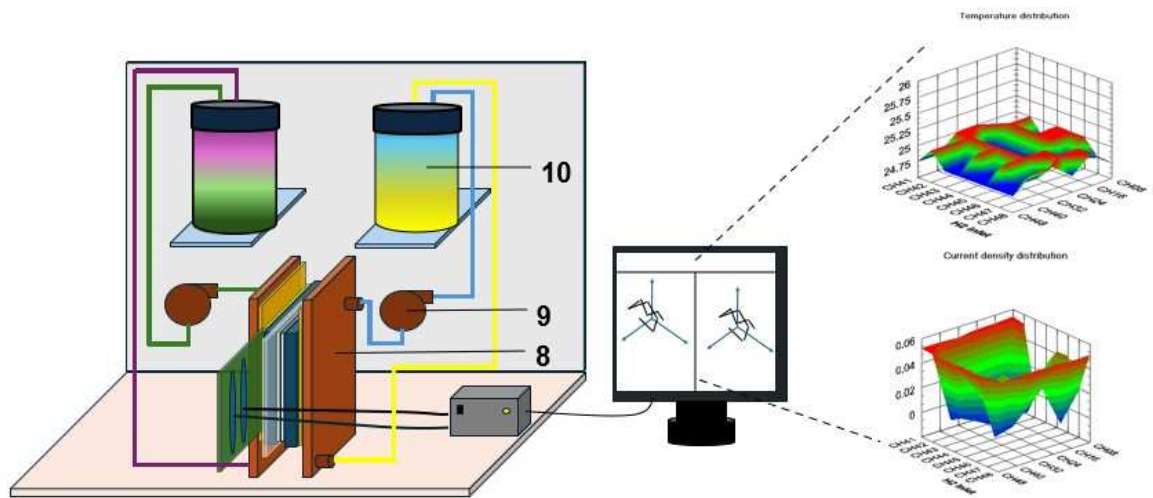


Fig. 8. Schematic diagram of Vanadium redox flow battery system.

The four different oxidation states of the Vanadium pentoxide are:



Fig. 9. Representation of Vanadium oxidation states [49].

4.4 Measurement of temperature and current.

The DiLiCo current and temperature density sensor from DiLiCo Engineering is used to detect the temperature and current distribution in the cell's electrolyte flow field. When mounted, the sensor's segmented front side contacts the monopolar plate's back side, while the unsegmented rear side holds the DiLiCo DAS connection plug. To seal the media supply's entrance and outlet, four gasket rings are positioned at each of the sensor layer's four corner segments. The gaskets of the Scribner cell's counter plate seal the circular channel on the rear. Similar in size to the active area of the galvanic element's membrane, the sensor layer's active area is 25 cm². Each of the 48 segments is 5.9 mm wide and 8 mm long. The limits of the insulated segments are 0.4 mm wide. For every section, both positive and negative currents are measured. The accuracy of the temperature sensor is $\pm 0.5^{\circ}\text{C}$.

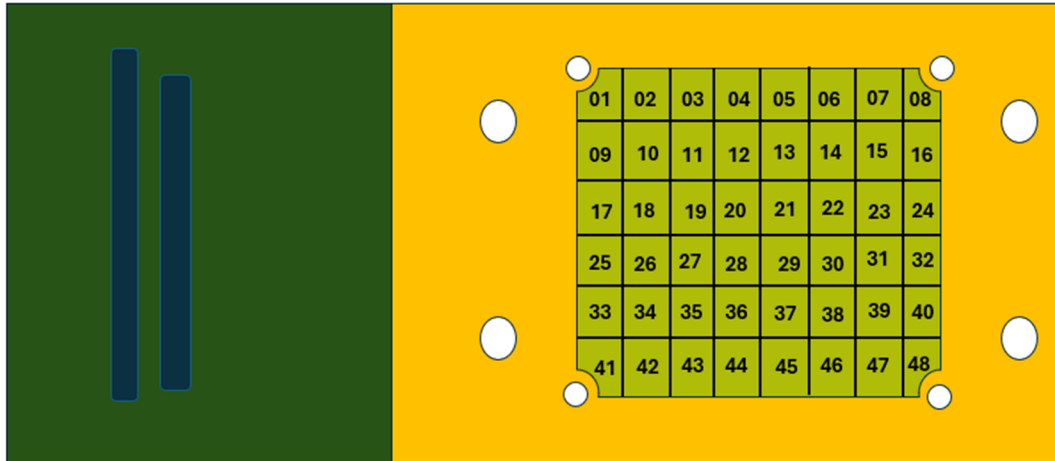


Fig. 10. DiLiCo current and temperature sensor with 48 segments.

4.5 Uncertainties and errors in measurements.

The uncertainties and errors in measurements are the fundamental concepts in scientific and engineering practices, where precise and accurate measurements are critical.

➤ Types of errors in measurements

- Systematic errors
- Random errors

• Systematic errors:

- 1) It affects the accuracy in measurement.
- 2) It affects all measurements similarly (all low or all high.)
- 3) Not revealed by repetition.
- 4) It can sometimes be eliminated.
- 5) It is often difficult to quantify.

• Random errors:

- 1) It affects the precision of measurement.

- 2) It affects the measurements randomly (some low and some high.)
- 3) Revealed by repetition.
- 4) It can never be eliminated.
- 5) It can always be quantified.

Uncertainty in temperature measurement can be categorized into two types.

Systematic error: The operating temperature for the cell can be considered as systematic error and an absolute uncertainty in the measurement is given as 25 ± 1 °C by the Scribner redox flow cell system.

Random error: The temperature measurement by the DiLiCo sensor at the electrodes can be considered a random error and a relative uncertainty in the measurement is given as $(\Delta x/x)$ where Δx is the accuracy of the sensor (0.5 °C) and x is the measured value.

CHAPTER 5

RESULTS

5.1 Pre-charge/formation of electrolytes before galvanostatic cycling and in-operando temperature measurement.

Pre-charge is essential to make the electrolyte suitable for galvanostatic cyclic. A stepwise electrolyte preparation is shown in Fig. 2. This shows how the colour of the electrolyte changes with stirring for a long time, and the colour of the electrolyte represents the oxidation states. When the vanadium precursor is completely dissolved in the presence of the reducing agent, it is blue, indicating V^{+4} oxidation states ([50] Fig. 9). Thus, further changing the oxidation states is required according to the reaction (1 & 2) for the preparation of catholyte and anolyte. 40 mL of the prepared electrolyte solution (+4 oxidation state) is placed in the negative tank, and 80 mL of the same electrolyte is placed in a positive tank. A current density of 40 mA cm^{-2} is applied during the pre-charging. The reaction occurs in this condition, and the cell gets fully charged with the upper potential window of 1.8 V cut-off. After pre-charging, the catholyte gets oxidized and reaches the V^{+5} oxidation state, and the anolyte gets reduced and tends to reach the V^{+2} oxidation state. Half of the electrolyte (40 mL) from the positive tank is removed to make the anolyte and catholyte capacity balance. This is followed by discharge (0.8 V lower cut-off) with the same current density to make subsequent galvanostatic cycling with in-operando temperature analysis at the bipolar plates.

5.2 In-operando temperature analysis at the electrodes: full-cell configuration.

The study represents a detailed analysis investigating the effects of various operating parameters such as current density, flow rate, and operating temperature to see the temperature behaviour at the negative and positive bipolar plates during the galvanostatic cycling in full-cell configuration. Three operating parameters were considered to make this detailed analysis. The temperature analysis is done on the following cases; (i) the cell and electrolyte tanks were kept at a constant operating temperature of 25 °C with the electrolyte flow rate of 50 mL min⁻¹ and the applied charge-discharge current density of 60 mA cm⁻², 75 mA cm⁻², and 90 mA cm⁻² (ii) operating temperature of 25 °C with the electrolyte flow rate of 100 mL min⁻¹ and the applied charge-discharge current density of 60 mA cm⁻², 75 mA cm⁻², and 90 mA cm⁻², and (iii) operating temperature of 30 °C with the electrolyte flow rate of 100 mL min⁻¹ and the applied charge-discharge current density of 60 mA cm⁻². In all the discussed cases, the temperature analysis is done at the negative and positive sides of the bipolar plate separately during the galvanostatic cycling.

5.2.1 In-operando temperature analysis at the negative electrode (anode) in full-cell during the galvanostatic cycling with different parameters.

A galvanostatic cycling with different current densities ranging from 60 mA cm⁻² to 90 mA cm⁻² for 15 cycles with an operating temperature of 25°C and electrolyte flow rate of 50 mL min⁻¹, is performed and represented in Fig. 11. A voltage profile vs. time is shown in Fig. 11a along with the temperature profile vs. time which is recorded at the negative electrode during the charge-discharge cycling. The temperature profile is similar at

different current densities (Fig. 11). It indicates that it increases during the charging process and reaches a maximum when the uppercut off voltage reaches 1.8 V. During the discharging process, the temperature starts decreasing. It reaches a lower value when the cell is completely discharged (i.e., 0.8 V). The temperature profile nature is quite like the voltage profile as depicted in Fig. 11a. The discharge capacity (mAh) vs. cycling is shown in Fig. 11b. A discharge capacity of ~940 mAh is observed after 5 cycles at the current density of 60 mA cm⁻² and when the current density was increased to 75 mA cm⁻², the discharge capacity was observed ~922 mAh after 10 cycles. A further increase of the current density, the discharge capacity was observed ~912 mAh after 15 cycles which is quite good even after applying the high current density. A 97% discharge capacity retention is observed from the 5th (considered 100%) to the 15th cycles when the current density is increased from 60 mA cm⁻² to 90 mA cm⁻². The Coulombic, energy, and Voltaic efficiency is calculated and depicted in Fig. 11c. It shows the Coulombic efficiency is slightly increased with increasing the current density from 60 mA cm⁻² to 90 mA cm⁻² and remains almost constant over the 15 cycles; however, the Coulombic efficiency is below the 90%. Voltaic efficiency is pretty good and observed at ~80% at the current density of 60 mA cm⁻². The Voltaic efficiency decreases with increasing the current density (Fig. 11c). At the current density of 75 mA cm⁻² the Voltaic efficiency decreases around 5% after 10 cycles concerning the initial applied current density. At the current density of 90 mA cm⁻², the Voltaic efficiency is observed ~71% after 15 cycles. These results show the highest Voltaic efficiency at the current density of 60 mA cm⁻². Similarly, a trend of energy efficiency decreased with increasing the current density is shown in Fig. 11c. At the current density of 60 mA cm⁻², the energy efficiency is recorded at ~69%, which decreased to ~62% after

15 cycles at the current density of 90 mA cm^{-2} . A single cycle, which is the 3rd cycle at the current density of 60 mA cm^{-2} for the voltage, temperature vs time, is shown in Fig. 12a, and the corresponding temperature distribution at the negative electrode (anode) of the cell is shown in Fig. 12b & Fig. 12c during the charge and discharge cycles. Fig. 12b represents the average temperature distribution in the area of 25 cm^2 at the negative electrode during the charge process. It shows the temperature is non-uniformly distributed in the electrodes and few localized hotspots can be seen in the electrodes due to resistive losses and localized heating in the electrodes. The temperature decreases during the discharge process at the negative electrode (Fig. 12a), and the temperature distribution seems non-uniform throughout the negative plate (Fig. 12c). Also, the voltage vs. time and temperature vs. time is plotted for each cycle along with its corresponding charge and discharge average temperature contours as shown in Fig. 13. The temperature during discharge is higher than the temperature during charge. This is because of the endothermic nature of the reaction during charge and exothermic reaction during discharge. This suggests that during the charge and discharge, the temperature increases and decreases with non-uniform distribution at the plate [47]. Similarly, 3rd cycle of voltage, temperature vs. time, is depicted in Fig. 14a for the higher current density of 75 mA cm^{-2} to see the temperature distribution behaviour at the negative electrode during the charge (Fig. 14b) and discharge (Fig. 14c). It indicates that the temperature changes abruptly at the negative electrode during the charge. Also, a sharp rise in temperature spots is visible at the edges side of the electrode (Fig. 14b). During the discharge, the temperature decreases with fluctuations, and the middle part of the negative cell seems slightly lower in the temperature distribution compared to the area near the edges. Fig. 15 shows the voltage vs. time and temperature

vs. time plots and their corresponding temperature distribution contours at charge and discharge for the individual cycle at 75 mA.cm^{-2} current density. Further, at the increased current density of 90 mA cm^{-2} , the 3rd voltage cycle, temperature vs. time, is shown in Fig. 16. The temperature rise and fall profiles are similar to the previous, current density, as discussed above. However, the temperature rise is slightly below during the charge (Fig. 16b) and discharge (Fig. 16c) at the current density of 90 mA cm^{-2} . Fig. 17 shows the voltage vs. time and temperature vs. time plots and their corresponding temperature distribution contours at charge and discharge for the individual cycle at 90 mA.cm^{-2} current density.

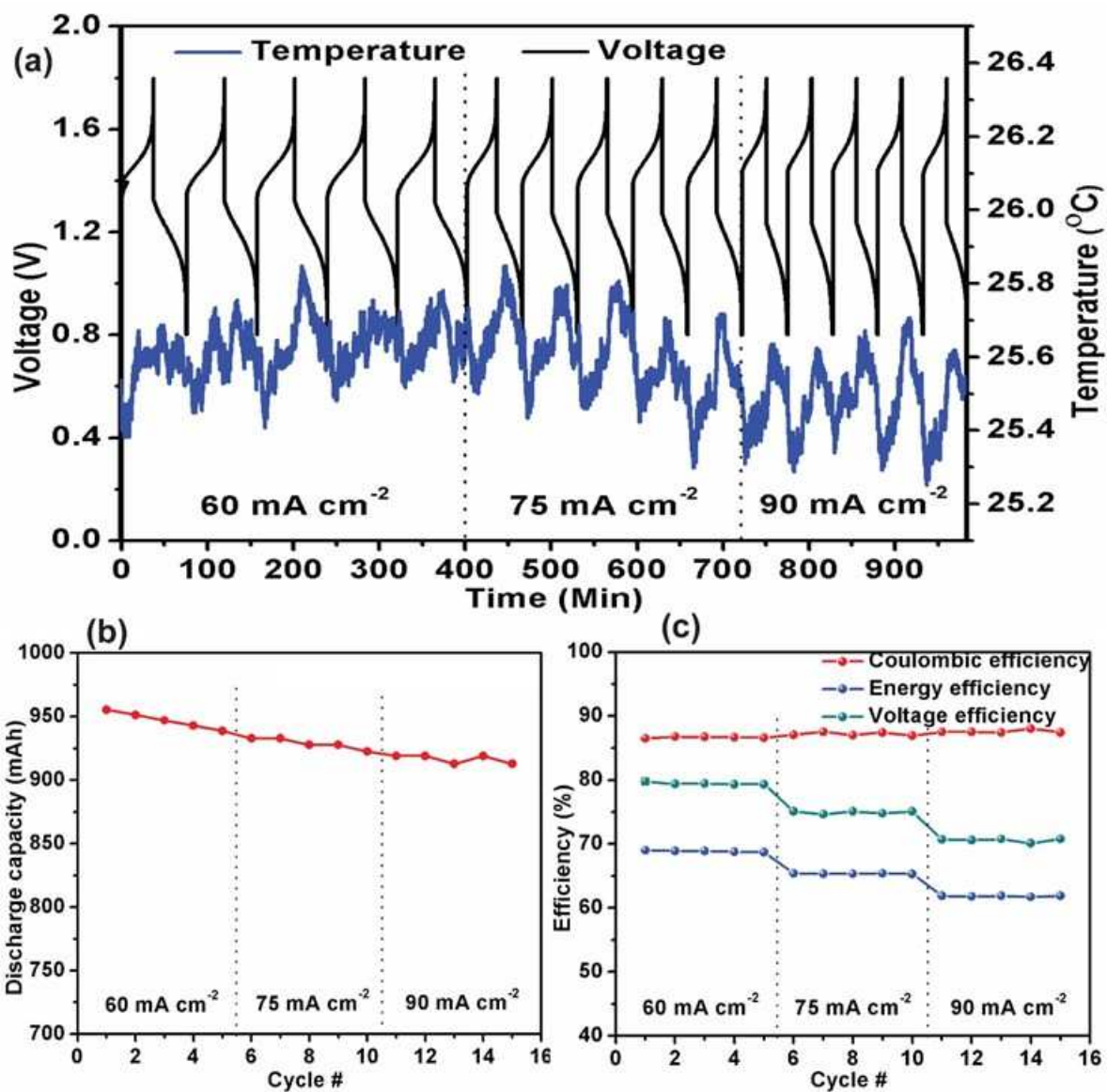


Fig. 11. Electrochemical performance in the full-cell configuration of VRFB at the negative side of the full cell at 50 ml/min. (a) Voltage and temperature vs. time plot at the different current densities ranging from 60 – 90 mA cm^{-2} , (b) discharge capacity vs. cycles at different current densities as given in Fig. a, (c) Coulombic, Energy, and Voltaic efficiencies vs. cycles.

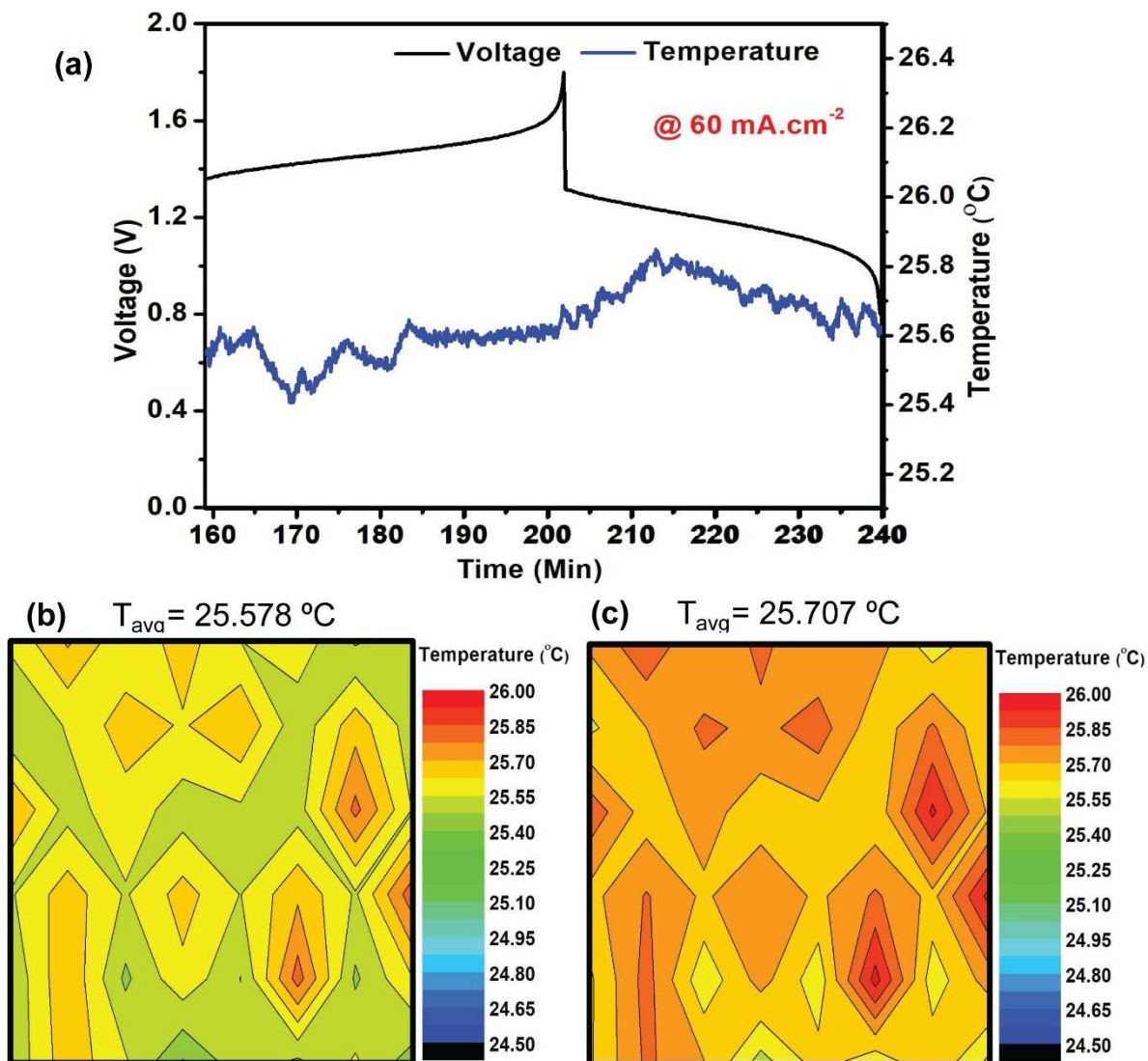


Fig. 12. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the negative side of the full cell at 50 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 60 mA cm⁻², (b) temperature contour plot at the negative side during the charging at 60 mA cm⁻², (c) temperature contour plot at the negative side during the discharge at 60 mA cm⁻².

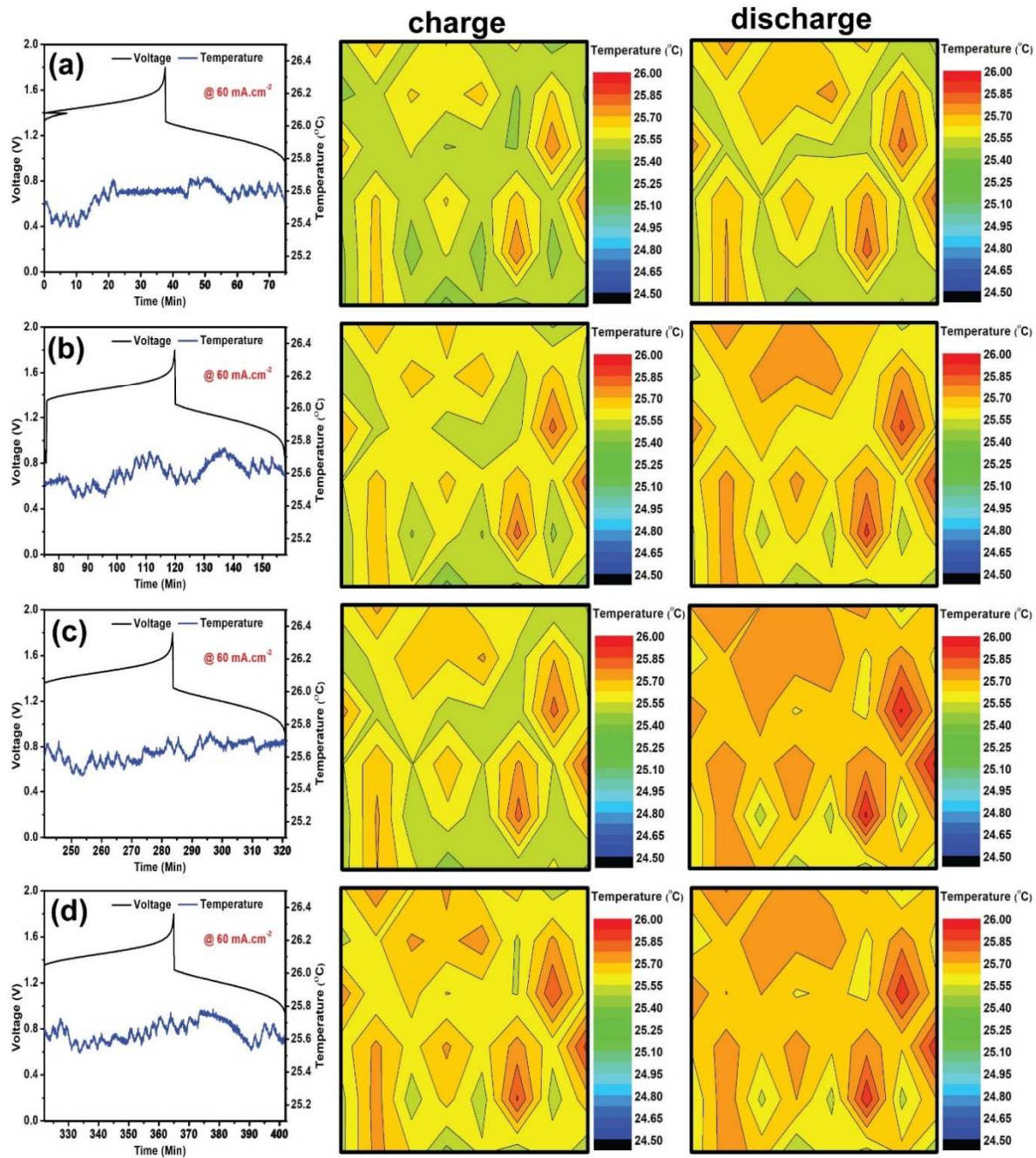


Fig. 13. (a) 1st cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours.

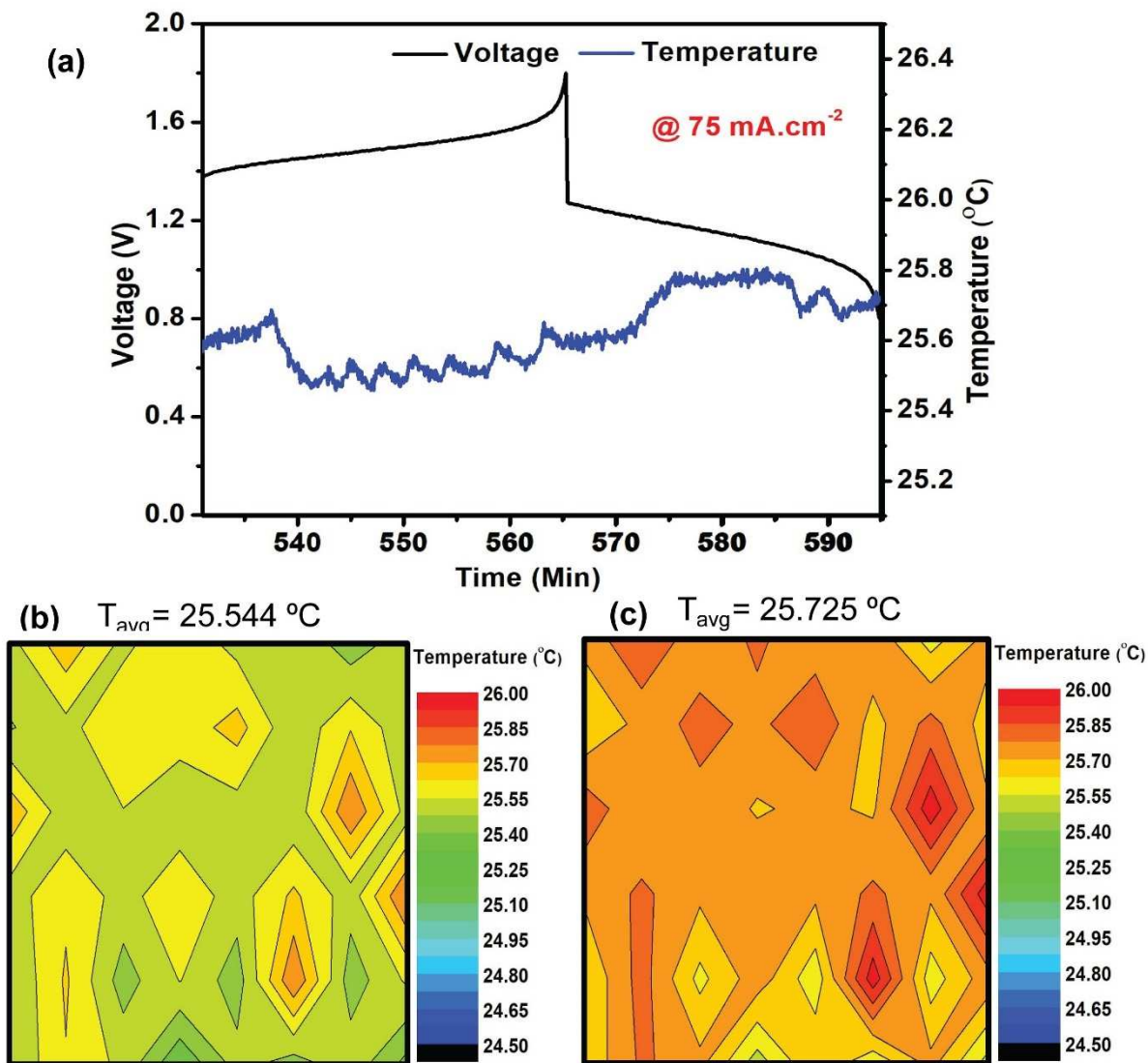


Fig. 14. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the negative side of the full cell at 50 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 75 mA cm^{-2} , (b) temperature contour plot at the negative side during the charging at 75 mA cm^{-2} , (c) temperature contour plot at the negative side during the discharge at 75 mA cm^{-2} .

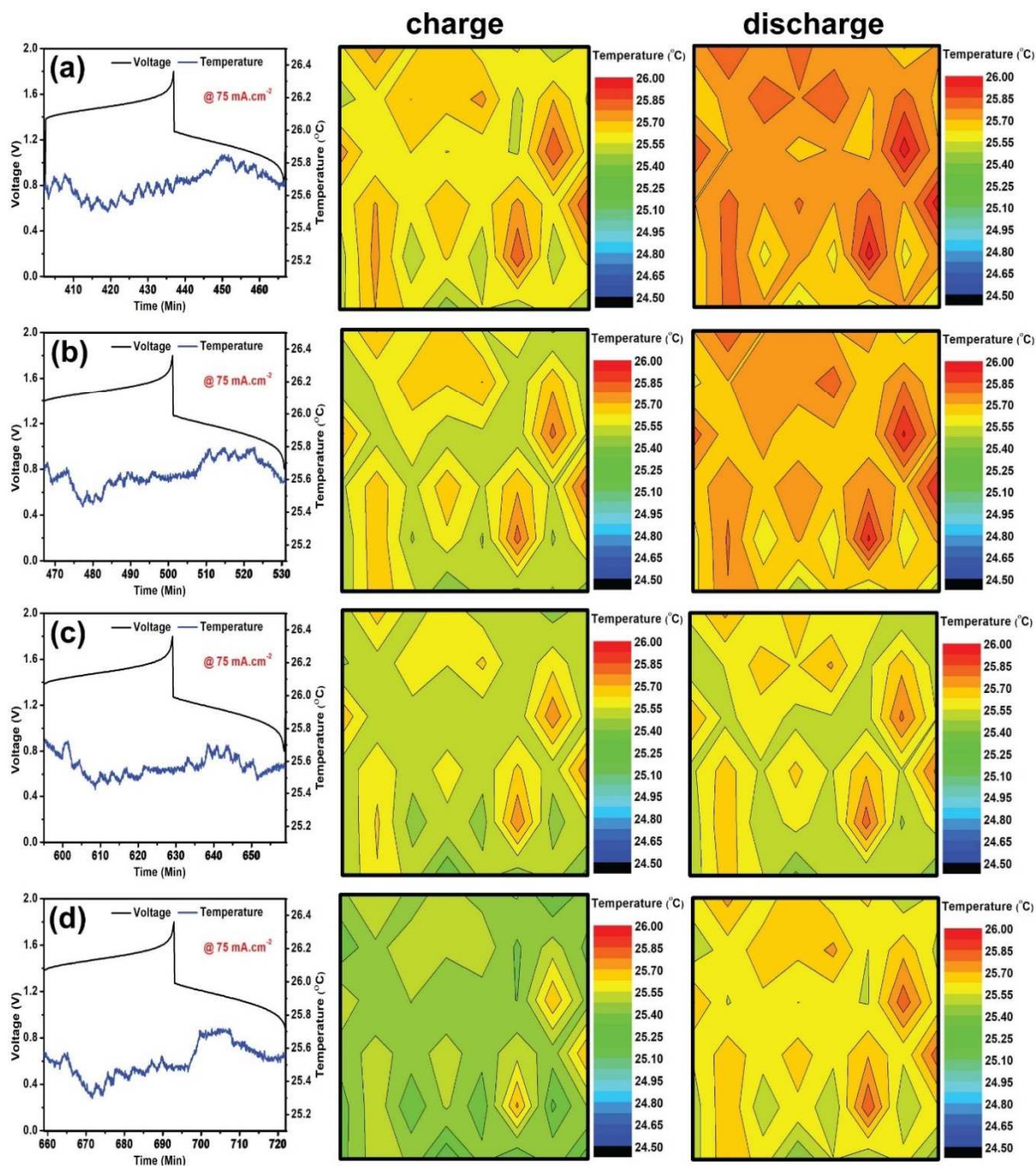


Fig. 15. (a) 1st cycle voltage and temperature vs. time at the current density of 75 mA cm⁻² and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 75 mA cm⁻² and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 75 mA cm⁻² and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 75 mA cm⁻² and its corresponding contours.

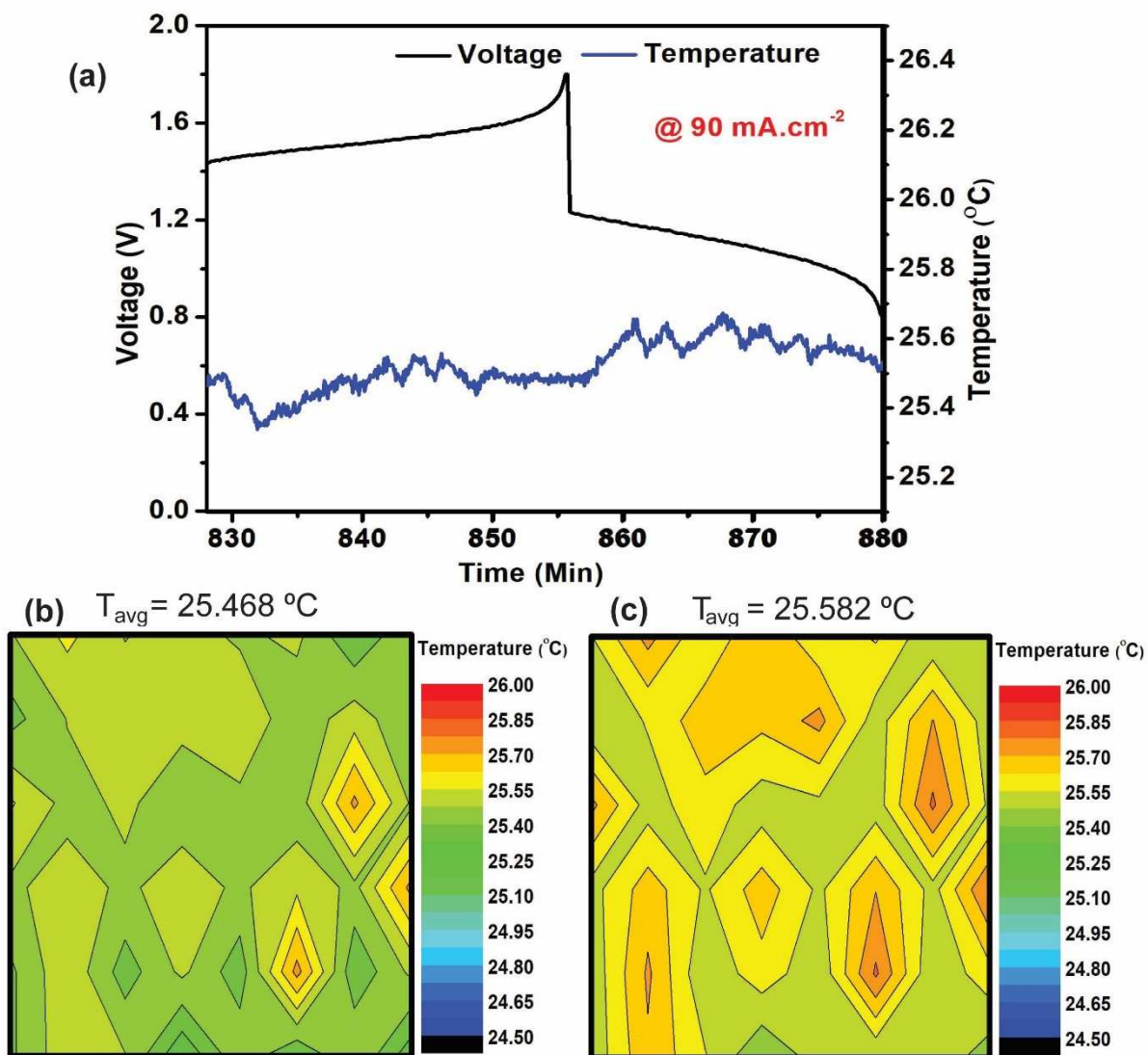


Fig. 16. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the negative side of the full cell at 50 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} , (b) temperature contour plot at the negative side during the charging at 90 mA cm^{-2} , (c) temperature contour plot at the negative side during the discharge at 90 mA cm^{-2} .

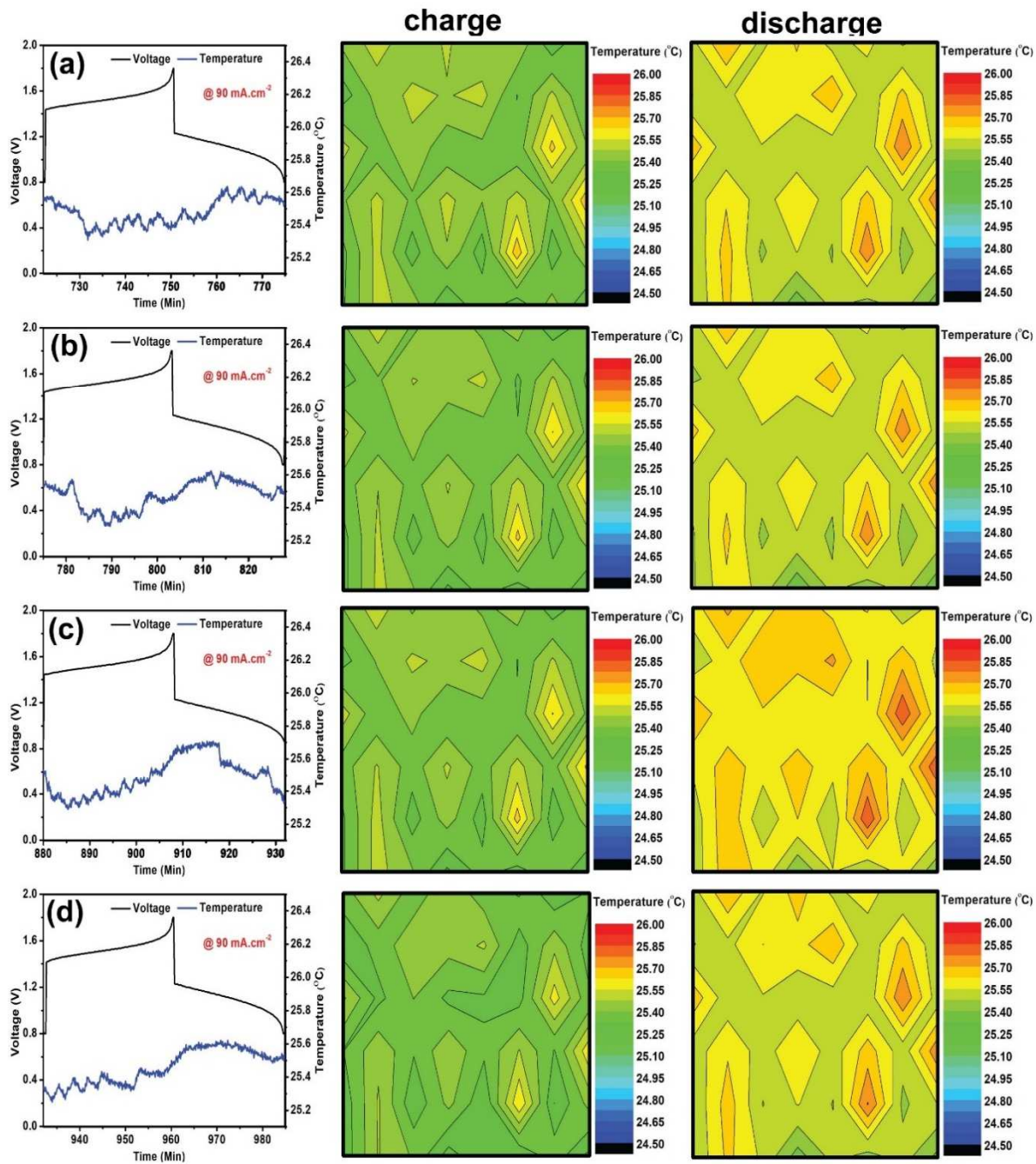


Fig. 17. (a) 1st cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours.

Temperature distribution at the negative side of the full cell during the charge and discharge is further measured when the flow rate is changed from 50 mL min⁻¹ to 100 mL min⁻¹. A total of 15 charge and discharge cycles are performed by varying the current densities of 60 mA cm⁻², 75 mA cm⁻², and 90 mA cm⁻², performing 5 cycles each, as shown in Fig. 18, along with voltage, temperature vs. time. The temperature increases along with the rise in voltage during the charging up to 1.8 V. The temperature decreases with discharging processing, as shown in Fig. 18a. These profiles are like the previously discussed case. The discharge capacity vs. cycling with the mentioned current density from the range of 60 mA cm⁻² to 90 mA cm⁻² is given in Fig. 18b. The discharge capacity over the 5th cycle at 60 mA cm⁻² is ~ 1185 mAh, whereas for the 10th cycle at 75 mA cm⁻² is ~ 1120 mAh and ~ 1050 mAh at 90 mA cm⁻² over the 15th cycle. The drop in the capacities for an increase in current density is expected with increasing the current density due to the kinetics and mass diffusion limitation [51]. The retention discharge capacity of 88% is observed from the 5th (considered 100%) cycle to the 15th cycle for a variation of current density from 60 mA cm⁻² to 90 mA cm⁻². Here, the discharge capacity is higher with the higher flow rate (100 mL min⁻¹) of the electrolyte compared with the flow rate of 50 mL min⁻¹ (Fig. 18b) [52]. This indicates that the flow rate can significantly impact the discharge capacity. The coulombic, energy, and voltaic efficiency are depicted in Fig. 18c. The coulombic efficiency remains nearly constant in all the cycles, varying from 60 mA cm⁻² to 90 mA cm⁻², but less than 90%. The voltaic efficiency vs. cycles is also shown in Fig. 18c, which decreases with increasing the current density; however, the voltaic efficiency is lower at a higher flow rate of 100 mL min⁻¹ compared to the lower flow rate of 50 mL min⁻¹ (Fig. 11c). The observed voltaic efficiency is ~ 72% for the 5th cycle at 60 mA cm⁻² and gradually

decreasing to ~ 65% for 10th cycle at 75 mA cm⁻² and ~ 60% for 15th cycle at 90 mA cm⁻². A similar trend is also observed for energy efficiency. The observed energy efficiencies are ~ 62%, ~ 57%, and ~ 52% for current densities 60 mA cm⁻², 75 mA cm⁻² and 90 mA cm⁻² as shown in Fig. 18c. A voltage, temperature vs. time plot for a single charge-discharge cycle for 60 mA cm⁻² is shown in Fig. 19a and the corresponding temperature contour plot at the negative cell (25 cm² area) for the charge and discharge process shown in Fig. 19b & Fig. 19c. It is observed from the temperature contour plot during the charging process (Fig. 19b) that domains of hot spots are distributed evenly and surrounded by slightly lower hot spots, as same is the case during the discharging process (Fig. 19c). A similar trend for the temperature profile (Fig. 21a) and the temperature contour plots (Fig. 21b & Fig. 21c) is observed when the current density of the charge-discharge process is increased to 75 mA cm⁻² from 60 mA cm⁻². Further, increasing the current density to 90 mA cm⁻², the temperature contour plots characteristics during the charging and discharging process remain the same, as shown in Fig. 23a-c. However, the temperature in the electrodes decreased slightly as current density increased due to limitations in mass transport [51]. Also, the temperature fluctuations can be seen at higher flow rates because of the variation of resistance and rate of heat absorption and release in chemical reactions during charge and discharge [41]. The voltage vs. time, temperature vs. time plots of all the cycles at 60 mA.cm⁻², 75 mA .cm⁻² and 90 mA.cm⁻² are shown in Fig. 20, Fig. 22, and Fig. 24 respectively.

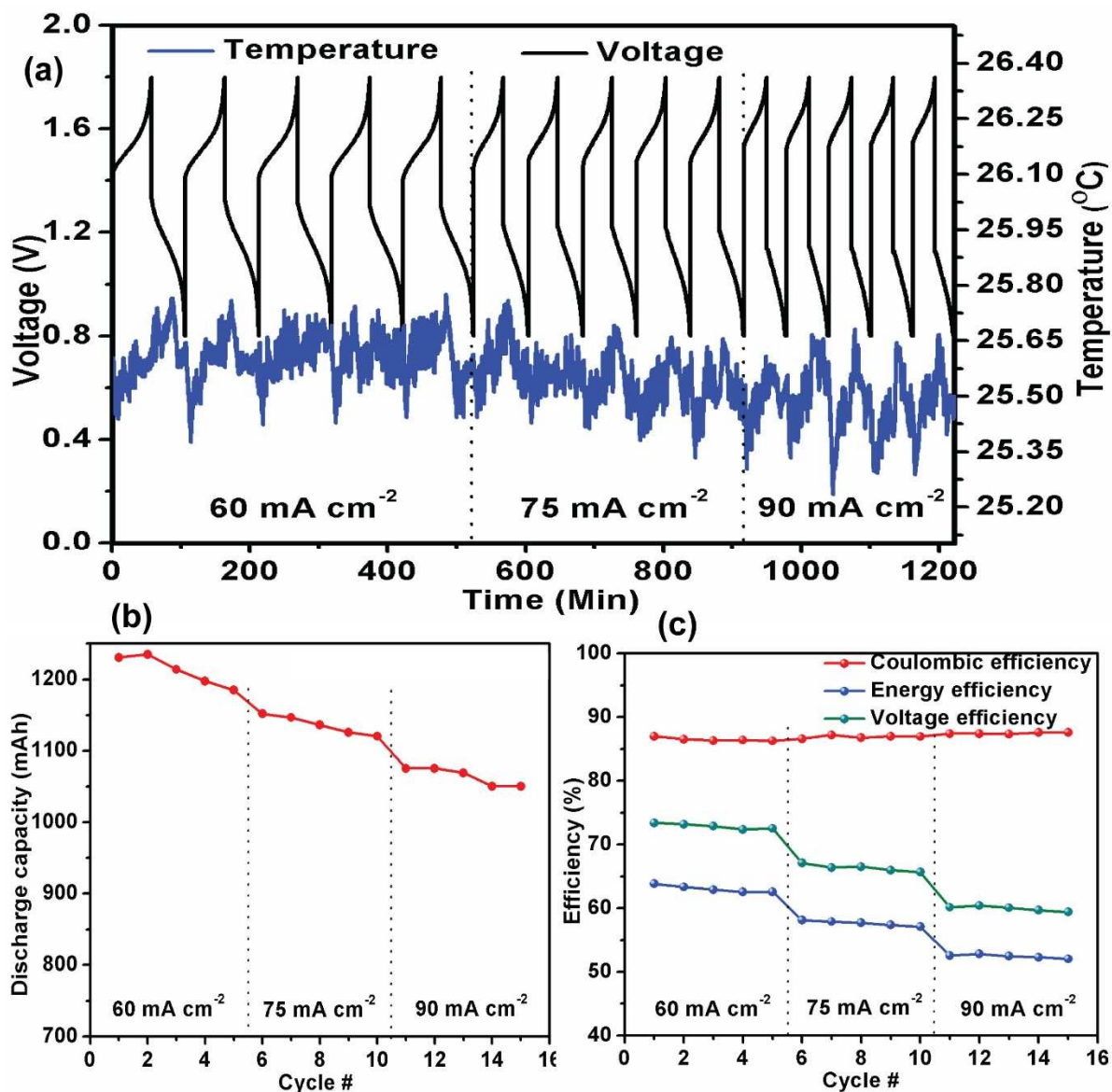


Fig. 18. Electrochemical performance in the full-cell configuration of VRFB at the negative side of the full cell at 100 ml/min. (a) Voltage and temperature vs. time plot at the different current densities ranging from 60 – 90 mA cm⁻², (b) discharge capacity vs. cycles at different current densities as given in Fig. a, (c) Coulombic, Energy, and Voltage efficiencies vs. cycles.

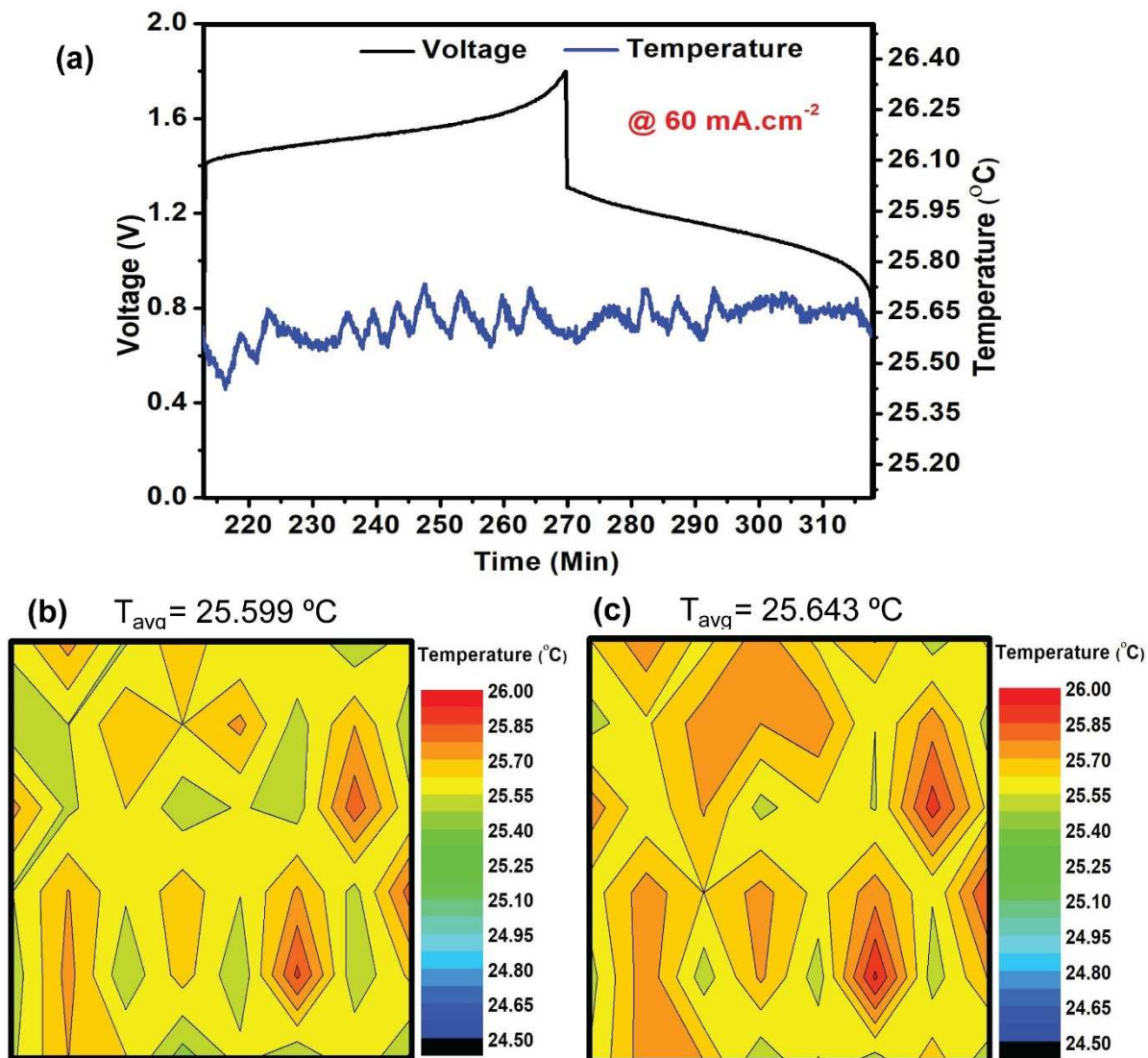


Fig. 19. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the negative side of the full cell at 100 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} , (b) temperature contour plot at the negative side during the charging at 60 mA cm^{-2} , (c) temperature contour plot at the negative side during the discharge at 60 mA cm^{-2} .

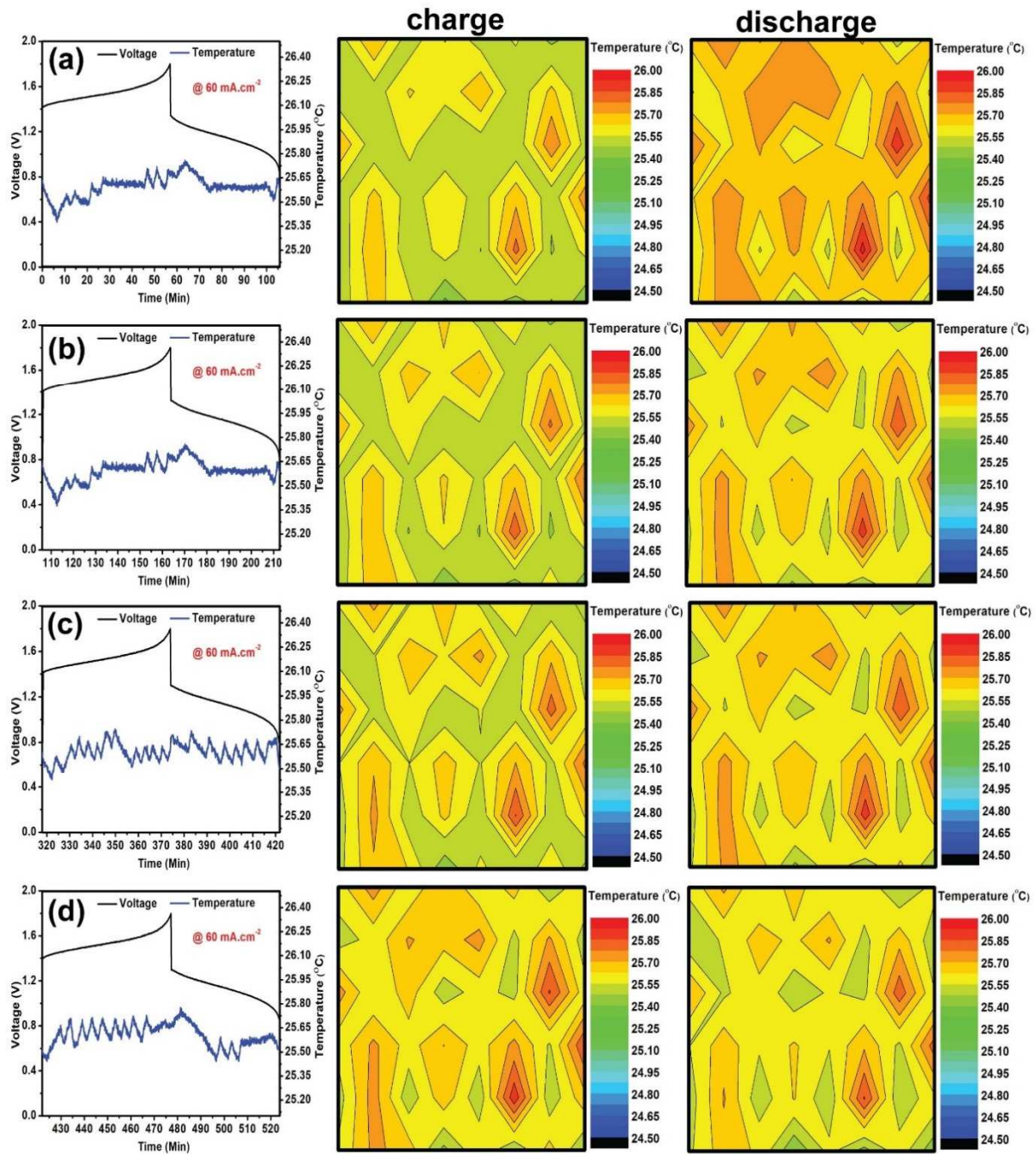


Fig. 20. (a) 1st cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours.

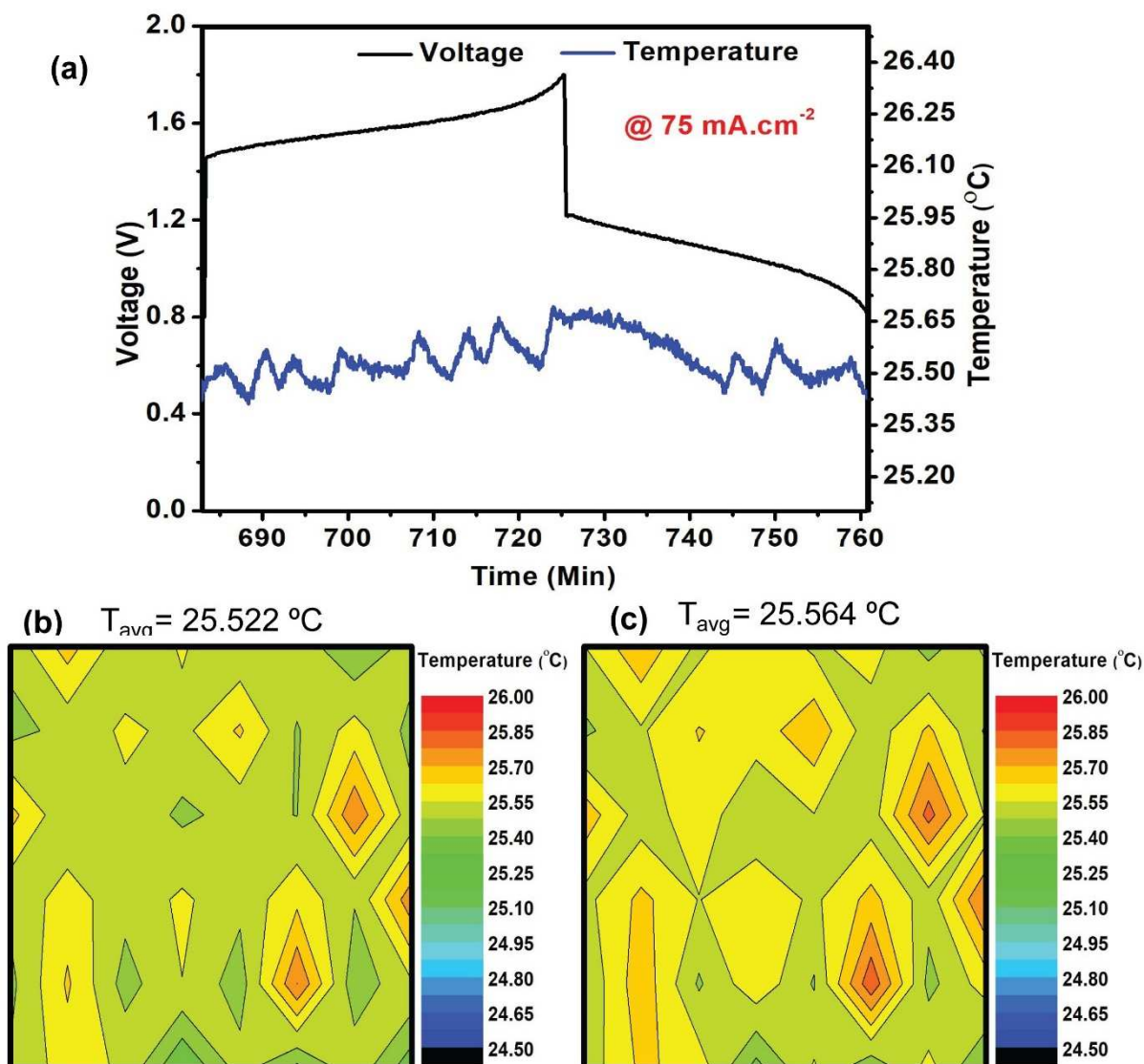
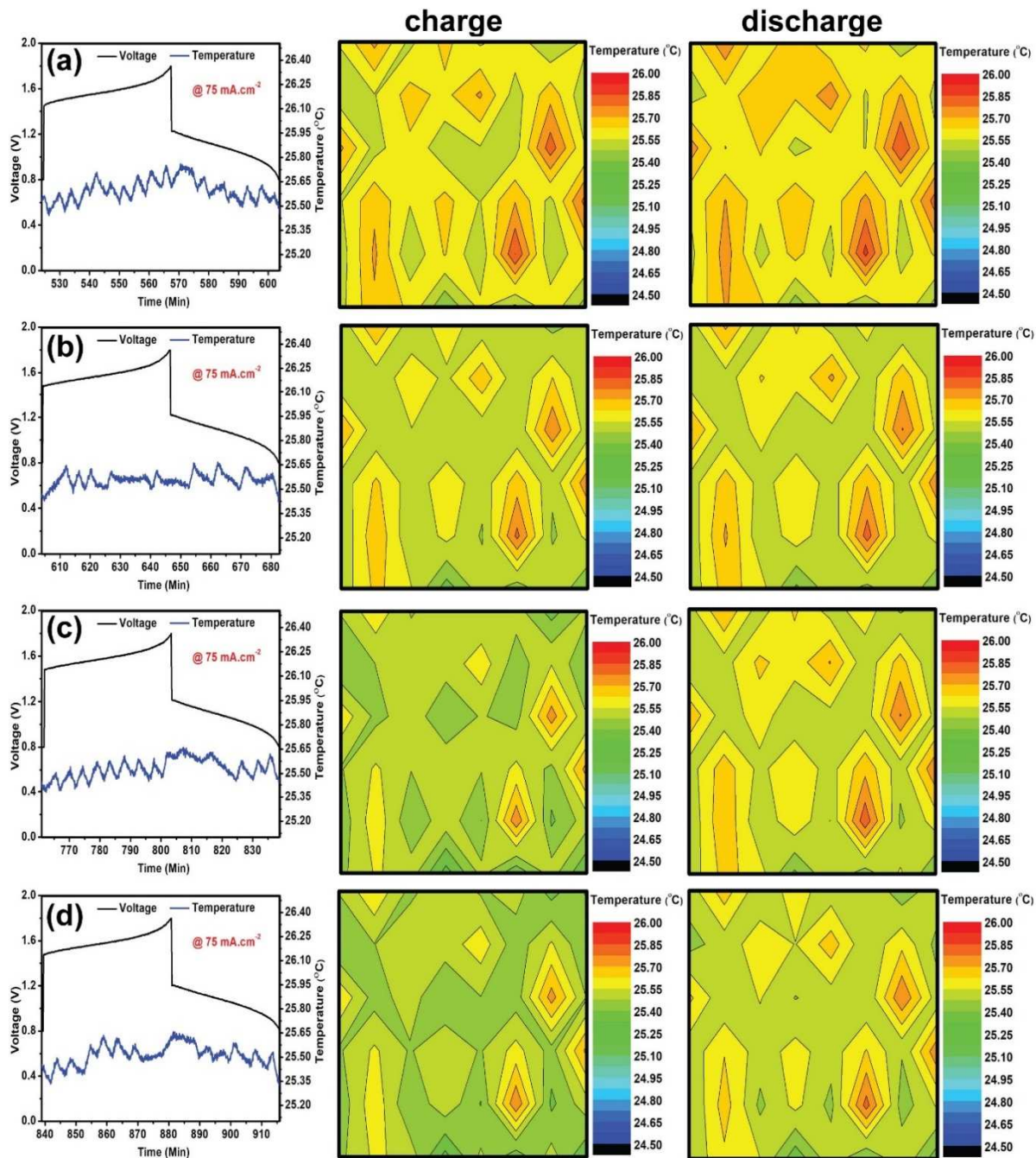


Fig. 21. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the negative side of the full cell at 100 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 75 mA cm^{-2} , (b) temperature contour plot at the negative side during the charging at 75 mA cm^{-2} , (c) temperature contour plot at the negative side during the discharge at 75 mA cm^{-2} .



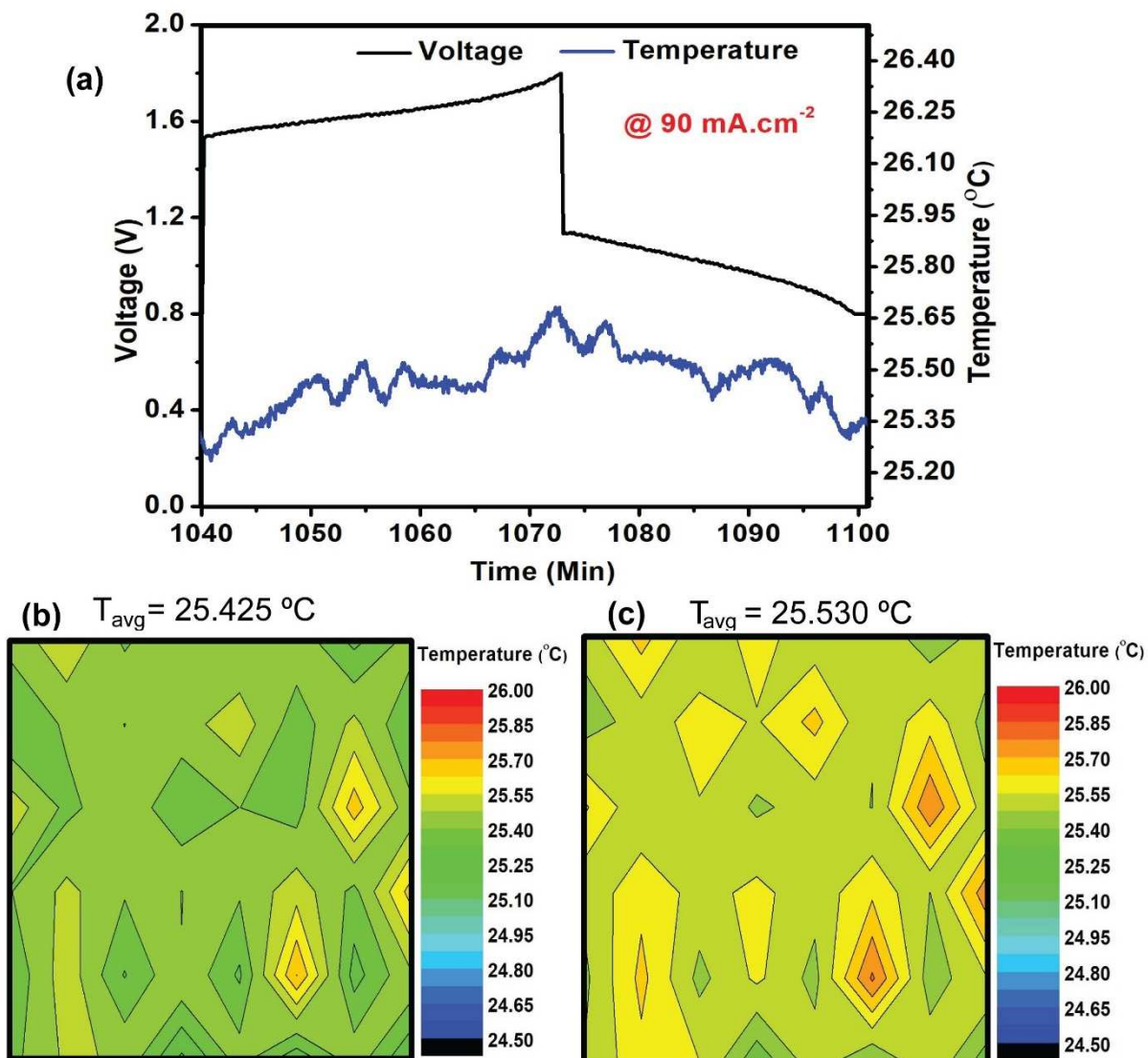


Fig. 23. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the negative side of the full cell at 100 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} , (b) temperature contour plot at the negative side during the charging at 90 mA cm^{-2} , (c) temperature contour plot at the negative side during the discharge at 90 mA cm^{-2} .

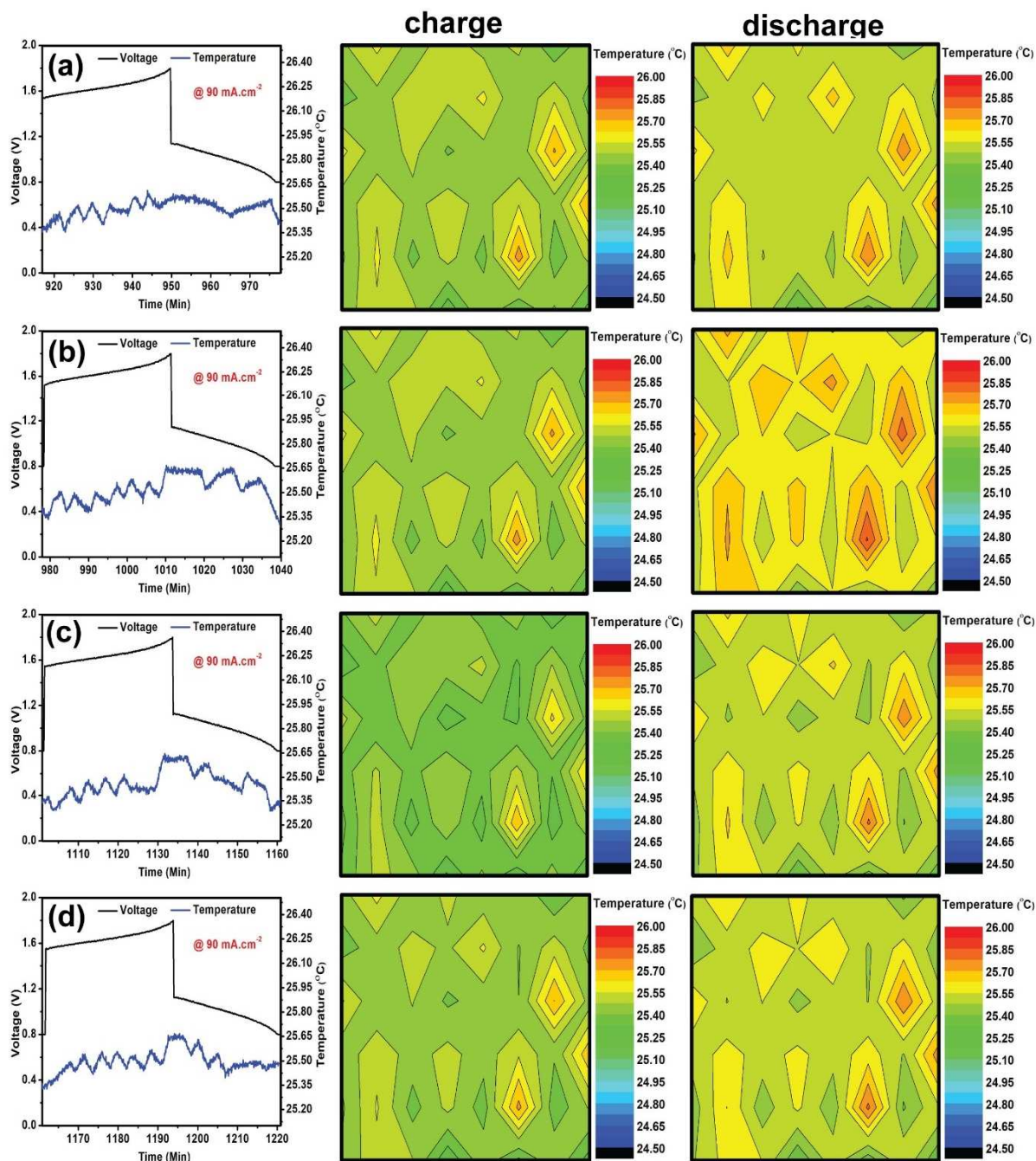


Fig. 24. (a) 1st cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours.

The temperature distribution analysis at the negative side of the cell is also done when the operating temperature is kept at 30°C instead of 25°C to see the behaviour during the galvanostatic cycling at the current density of 60 mA cm⁻² for the 10 cycles as shown in Fig. 25. The voltage, temperature vs. time plot is depicted in Fig. 25a. where the temperature is recorded at the negative electrode of the cell. During charging, the temperature increases with the increase in the voltage, and during discharge, the temperature decreases with a decrease in the voltage. The discharge capacity vs. cycles is shown in Fig. 25b. The discharge capacity of ~ 975 mAh is observed for the 10th cycle at 60 mA cm⁻². The efficiency calculation in terms of Coulombic, voltaic, and energy is represented in Fig. 25c. The Coulombic efficiency is nearly the same as when the cell operated at 25°C (Fig. 18c) with similar experimental conditions except for operating temperature. This indicates that a rise of 5 °C does not affect Coulombic efficiency. However, the voltaic efficiency increased slightly by ~2.5% (Fig. 25c) when the operating temperature increased from 25°C (Fig. 18c) to 30°C while other experimental parameters kept the same. However, the energy efficiency has changed insignificantly with the increased operating temperature of 30°C [53]. A single cycle voltage, temperature vs. time plot (Fig. 26a), and the related temperature contours plot at the negative electrode during charge and discharge are shown in Fig. 26b & Fig. 26c. Higher temperature hot spots domains are visible near the edges of while little lower hot spots are centred to the middle part of the cell during the charge (Fig. 26b). During discharge size of little lower temperature domains decreases in the middle part while also visible at the edges (Fig. 26c) and fig. Also, there are a lot of fluctuations in the temperature during charge and discharge for every cycle shown in Fig. 27.

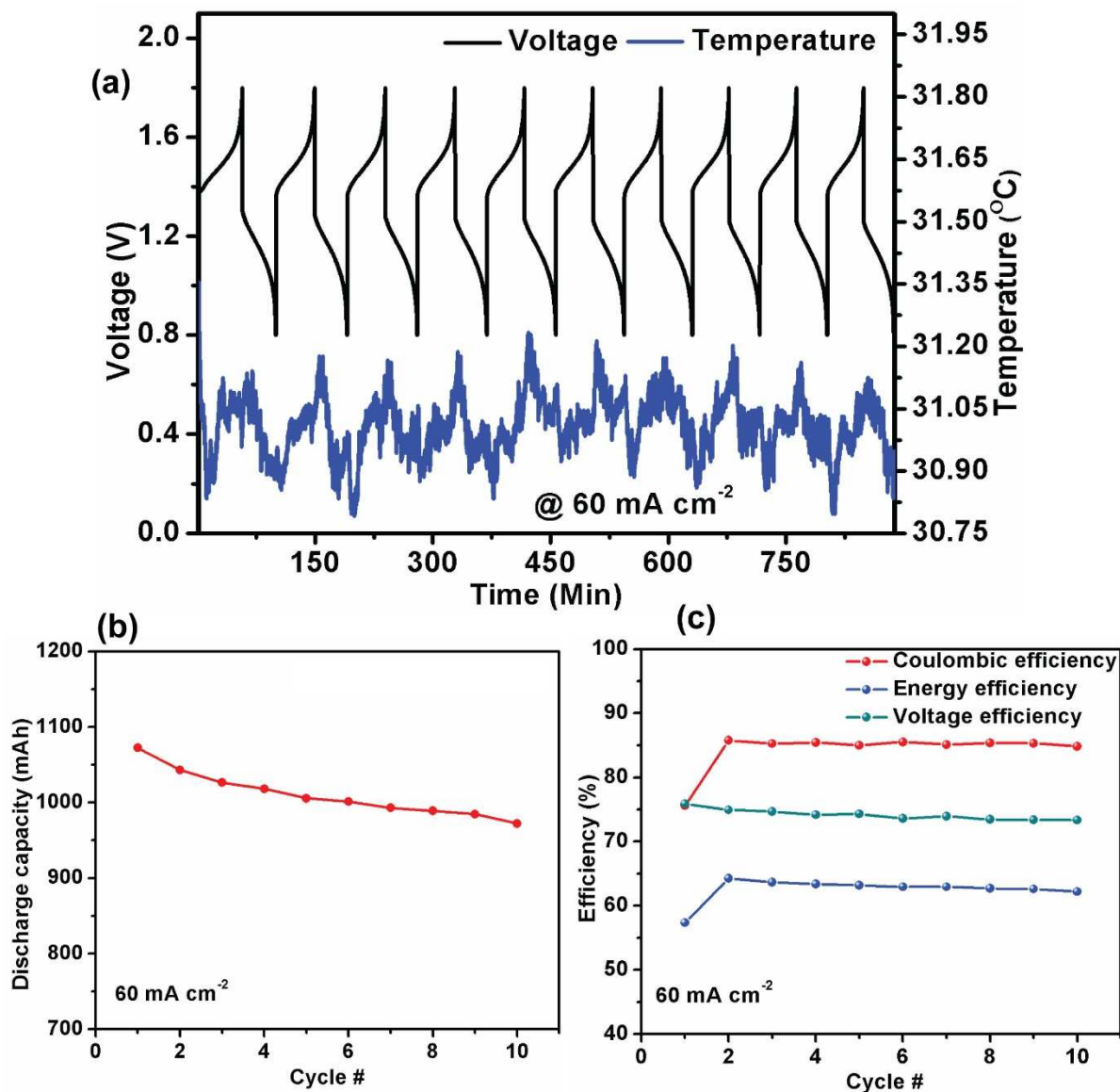


Fig. 25. Electrochemical performance in the full-cell configuration of VRFB at the negative side of the full cell at 100 ml/min. (a) Voltage and temperature vs. time plot at the current density 60 mA cm^{-2} , (b) discharge capacity vs. cycles current density as given in Fig. a, (c) Coulombic, Energy, and Voltaic efficiencies vs. cycles.

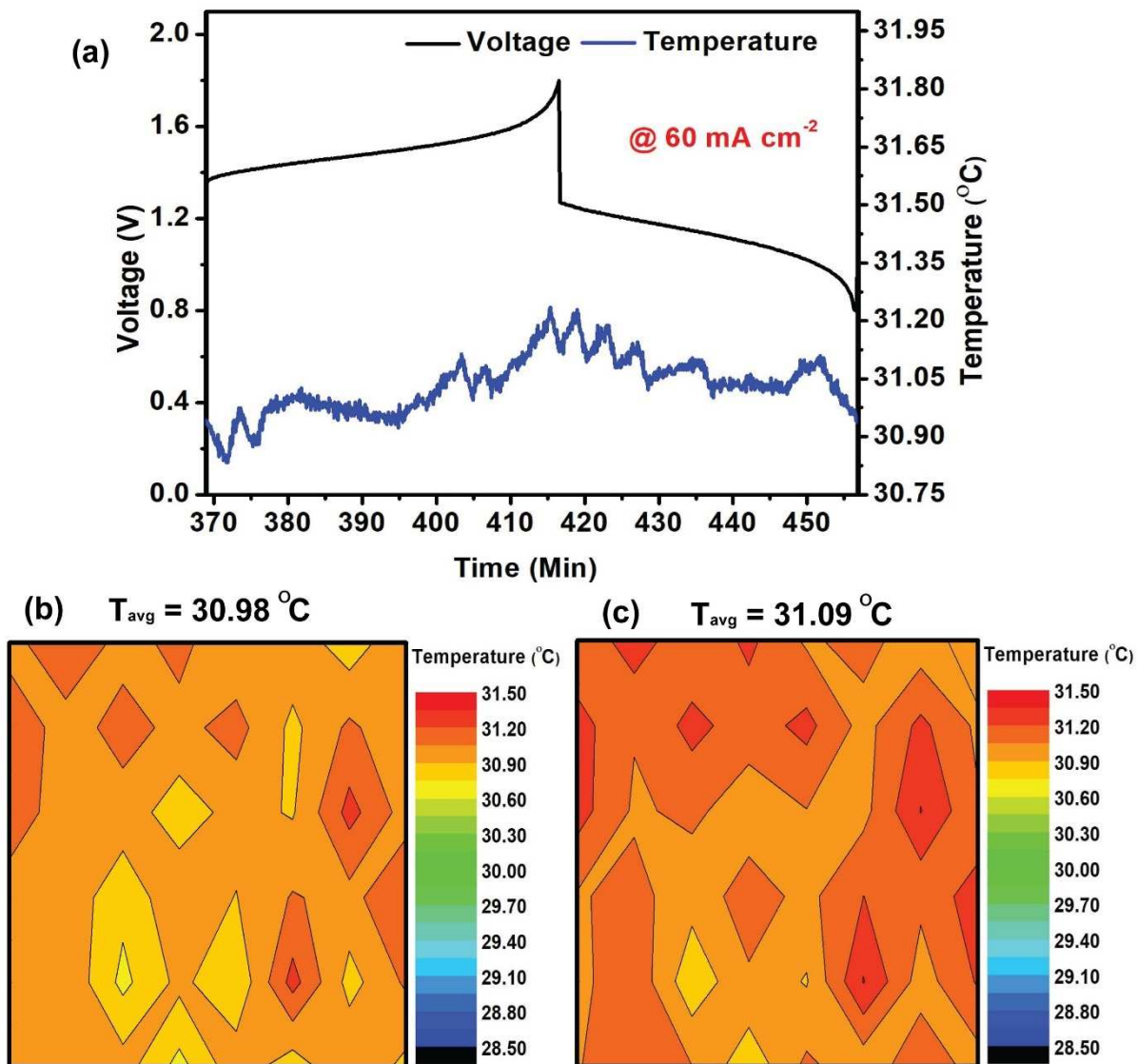


Fig. 26. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the negative side of the full cell at 100 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 60 mA cm⁻², (b) temperature contour plot at the negative side during the charging at 60 mA cm⁻², (c) temperature contour plot at the negative side during the discharge at 60 mA cm⁻².

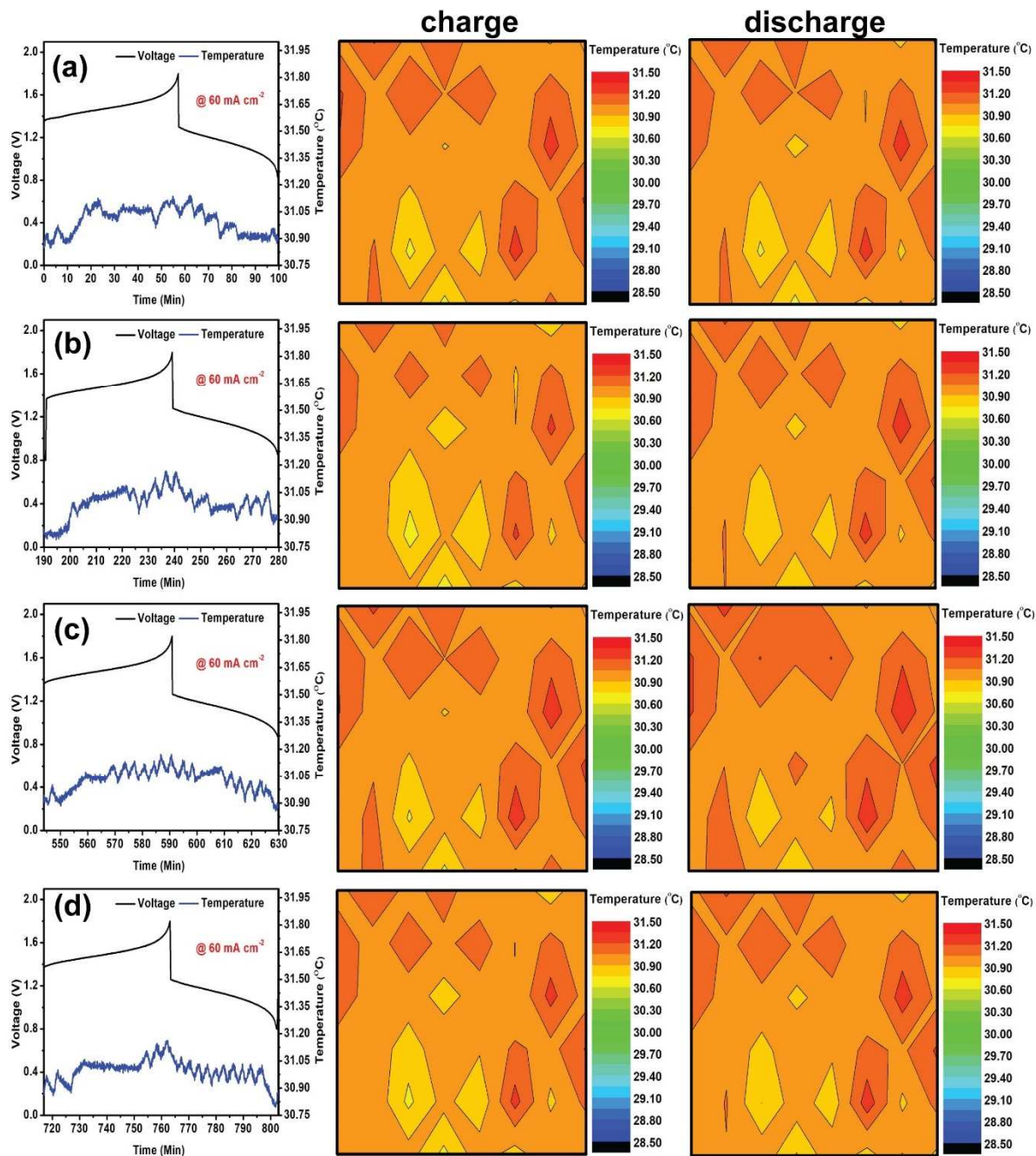


Fig. 27. (a) 1st cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (b) 3rd cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (c) 7th cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (d) 9th cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours.

5.2.2 In-operando temperature analysis at the negative electrode (anode) in full-cell during the galvanostatic cycling with different parameters.

In this case, the temperature sensor was placed at the positive side of the cell (bipolar plate) in full-cell and repeated with similar previous experimental conditions such as current density, electrolyte flow rate, and operating temperature to see the thermal distribution behaviour. A galvanostatic cycling behaviour for various current densities ranges from 60 mA cm⁻² to 90 mA cm⁻² for 15 cycles, and related temperature contour plots at the positive side of the cell are represented in Fig. 28. The operating temperature for the cell is 25°C and the electrolyte flow rate of 50 mL min⁻¹. Fig. 28a. shows the voltage vs. time for the charge-discharge process at various current densities along with temperature vs. time at the positive side of the cell. The 5 charge and discharge cycles are obtained at each current densities 60 mA cm⁻², 75 mA cm⁻², and 90 mA cm⁻². It is observed from the plots (Fig. 28a). The temperature at the positive side of the cell decreases during charging with increasing the charging voltage. It reaches a minimum value when the voltage reaches to upper cut off which is 1.8 V and increases during discharge with decreasing the discharging voltage and reaches a maximum value at the end of the discharge process at a lower cut-off voltage of 0.8 V. The temperature vs. time plots nature is similar to all the applied current densities. It indicates that the temperature concerning time decreases during charging and increases during discharging, which is the temperature patterns are opposite of the case discussed for the negative electrode in Fig. 11. The discharge capacity vs. cycles are depicted in Fig. 28b. A discharge capacity of ~ 890 mAh is observed over the 5th cycle for 60 mA cm⁻², whereas ~ 885 mAh is observed over the 10th cycle for 75 mA cm⁻², and for 90 mA cm⁻² at the end of 15th cycle it is ~ 870 mAh. The discharge capacity retention

of 98% is behold compared to 5th cycle (considering 100%) and 15th cycle which is pretty good even after applying for higher current densities. The coulombic, voltaic and energy efficiency are depicted in Fig. 28c. The various current densities does not have any effect on the coulombic efficiency of the cell. It maintains a constant value for all the cycling processes. The voltaic efficiency decreases with an increase in current density as shown in Fig. 28c. The voltaic efficiency for a current density of 60 mA cm⁻² is observed to be ~ 80% at the end of 5th cycle which is excellent. As the current density is increased to 75 mA cm⁻² a decrease in 5% of the voltaic efficiency is observed and a further decrease of 3% for 90 mA cm⁻² current density (Fig. 28c). Similarly, the energy efficiency also follows the same trend as the voltaic efficiency where the energy efficiency of 70% is observed at the end of 5th cycle for 60 mA cm⁻², with a reduction of 4% for 75 mA cm⁻² at the end of 10th cycle and 8% reduction for 90 mA cm⁻² at the end of 15th cycle compared with 60 mA cm⁻² current density (Fig. 28c). In summary, these results are closely matching with the electrochemical performance represented in Fig. 11. Thus, the difference in the measurement of temperature distribution in real-time at the negative and positive side of the cell makes meaningful sense in this scenario. A single cycle charge-discharge voltage, temperature vs. time profile at various current densities (i.e., 60 mA cm⁻², 75 mA cm⁻², and 90 mA cm⁻²) is shown in Fig. 29a, Fig. 31a & Fig. 33a and their respective charge-discharge temperature contour plots for the electrode area of 25 cm² are shown in Fig. 29b & Fig. 29c for 60 mA cm⁻², Fig. 31b & Fig. 31c for 75 mA cm⁻², and Fig. 33b & Fig. 33c for 90 mA cm⁻². A decrease in the temperature during the charging is clearly visible in Fig. 29a (60 mA cm⁻²) while increasing during the discharge. The corresponding temperature contour plot at the positive electrode of the cell (Fig. 29b) validates the same when

compared with the temperature contour plots during the discharging (Fig. 29c). A similar observation is recorded for the higher current densities at 75 mA cm^{-2} and 90 mA cm^{-2} (Fig. 31b-c & Fig. 33b-c). The temperature distribution in the positive electrode is uniform during charge. However, there are few hotspot regions in the electrode during discharge.

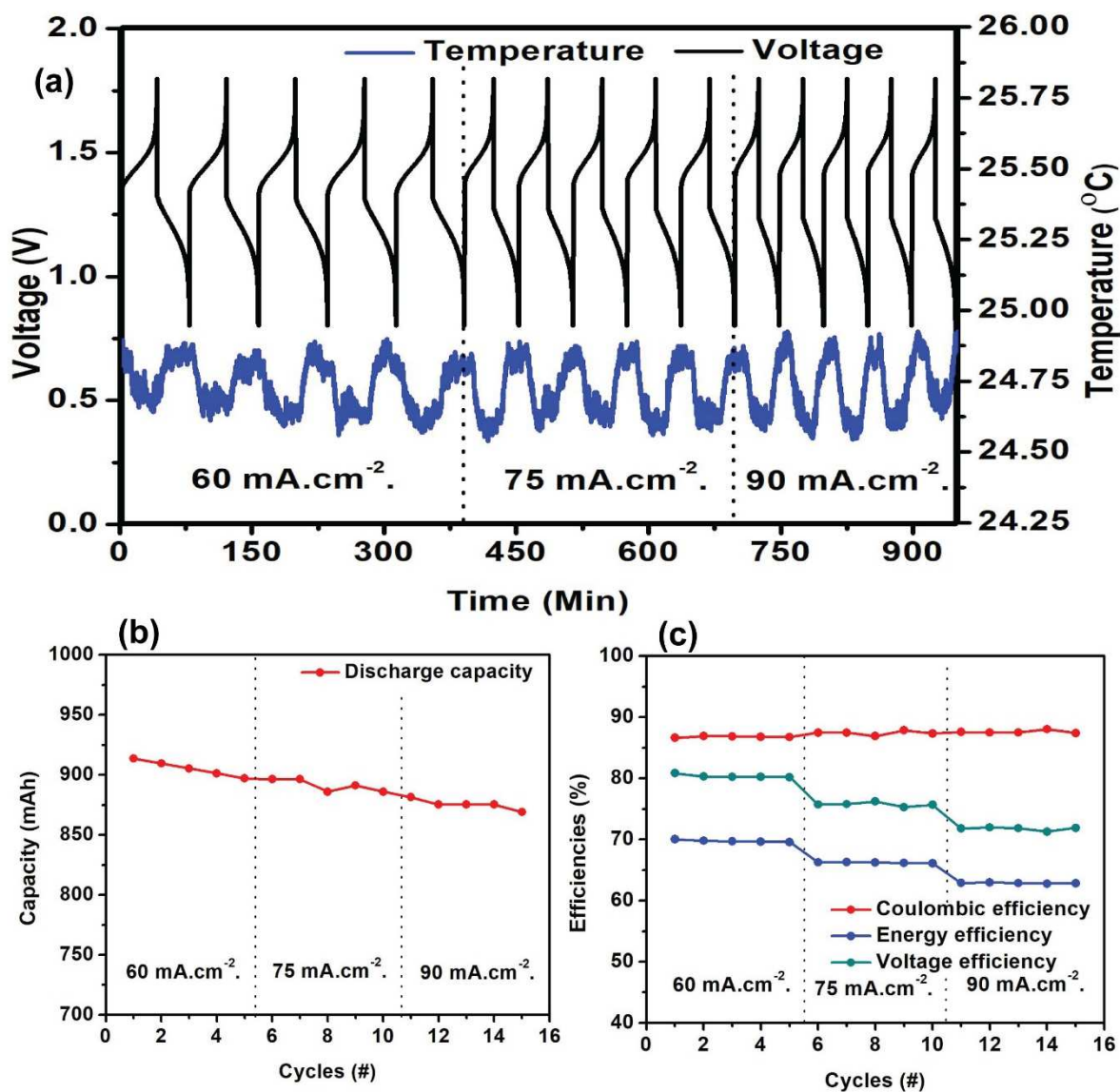


Fig. 28. Electrochemical performance in the full-cell configuration of VRFB at the positive side of the full cell at 50 ml/min. (a) Voltage and temperature vs. time plot at the different current densities ranging from 60 – 90 mA cm⁻², (b) discharge capacity vs. cycles at different current densities as given in Fig. a, (c) Coulombic, Energy, and Voltaic efficiencies vs. cycles.

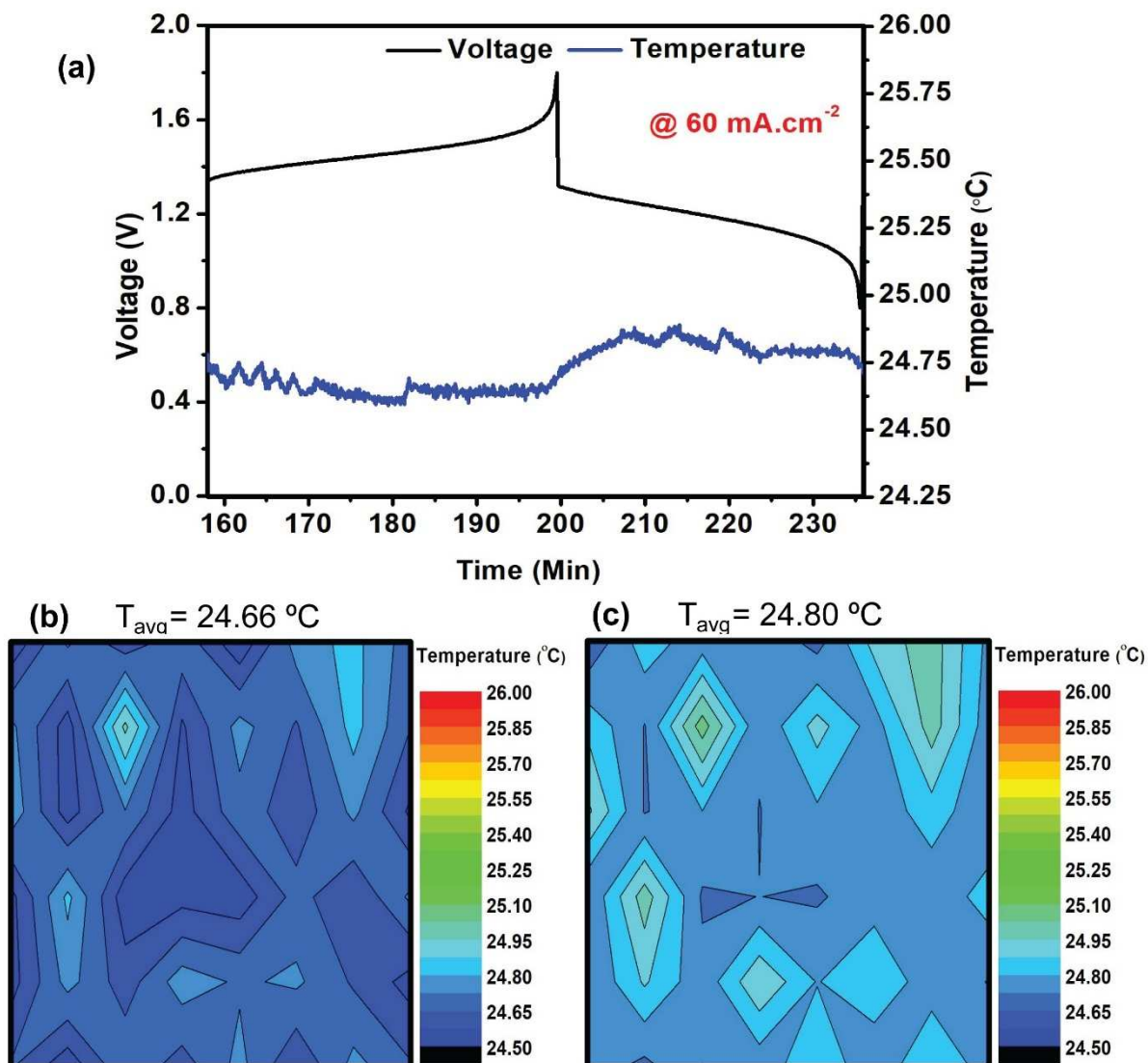


Fig. 29. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the positive side of the full cell at 50 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 60 mA cm⁻², (b) temperature contour plot at the negative side during the charging at 60 mA cm⁻², (c) temperature contour plot at the negative side during the discharge at 60 mA cm⁻².

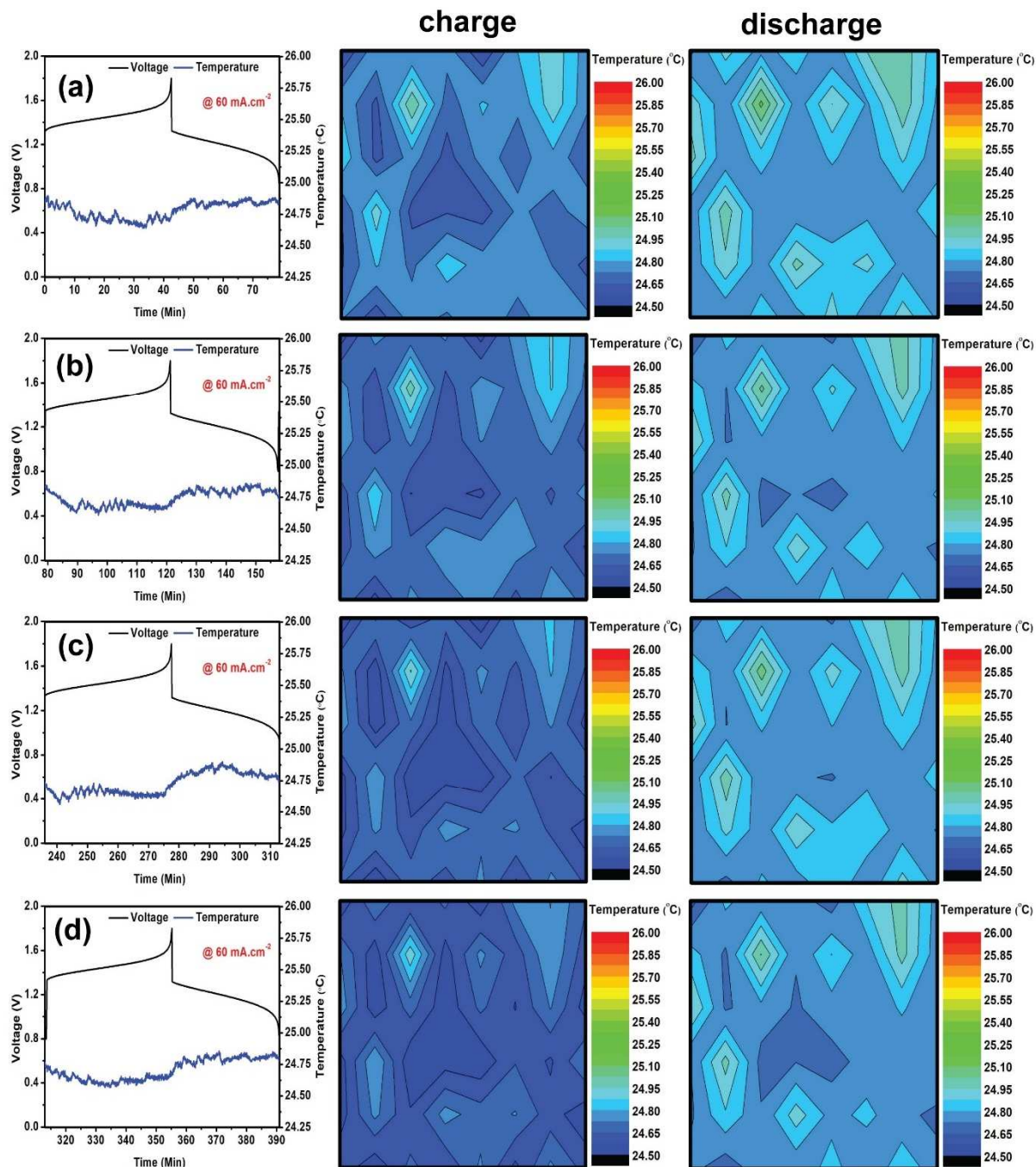


Fig. 30. (a) 1st cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours.

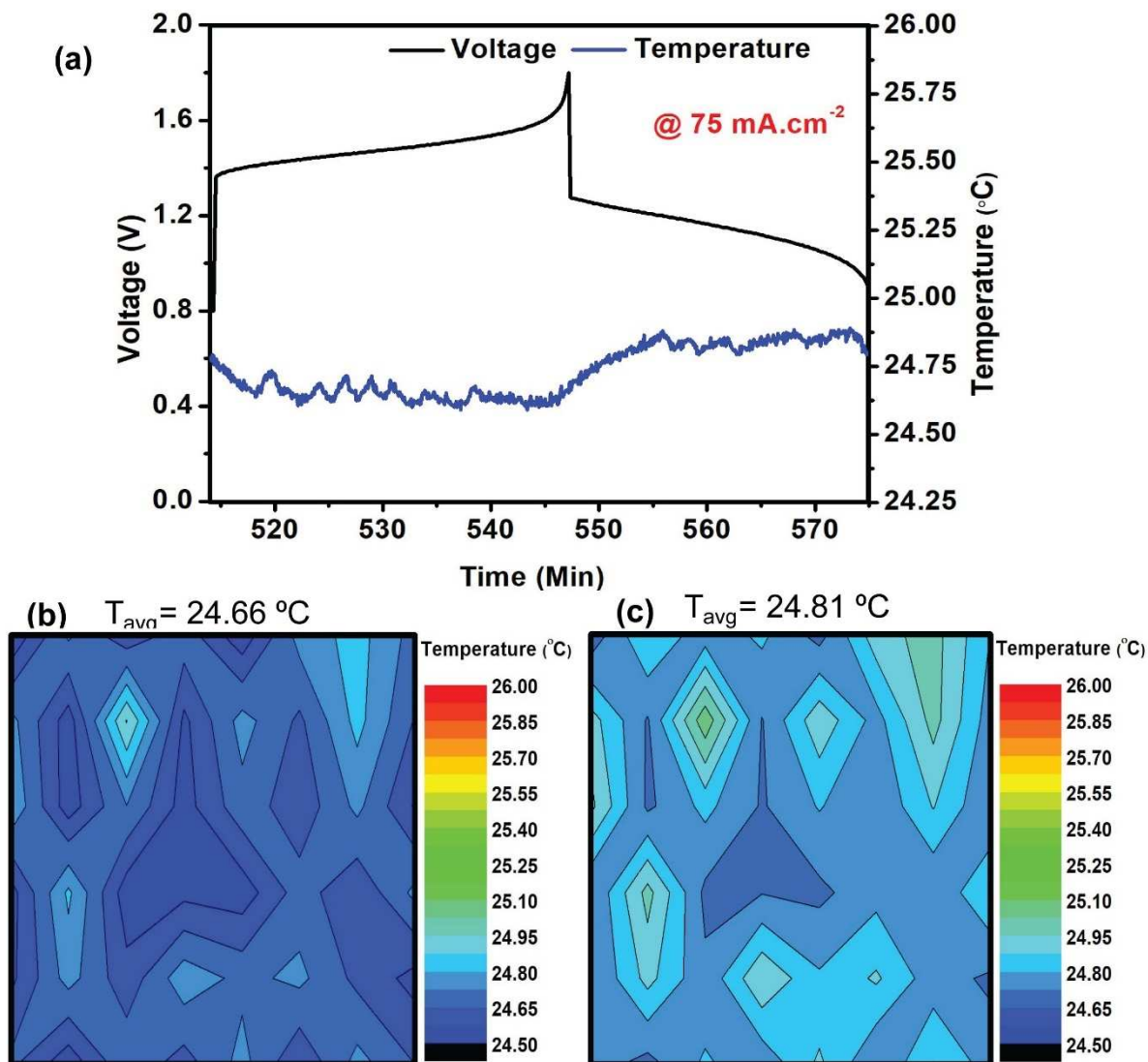


Fig. 31. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the positive side of the full cell at 50 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 75 mA cm⁻², (b) temperature contour plot at the negative side during the charging at 75 mA cm⁻², (c) temperature contour plot at the negative side during the discharge at 75 mA cm⁻².

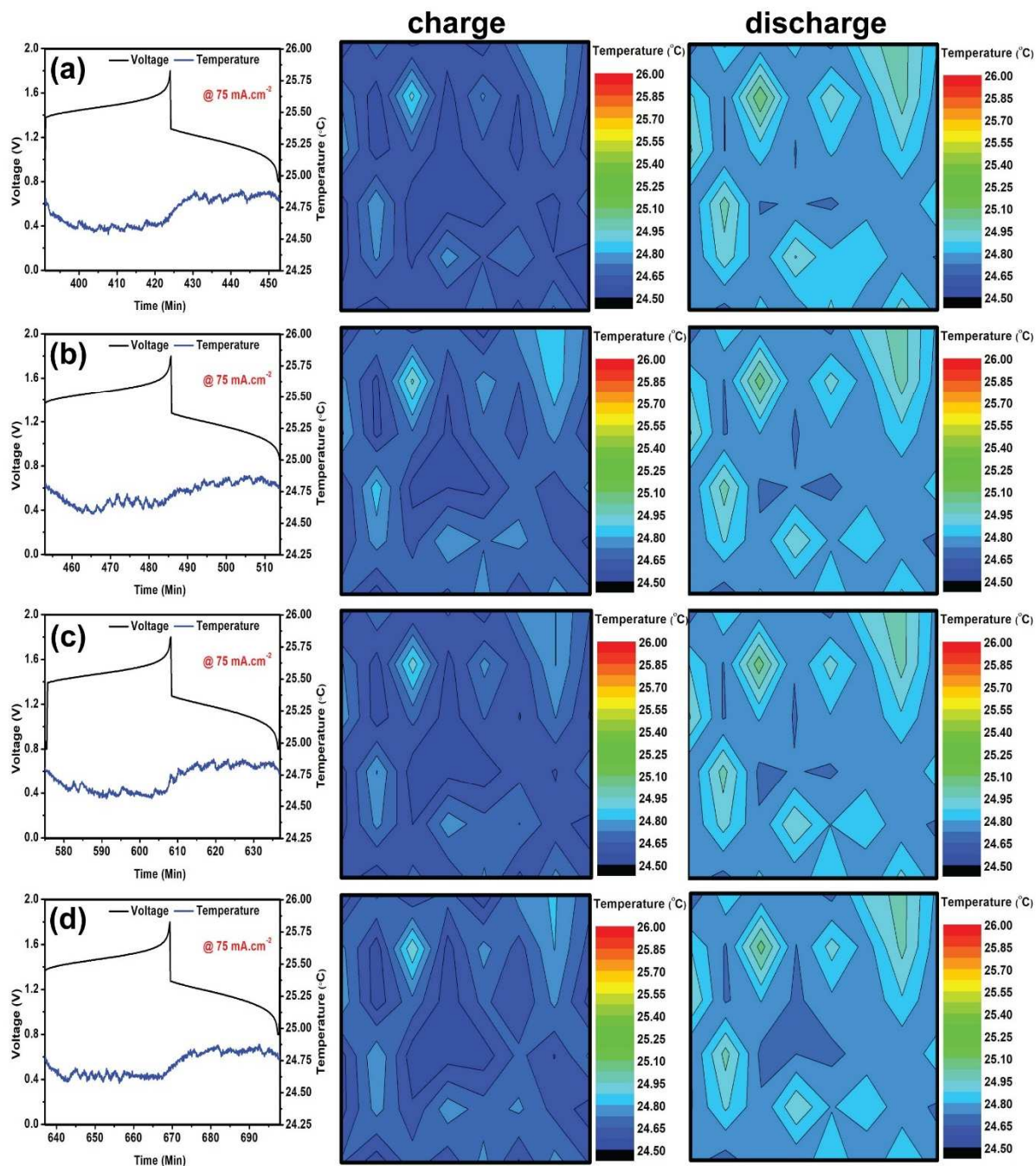


Fig. 32. (a) 1st cycle voltage and temperature vs. time at the current density of 75 mA cm^{-2} and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 75 mA cm^{-2} and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 75 mA cm^{-2} and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 75 mA cm^{-2} and its corresponding contours.

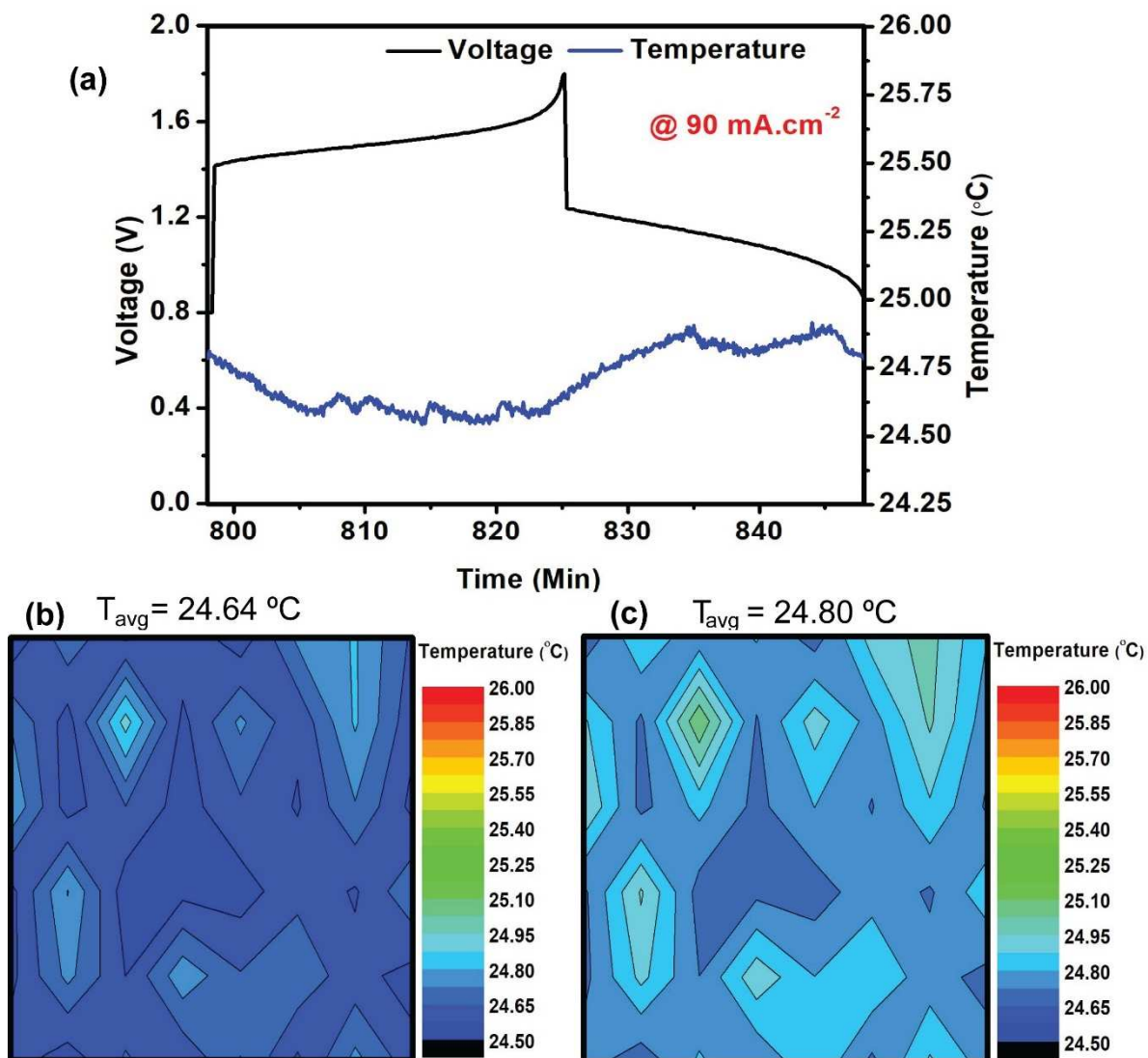


Fig. 33. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the positive side of the full cell at 50 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 90 mA cm⁻², (b) temperature contour plot at the negative side during the charging at 90 mA cm⁻², (c) temperature contour plot at the negative side during the discharge at 90 mA cm⁻².

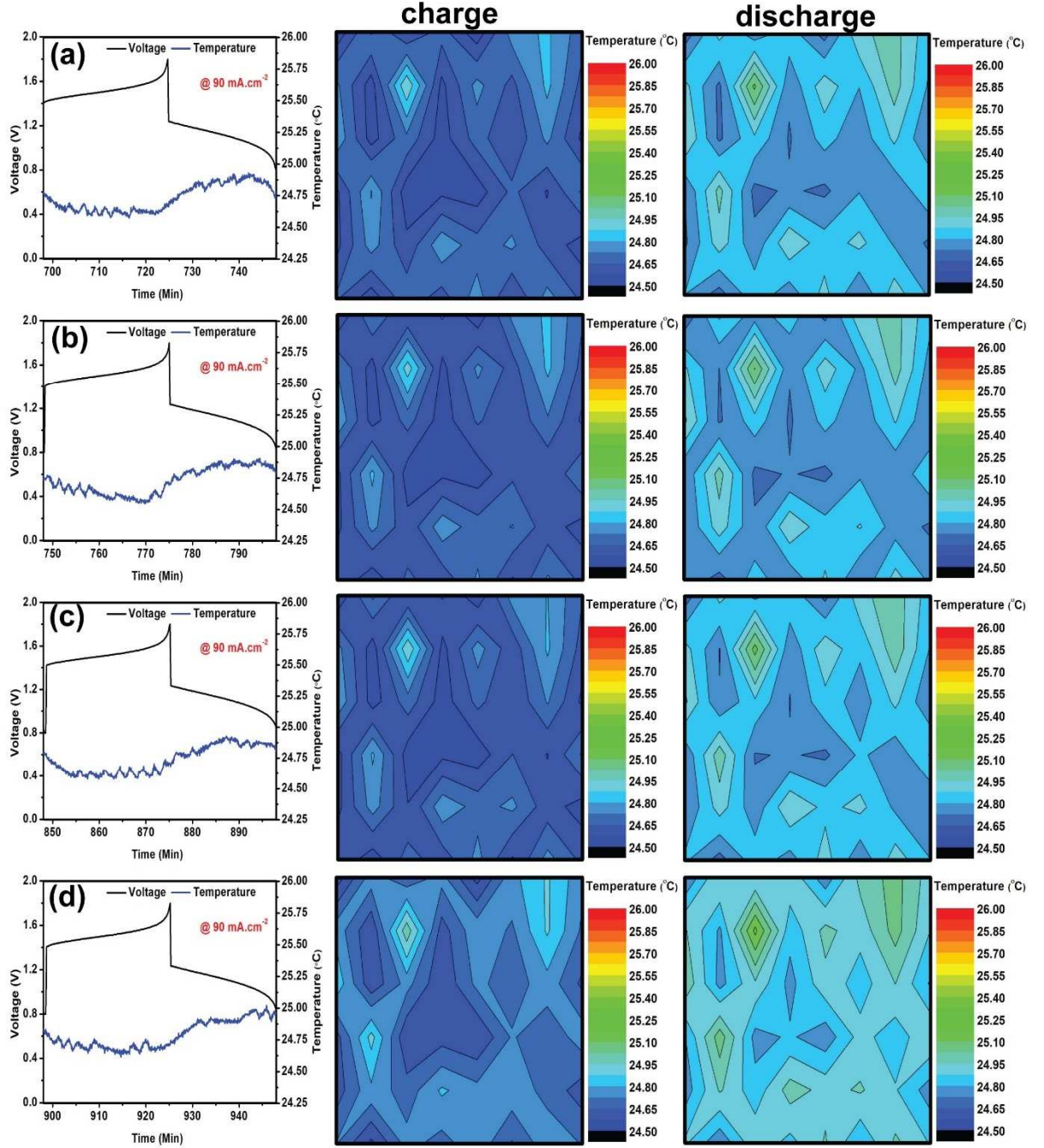


Fig. 34. (a) 1st cycle voltage and temperature vs. time at the current density of 90 mA cm⁻² and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 90 mA cm⁻² and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 90 mA cm⁻² and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 90 mA cm⁻² and its corresponding contours.

The temperature distribution at the cell's positive electrode was further studied at a higher flow rate of 100 mL min⁻¹ during charge and discharge by keeping all other operating parameters constant, such as operating temperature (25°C) and current density. The electrochemical performance and temperature distribution at the electrode of the cell are shown in Fig. 35. The voltage vs. time for the cell and temperature vs. time at the positive electrode is shown in Fig. 35a. A total of 15 charge-discharge cycles were examined for current densities of 60 mA cm⁻², 75 mA cm⁻², and 90 mA cm⁻². The temperature at the positive side of the cell decreases as voltage increases during charge and increases as voltage decreases during discharge as shown in Fig. 35a. The corresponding discharge capacity vs. cycles at various current densities are shown in Fig. 35b. At 60 mA cm⁻², the discharge capacity over 5th cycle is ~1098 mAh. At a higher current density of 75 mA cm⁻² over the 10th cycle, the discharge capacity is ~1068 mAh, and for 90 mA cm⁻² over the 15th cycle, it is ~1023 mAh. Retention of ~95% after 15 cycles (considering 100% at the 5th cycle) of discharge capacity is beheld by increasing the current densities by 30 mA cm⁻². The performance parameters such as Coulombic efficiency, voltaic efficiency, and energy efficiency are depicted in Fig. 35c. The Coulombic efficiency maintains itself constant throughout the 15 cycles, thereby showing no effect of current densities. The voltaic efficiency decreases at current density increases. The observed voltaic and energy efficiencies degraded when the flow rate increased from 50 mL min⁻¹ (Fig. 28c) to 100 mL min⁻¹ (Fig. 35c). A similar degradation of voltaic and energy efficiency is noted in the electrochemical performance of the cell at a similar experimental condition when the temperature distribution was analyzed at the negative electrode of the cell (Fig. 18c). A single charge-discharge voltage plots selected from the Fig. 35a for the three current

densities and is shown in Fig. 36a, Fig. 38a & Fig. 40c with the temperature plot at the positive electrode of the cell. Their respective temperature contour plots at the electrodes during charge and discharge are shown in Fig. 36b & 36c at 60 mA cm^{-2} , Fig. 38b & 38c at 75 mA cm^{-2} and Fig. 40b & 40c at 90 mA cm^{-2} . The three plots, Fig. 36a, Fig. 38a & Fig. 40a, follow the same trend of temperature decrease at charging and increase during discharging. The corresponding temperature contour plot validates the pictorial representation of the temperature distribution (Fig. 36b, Fig. 38b & Fig. 40b) during charge when compared with the temperature distribution (Fig. 36c, Fig. 38c, & Fig. 40c) during discharge for the different current densities. In the positive electrode, the temperature is uniformly distributed compared to the temperature distribution of the negative electrode. The difference in the rise in temperature distribution during charge and discharge is also insignificant. The temperature vs. time and average charge-discharge temperature contours are shown in Fig. 37 (60 mA.cm^{-2}), Fig. 39 (75 mA.cm^{-2}), and Fig. 41 (90 mA.cm^{-2}). At higher flow rate, the temperature in the electrodes increases during charge and discharge, due to an increase in the electrochemical activity of vanadium species.

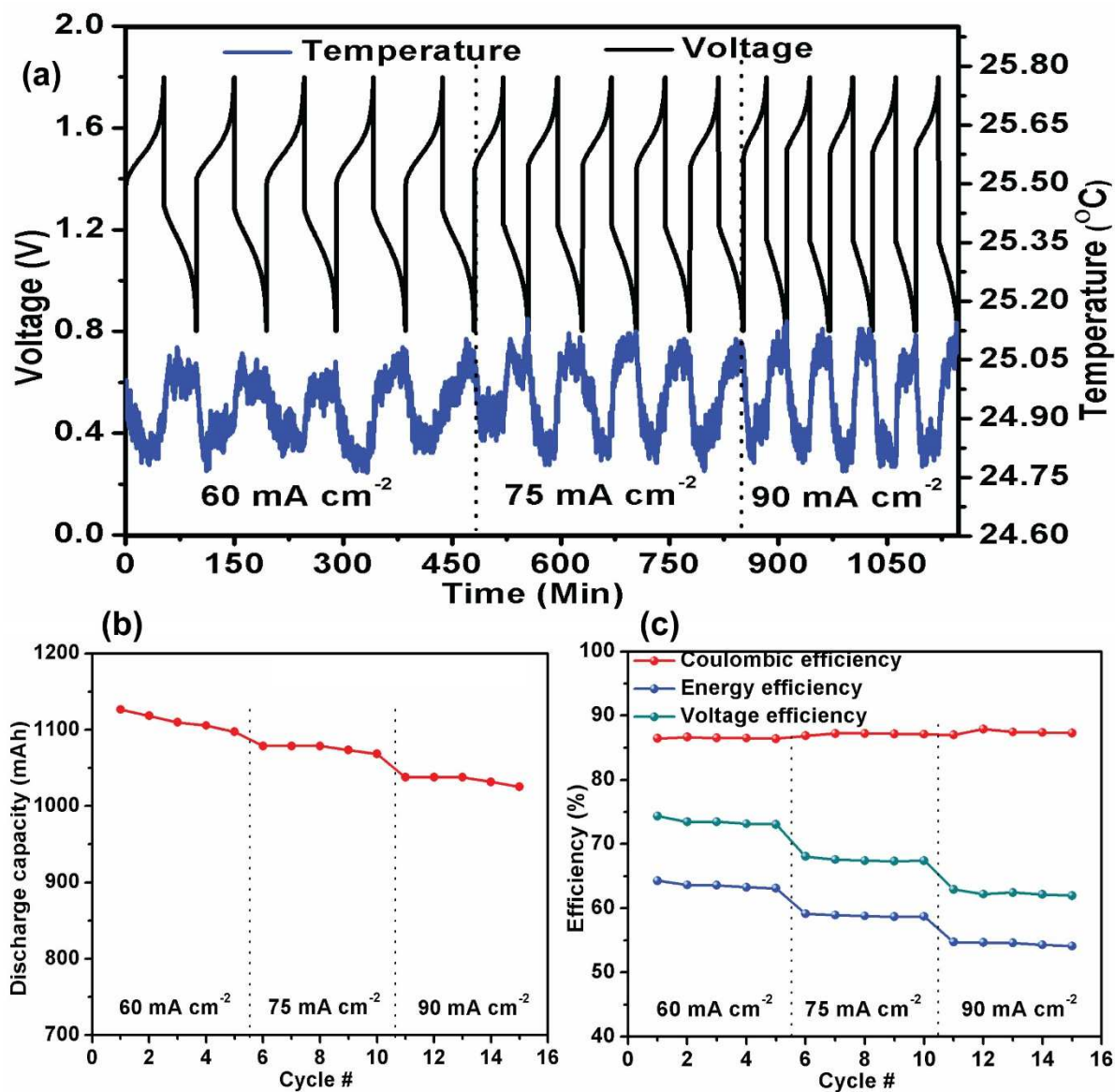


Fig. 35. Electrochemical performance in the full-cell configuration of VRFB at the positive side of the full cell at 100 ml/min. (a) Voltage and temperature vs. time plot at the different current densities ranging from 60 – 90 mA cm⁻², (b) discharge capacity vs. cycles at different current densities as given in Fig. a, (c) Coulombic, Energy, and Voltaic efficiencies vs. cycles.

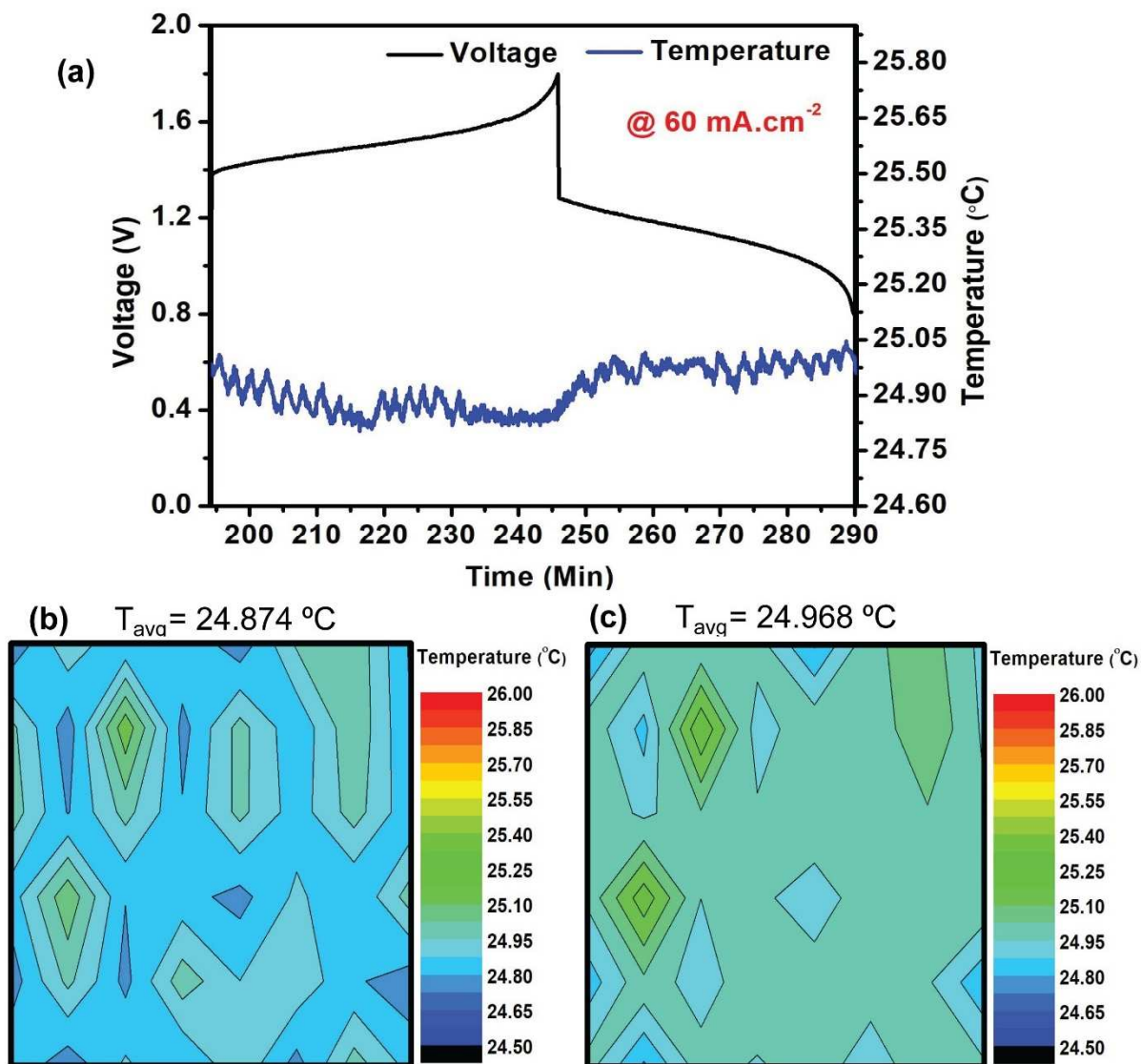


Fig. 36. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the positive side of the full cell at 100 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 60 mA cm⁻², (b) temperature contour plot at the negative side during the charging at 60 mA cm⁻², (c) temperature contour plot at the negative side during the discharge at 60 mA cm⁻².

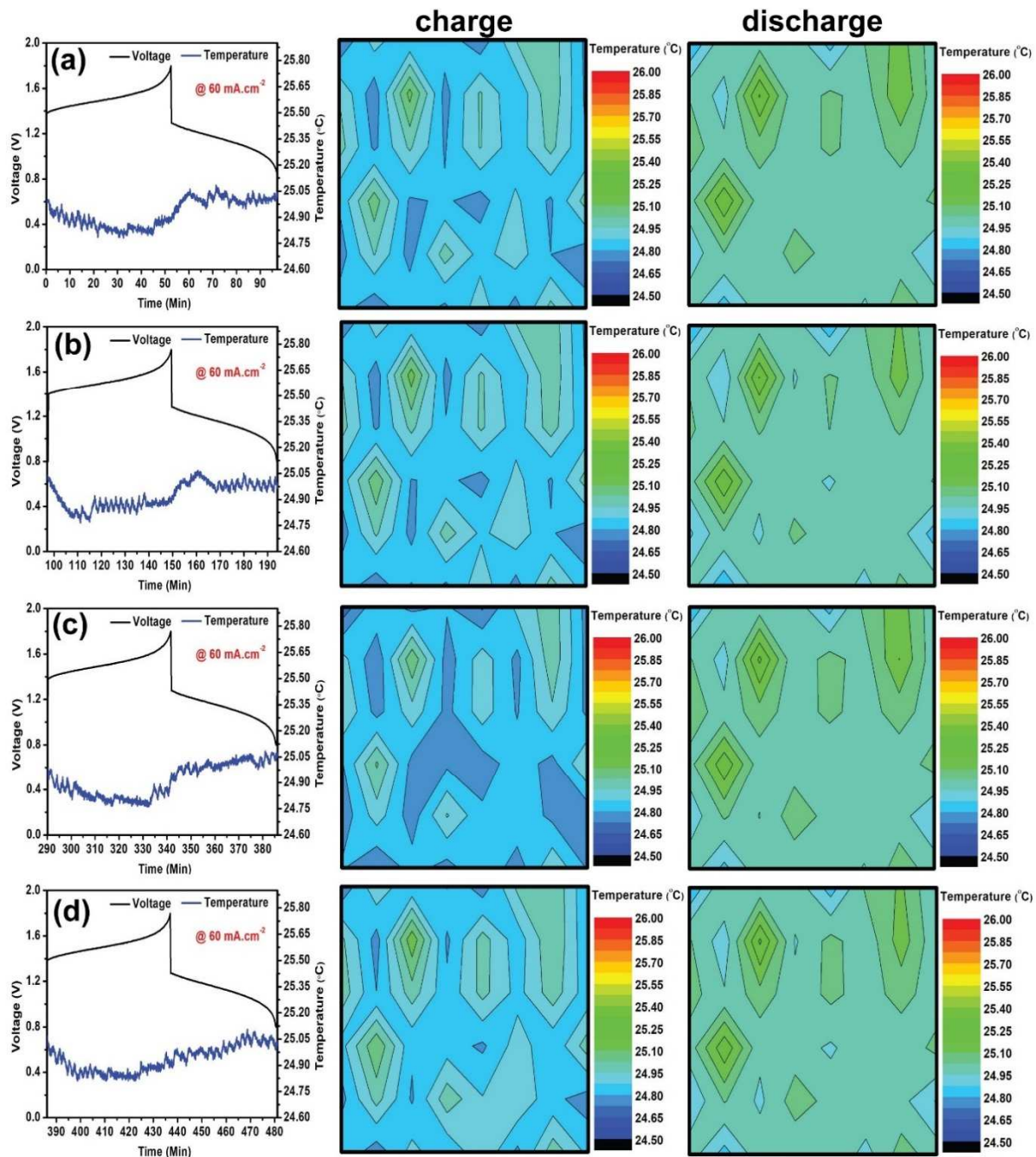


Fig. 37. (a) 1st cycle voltage and temperature vs. time at the current density of 60 mA cm⁻² and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 60 mA cm⁻² and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 60 mA cm⁻² and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 60 mA cm⁻² and its corresponding contours.

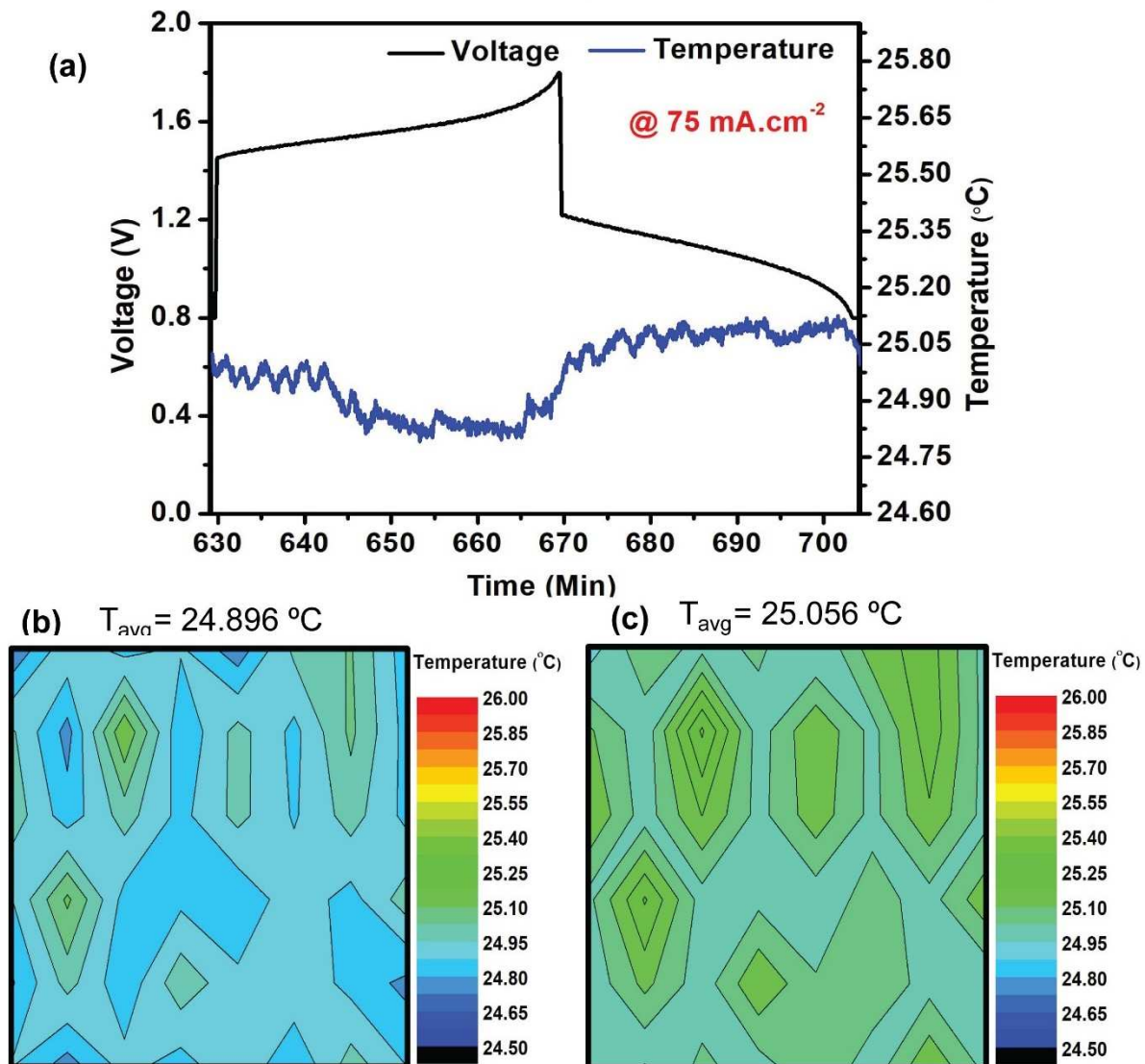


Fig. 38. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the positive side of the full cell at 100 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 75 mA cm⁻², (b) temperature contour plot at the negative side during the charging at 75 mA cm⁻², (c) temperature contour plot at the negative side during the discharge at 75 mA cm⁻².

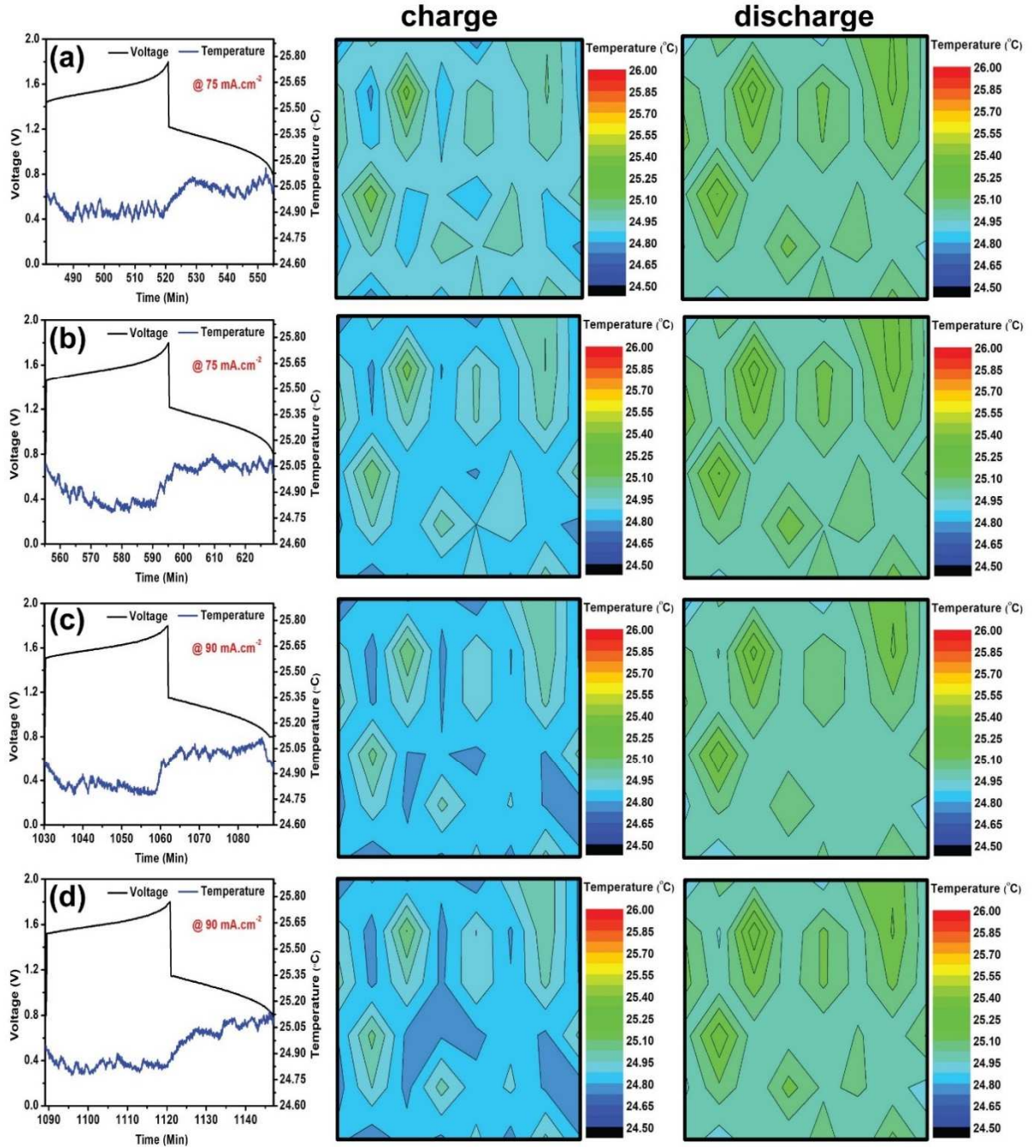


Fig. 39. (a) 1st cycle voltage and temperature vs. time at the current density of 75 mA cm⁻² and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 75 mA cm⁻² and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 75 mA cm⁻² and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 75 mA cm⁻² and its corresponding contours.

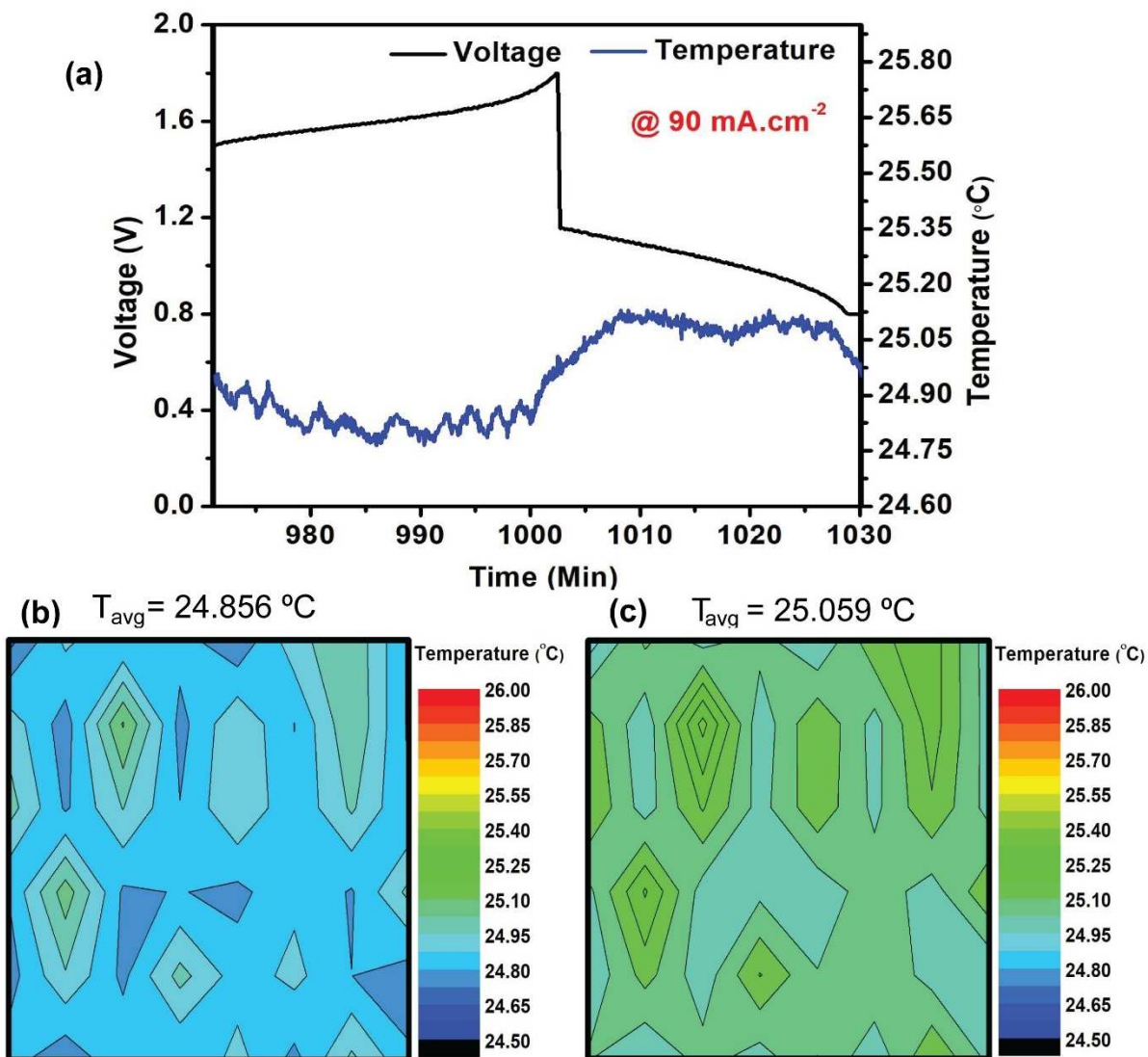


Fig. 40. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the positive side of the full cell at 100 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 90 mA cm⁻², (b) temperature contour plot at the negative side during the charging at 90 mA cm⁻², (c) temperature contour plot at the negative side during the discharge at 90 mA cm⁻².

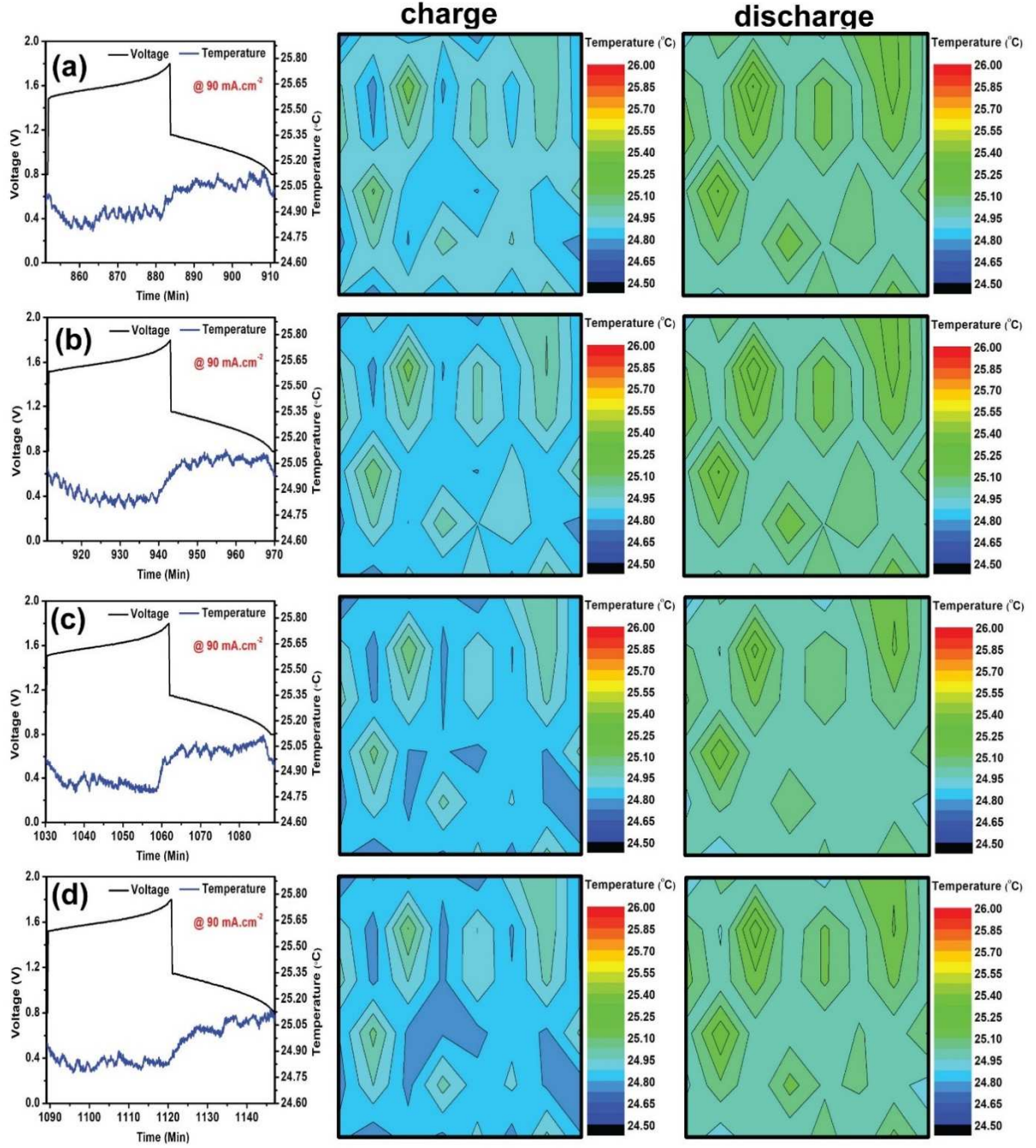


Fig. 41. (a) 1st cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours, (b) 2nd cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours, (c) 4th cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours, (d) 5th cycle voltage and temperature vs. time at the current density of 90 mA cm^{-2} and its corresponding contours.

The temperature distribution is also studied for another case where the cell's operating temperature has been increased to 30°C from 25°C by keeping the electrolyte flow rate at 100 mL min⁻¹. This case has been studied at a current density of 60 mA cm⁻². The 10 cycles of charge-discharge have been recorded along with the temperature distribution as shown in Fig. 42. The voltage vs. time for the cell and temperature vs. time at the positive electrode is shown in Fig. 42a. The temperature distribution follows the same pattern as discussed in Fig. 25a. The discharge capacity vs. cycle for 10 cycles is shown in Fig. 42b. The discharge capacity after 10 cycles is ~ 1020 mAh. Fig. 42c represents the Coulombic, voltaic, and energy efficiencies recorded for the experiment. The Coulombic efficiency throughout 10 cycles remains nearly constant at ~86%. It does not affect the Coulombic efficiency when the temperature increases (30 °C) and is similar to the discussed in Fig. 25c (30 °C). The voltaic and energy efficiency also remain constant over the 10 cycles. The selected single cycle of voltage, temperature vs. time plot is shown in Fig. 43a, and its respective temperature contour plots at the positive electrode of the cell during charge and discharge are given in Fig. 43b & Fig. 43c. From the contour plot, it is observed that the temperature decreases during charge and rises during discharge. However, a sharp difference in the temperature distribution is merely visible (Fig. 44).

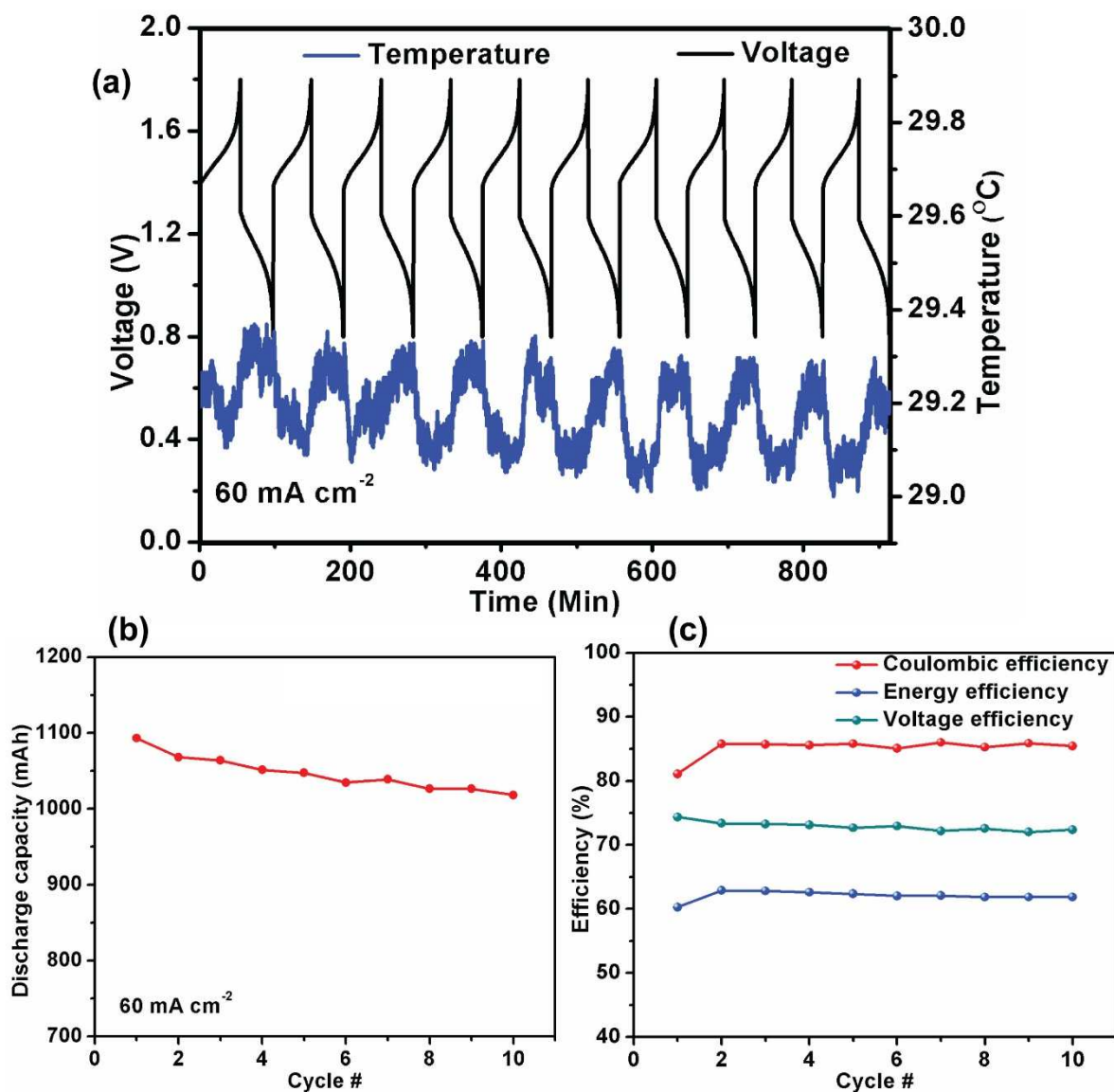


Fig. 42. Electrochemical performance in the full-cell configuration of VRFB at the positive side of the full cell at 100 ml/min. (a) Voltage and temperature vs. time plot at the current density 60 mA cm^{-2} , (b) discharge capacity vs. cycles current density as given in Fig. a, (c) Coulombic, Energy, and Voltaic efficiencies vs. cycles.

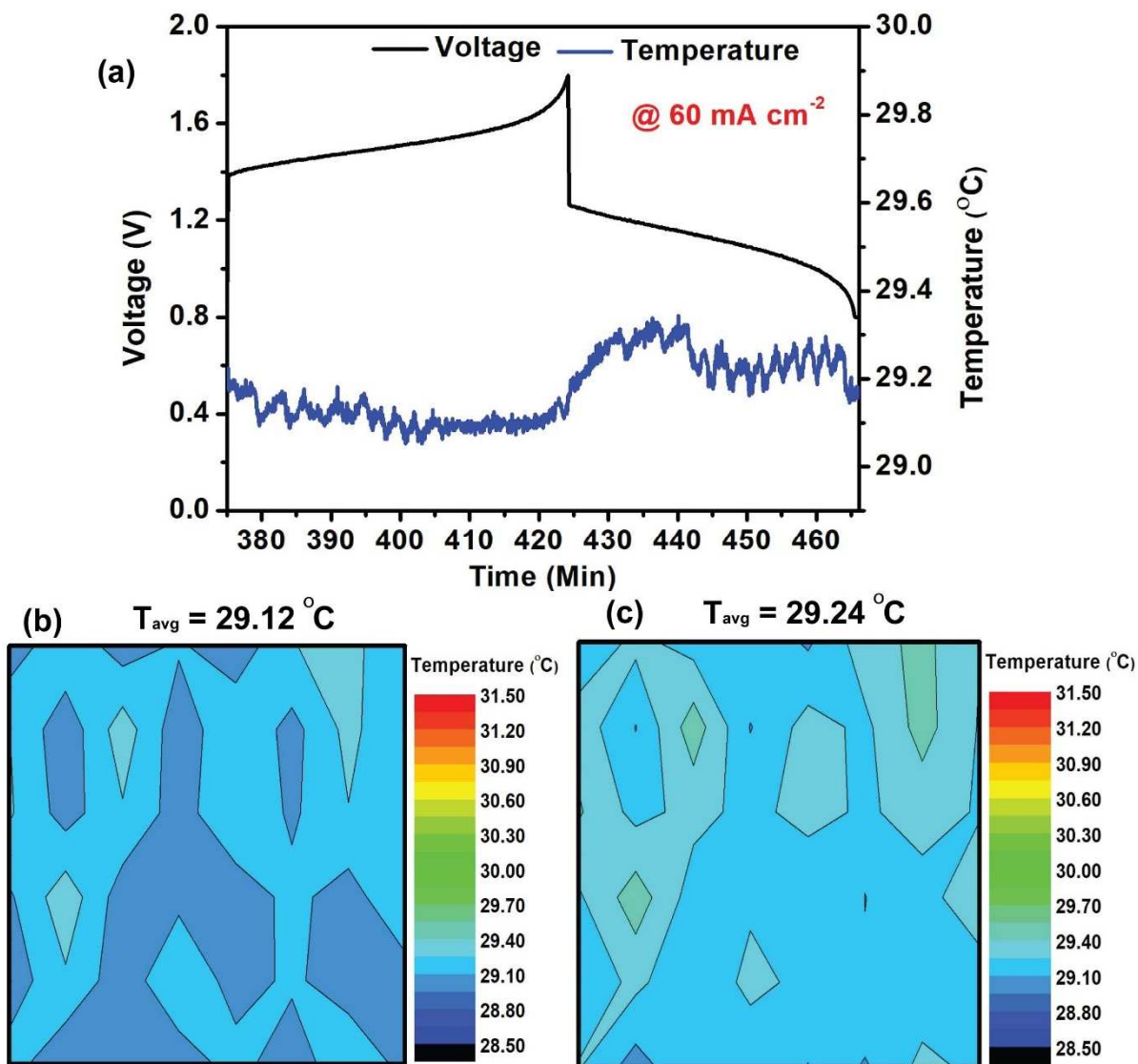


Fig. 43. Electrochemical performance in the full-cell configuration of VRFB and real-time temperature contour plots at the positive side of the full cell at 100 ml/min. (a) 3rd cycle voltage and temperature vs. time at the current density of 60 mA cm⁻², (b) temperature contour plot at the negative side during the charging at 60 mA cm⁻², (c) temperature contour plot at the negative side during the discharge at 60 mA cm⁻².

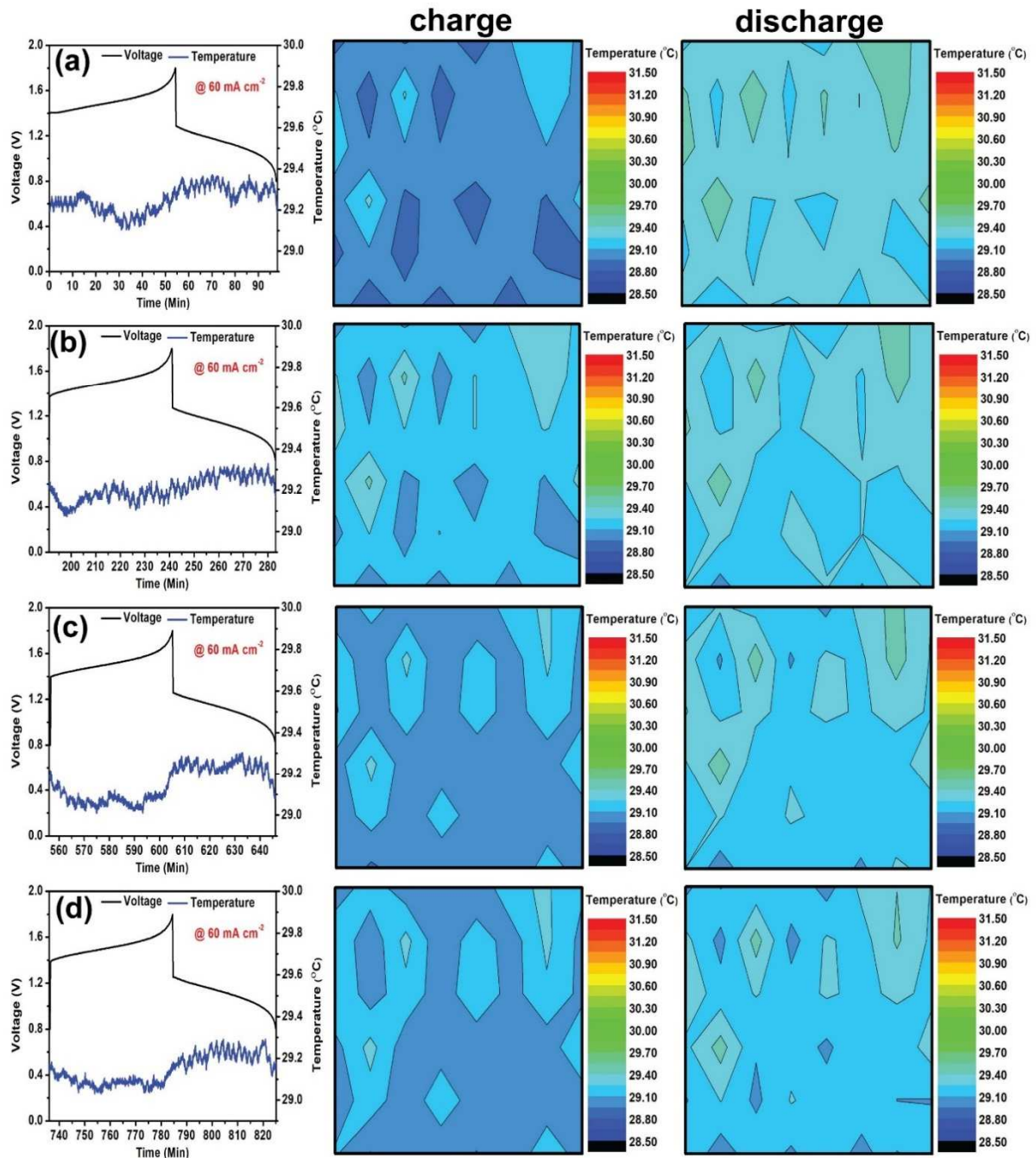


Fig. 44. (a) 1st cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (b) 3rd cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (c) 7th cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours, (d) 9th cycle voltage and temperature vs. time at the current density of 60 mA cm^{-2} and its corresponding contours.

5.2.3 A comparative in-operando temperature distribution analysis at the positive and negative sides of the full cell during the galvanostatic cycling.

Here, the comparative analysis of temperature plots vs time for both positive (cathode) electrode and negative electrode (anode) is done at the discussed above three current densities of 60 mA cm^{-2} , 75 mA cm^{-2} , and 90 mA cm^{-2} and thus represented in Fig. 45a-b and Fig. 46 represents the temperature plot at a particular current density of 60 mA cm^{-2} having different

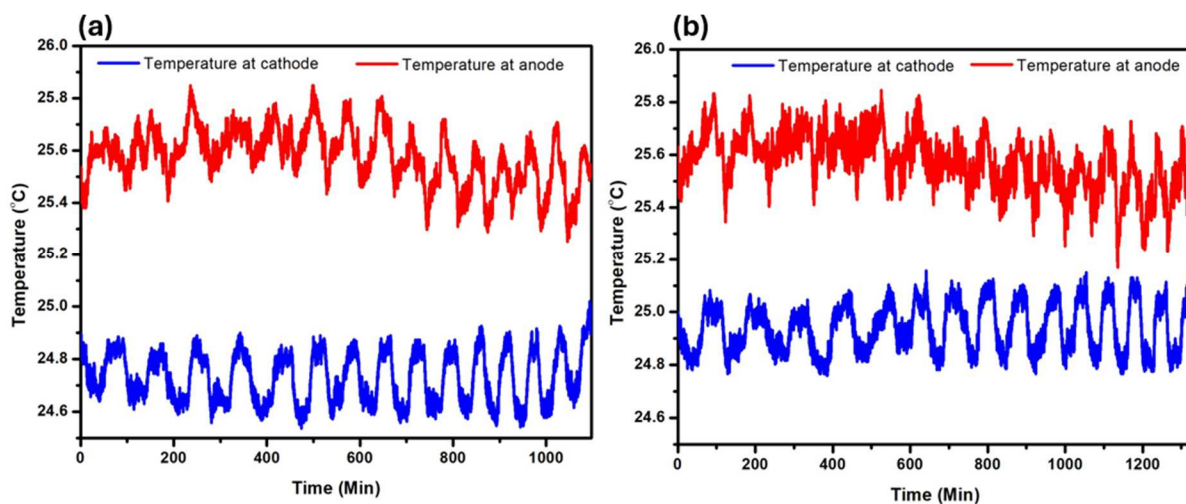


Fig. 45. Real time temperature distribution of electrochemical cell at anode and cathode: (a) Temperature distribution at anode and cathode at temperature 25°C and flow rate 50 ml min^{-1} , (b) Temperature distribution at anode and cathode at temperature 25°C and flow rate 100 ml min^{-1} .

operating temperature and flow rate. Fig. 45a shows the temperature vs. time plot at the operating temperature of 25°C and electrolyte flow rate of 50 mL min^{-1} and Fig. 45b shows the temperature vs. time plot at the operating temperature of 25°C and electrolyte flow rate of 100 mL min^{-1} . It can be observed that the temperature distribution in the negative side is higher than the operating temperature of the cell because of the higher overpotentials in the negative electrode than positive electrode [25]. The temperature in the positive electrode is slightly lower than the operating temperature of the cell. However, a lower

temperature than the operating temperature could be possible due to imperfect isolation between the cell and room temperature ($25 \pm 1\text{ }^{\circ}\text{C}$). The detailed experiments conducted with different parameters confirm that the temperature distribution shows the opposite trend for both the cell electrodes, which means the temperature increases and decreases with the rise and fall of the voltage at the negative side, but it decreases and increases with the rise and fall of the voltage at the positive side during the charge-discharge cycles [26].

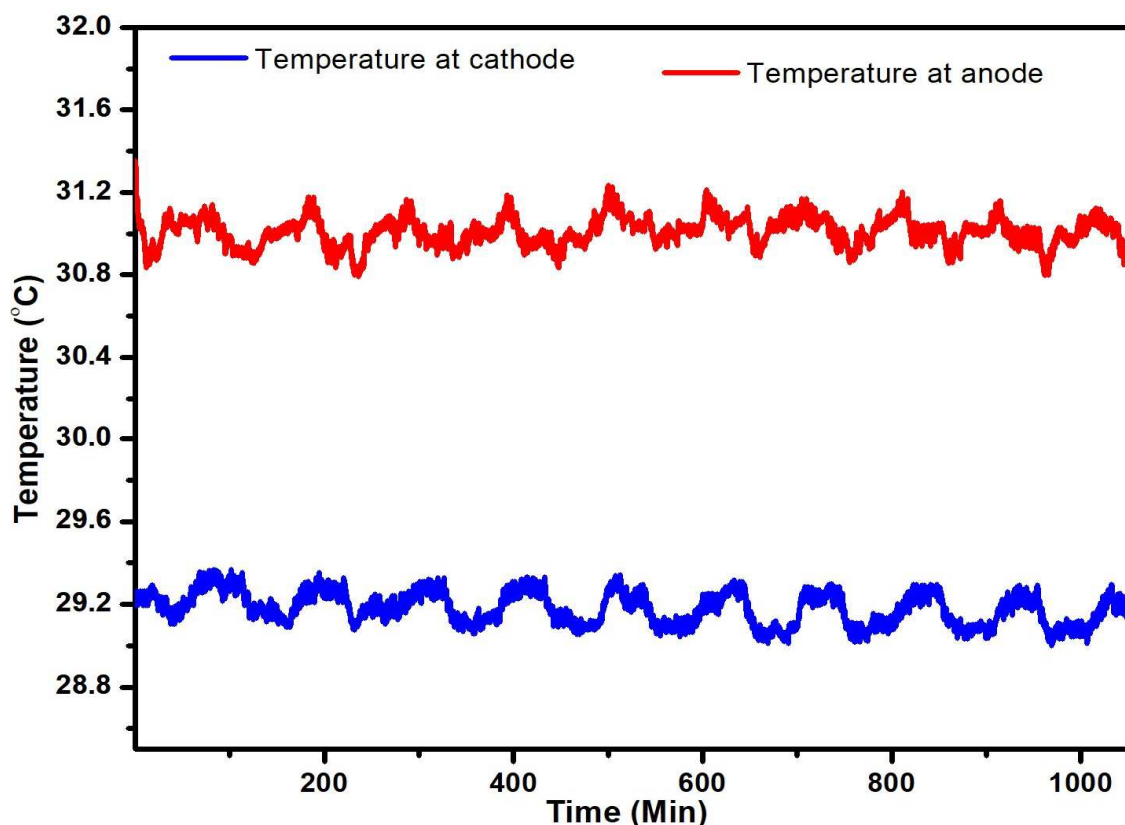


Fig. 46. Real time temperature distribution of electrochemical cell at anode and cathode at temperature 30°C and flow rate 100 ml min^{-1} .

During discharge at the negative electrode, the oxidation of V^{+2} to V^{+3} is thermodynamically favourable, requiring less energy input, and any heat generated is less localized due to the exothermic nature of the reaction [54]. The enthalpy change at the

negative electrode is very less compared to the positive electrode. The change in the enthalpy at the negative and positive electrodes are -33 KJ/mol and -122.8 KJ/mol during discharge. The entropy changes in the negative and positive electrodes are -0.0379 KJ/mol/K and -0.0884 KJ/mol/K during discharge [55]. At the negative electrode, the electrochemical reaction heat is much less compared to the positive electrode and the reaction V^{+3} to V^{+2} is thermodynamically unfavourable, and the charge requires overcoming activation energy for the reduction which generates heat due to polarisation and resistive effects. Also, the rate of heat dissipation is less at the negative electrode compared to the positive electrode as given by the entropy values, so the heat accumulates at the negative electrode during the charge. At the positive electrode, the activation overpotential is less and the enthalpy change for the electrochemical reaction is high. The rate of heat dissipation is also higher. So, there is no heat accumulation in the positive electrode. The change in temperature in the positive electrode is due to the nature of the chemical reaction [56].

5.2.4 A comparative in-operando current distribution analysis at the positive and negative sides of the full cell during the galvanostatic cycling.

The current density distribution applied to the full cell is also mapped using the sensor at the positive and negative electrodes during the charge-discharge cycling at 60 mA cm^{-2} , 75 mA cm^{-2} , 90 mA cm^{-2} , and is given in Fig. 47 & Fig. 48. The Fig. 47a (60 mA cm^{-2}), Fig. 47c (75 mA cm^{-2}), and Fig. 47e (90 mA cm^{-2}) represent the current density distribution at the positive side of the cell during charge and indicate the current density is higher near the edges of the electrodes. Similarly, during the discharge also, the current density is higher near the edges and is mapped to Fig. 47b (60 mA cm^{-2}), Fig. 47d (75 mA cm^{-2}), and Fig. 47f (90 mA cm^{-2}). Similarly, for the negative cell, the current density distribution is mapped and is given in Fig. 48 during charge and discharge. Fig. 48a (60 mA cm^{-2}), Fig. 48c (75 mA cm^{-2}), and Fig. 48e (90 mA cm^{-2}) represents the current density contour plot during charge and Fig. 48b (60 mA cm^{-2}), Fig. 48d (75 mA cm^{-2}), and Fig. 48f (90 mA cm^{-2}) during discharge. The current density distribution in the negative electrode is more inclined toward uniformity at the surface rather than the edges compared to the positive electrode. The lower current density distribution (blue) size is also lesser than the positive side. This is due to the velocity gradient across the electrode at low flow rate. The velocity of the electrolyte under the rib is higher than the velocity near the membrane. This is why we see the current distribution concentrated at the edges of electrode[52].

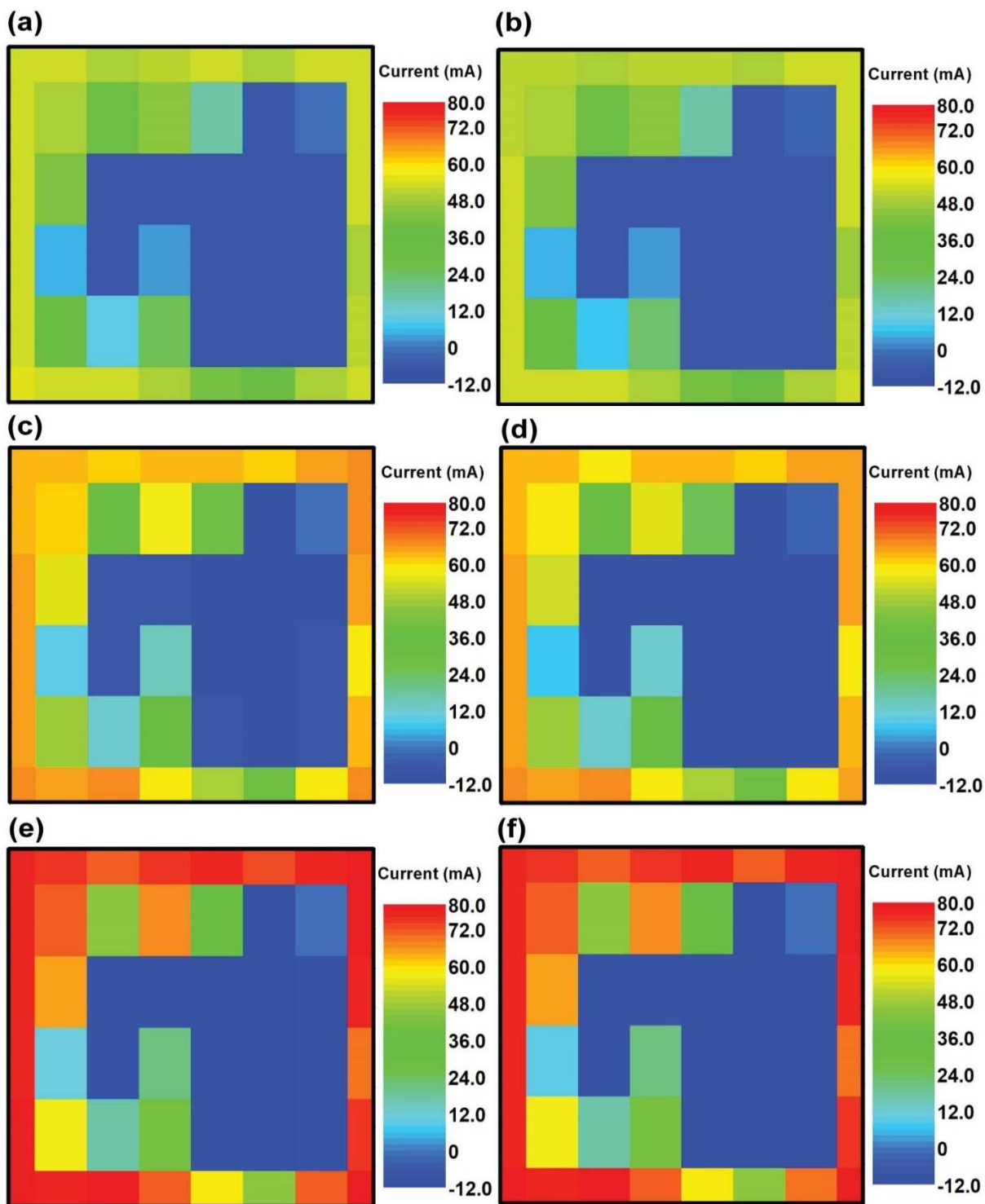


Fig. 47. Real-time current distribution of electrochemical cell at cathode at temperature 25°C and flow rate 50 ml min⁻¹: (a) current contour plot at 60 mA cm⁻² charge, (b) current contour plot at 60 mA cm⁻² discharge, (c) current contour plot at 75 mA cm⁻² charge, (d) current contour plot at 75 mA cm⁻² discharge, (e) current contour plot at 90 mA cm⁻² charge, (f) current contour plot at 90 mA cm⁻² discharge.

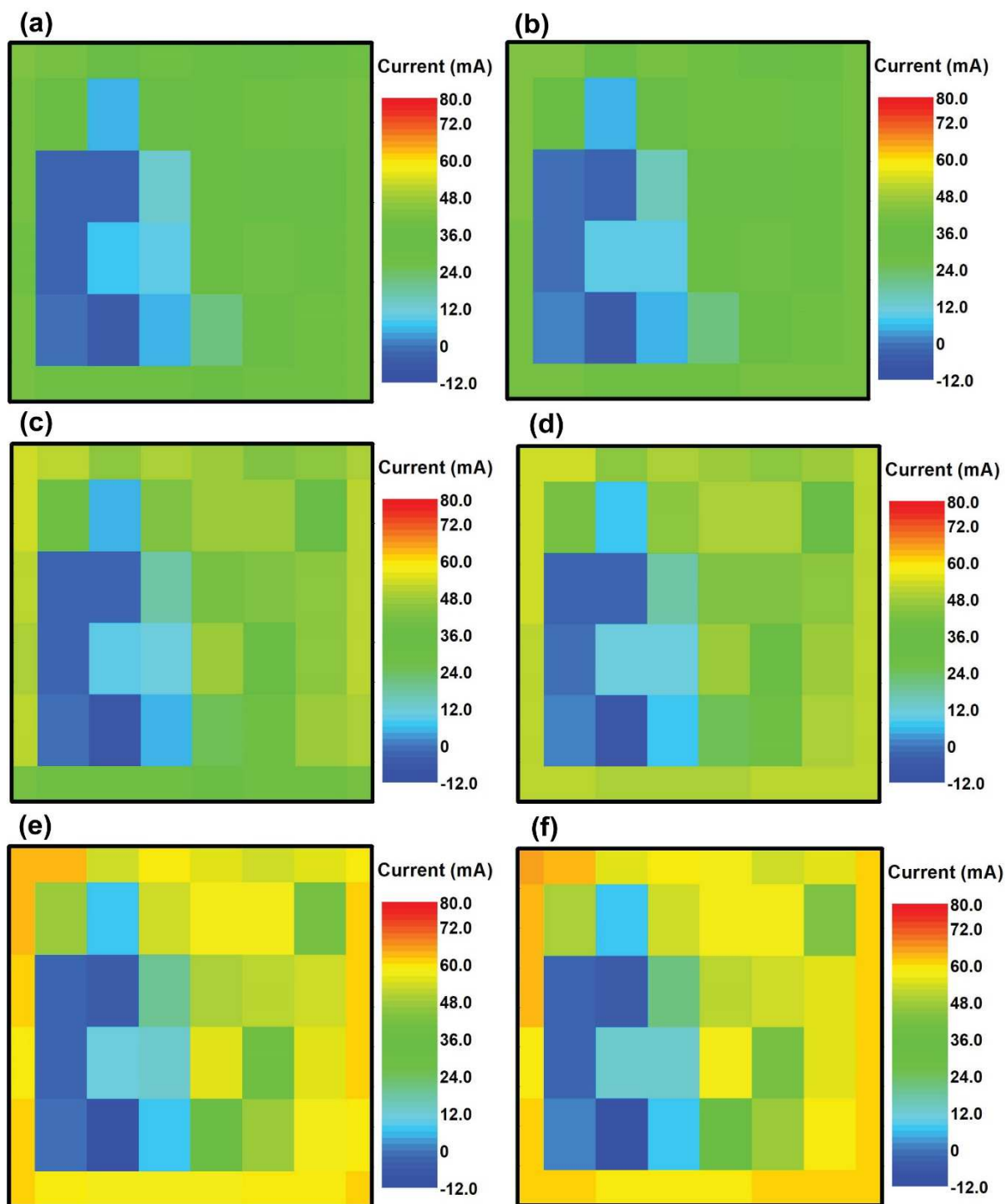


Fig. 48. Real-time current distribution of electrochemical cell at anode at temperature 25°C and flow rate 50 ml min⁻¹: (a) current contour plot at 60 mA cm⁻² charge, (b) current contour plot at 60 mA cm⁻² discharge, (c) current contour plot at 75 mA cm⁻² charge, (d) current contour plot at 75 mA cm⁻² discharge, (e) current contour plot at 90 mA cm⁻² charge, (f) current contour plot at 90 mA cm⁻² discharge.

For another case, to study the effect of electrolyte flow rate on current distribution at the positive and negative sides of the full-cell, the flow rate of cell has been increased from 50 mL min⁻¹ to 100 mL min⁻¹. The current density distribution contour plots are mapped for current densities 60 mA cm⁻², 75 mA cm⁻², and 90 mA cm⁻² during charge and discharge at both the electrodes and is shown in Fig. 49 & Fig. 50. The Fig. 49a, Fig. 49c, Fig. 49e shows the contour plot for current density distribution for the positive cell during charge at 60 mA cm⁻², 75 mA cm⁻², and 90 mA cm⁻². The current density distribution in these plots are uniformly distributed along the surface of the electrode (area 25 cm²) unlike the case discussed above [52]. Similarly, during discharge at positive side the current density distribution plot is shown in Fig. 49b (60 mA cm⁻²), Fig. 49d (75 mA cm⁻²), Fig. 49f (90 mA cm⁻²). The current density distribution follows the same pattern of uniformity during discharge as discussed above for charge. The current distribution in the electrodes have lesser magnitude and is distributed throughout the electrode surface area rather at the edges as discussed for a flow rate of 50 mL min⁻¹. However, there are still few lower current density areas at the center of the electrode area. The current density distribution at negative electrode during charge and discharge is depicted in Fig. 50. There is very little difference in the current density distribution at negative side during charge and discharge at both the flow rates 100 mL min⁻¹ and 50 mL min⁻¹ (Fig. 48) and the distribution is uniform for all the current densities.

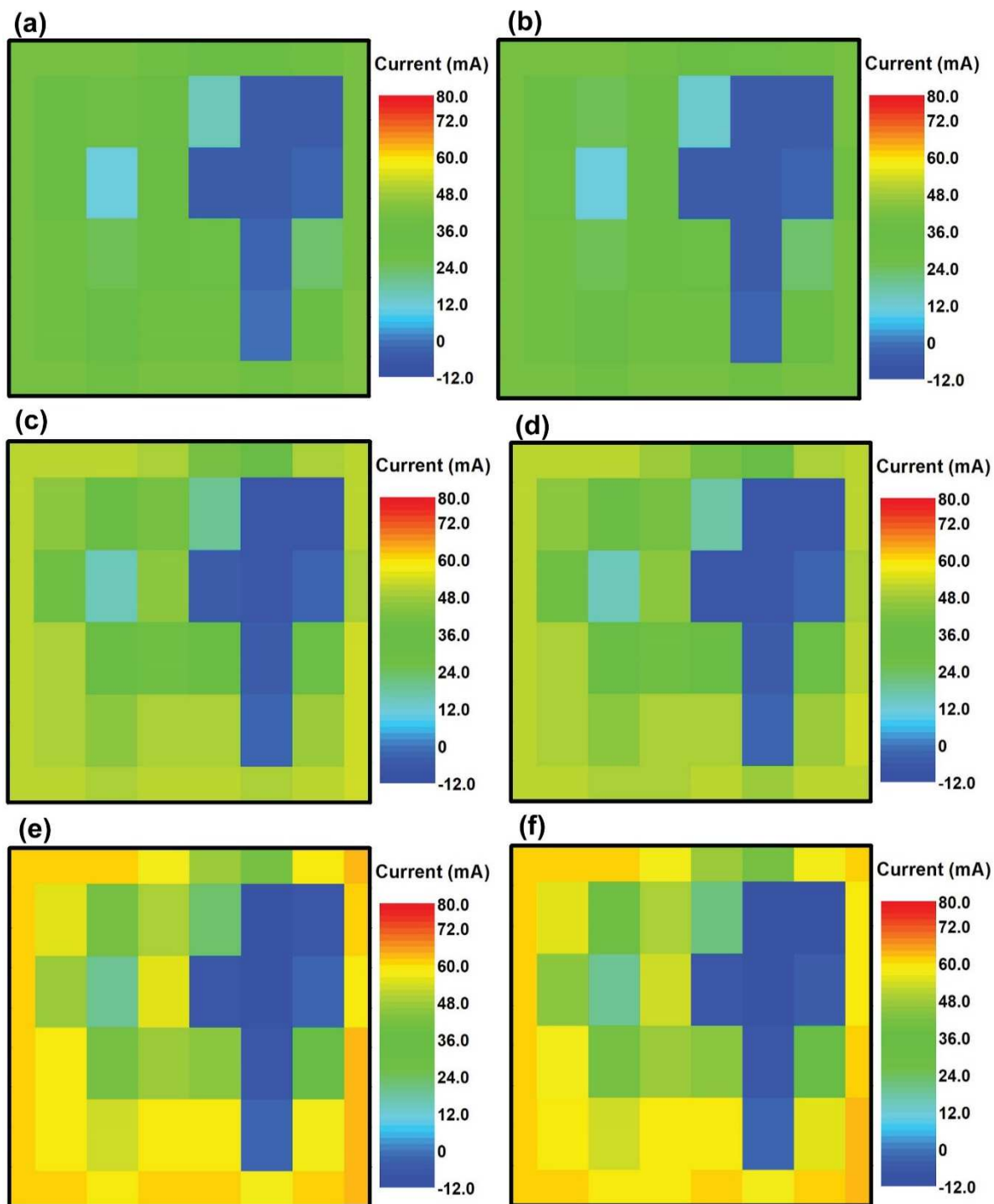


Fig. 49. Real-time current distribution of electrochemical cell at cathode at temperature 25°C and flow rate 100 ml min⁻¹: (a) current contour plot at 60 mA cm⁻² charge, (b) current contour plot at 60 mA cm⁻² discharge, (c) current contour plot at 75 mA cm⁻² charge, (d) current contour plot at 75 mA cm⁻² discharge, (e) current contour plot at 90 mA cm⁻² charge, (f) current contour plot at 90 mA cm⁻² discharge.

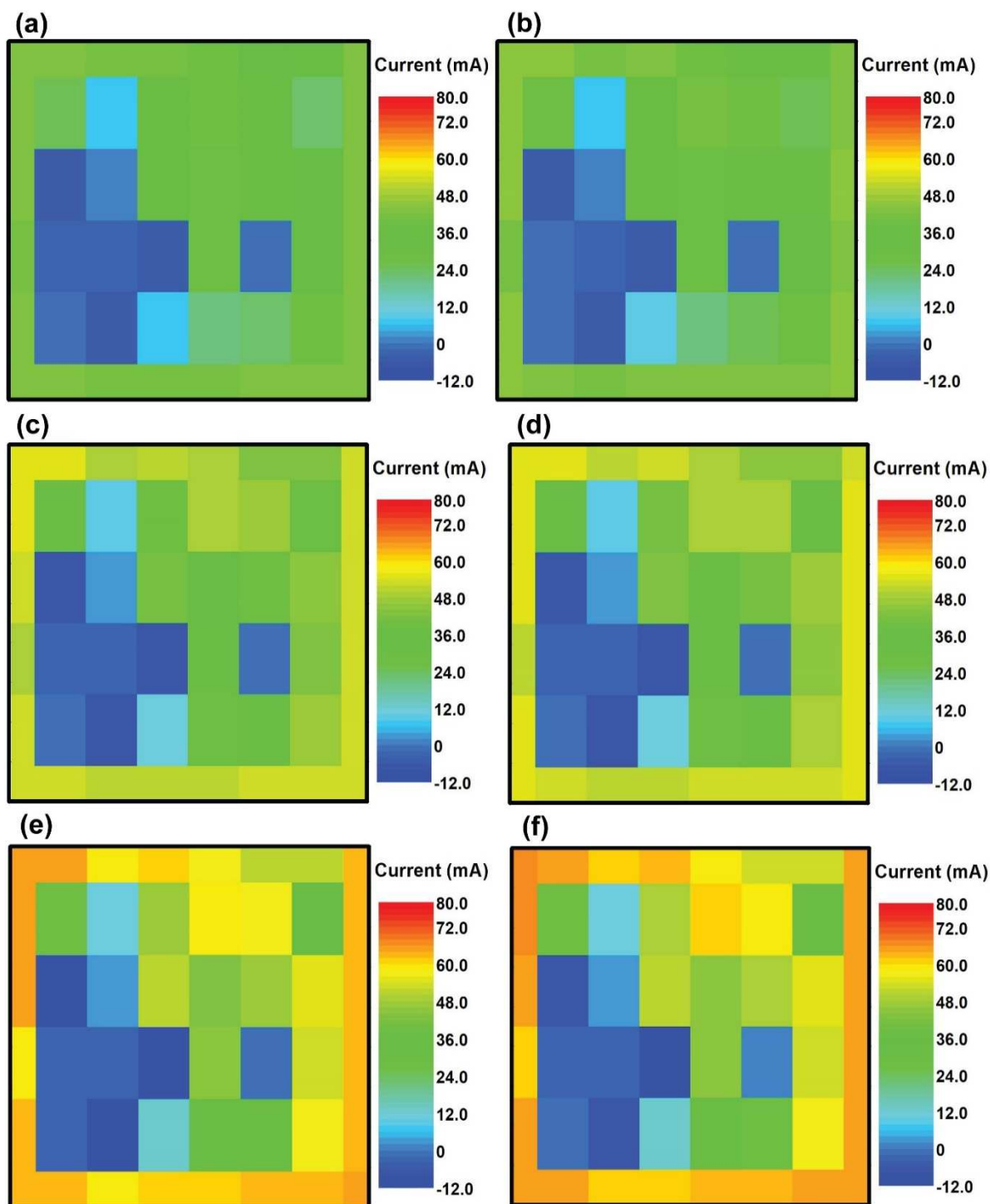


Fig. 50. Real-time current distribution of electrochemical cell at anode at temperature 25°C and flow rate 100 ml min⁻¹: (a) current contour plot at 60 mA cm⁻² charge, (b) current contour plot at 60 mA cm⁻² discharge, (c) current contour plot at 75 mA cm⁻² charge, (d) current contour plot at 75 mA cm⁻² discharge, (e) current contour plot at 90 mA cm⁻² charge, (f) current contour plot at 90 mA cm⁻² discharge.

5.3 In-operando temperature analysis at the negative electrode (anode) in full-cell during the galvanostatic cycling at higher vanadium concentration.

Galvanostatic cycling with higher vanadium concentration of 1.5 M V_2O_5 , 3 M H_2SO_4 and 1.5 M Oxalic acid is performed. The current density of 40 mA cm^{-2} with an operating temperature of 25°C and electrolyte flow rate of 100 mL min^{-1} are used. The number of galvanostatic cycles performed is 52 cycles represented in Fig. 52. A voltage profile vs. time is shown Fig. 52a along with the temperature profile vs. time recorded at the negative electrode during the charge-discharge cycling for 52 cycles. It indicates that it increases during the charging process and gets maximized when the uppercut-off voltage reaches 1.8 V. During the discharging process, the temperature starts decreasing. It minimizes when the cell is completely discharged (i.e., 0.8 V). To analyse the temperature distribution, the first 10 cycles for charge and discharge are plotted and shown in Fig. 52b. The temperature profile nature is quite like the voltage profile as depicted in previous cases. The discharge capacity (mAh) vs. cycling is shown in Fig. 51a. A discharge capacity of $\sim 1500 \text{ mAh}$ is observed after 10 cycles and a discharge capacity of $\sim 1250 \text{ mAh}$ is observed after 50 cycles which is quite good even after 40 charge-discharge cycles. An 83% discharge capacity retention is observed from the 10th (considered 100%) to the 50th cycle. The Coulombic, energy, and Voltaic efficiency is calculated and depicted in Fig. 51b. The Coulombic efficiency remains constant throughout the cyclic process which is $\sim 87\%$. However, it is less compared to the previous experimental setup. Voltaic efficiency is observed at $\sim 64\%$ at the 1st cycle and gradually decreases to $\sim 53\%$ at the end of the 50th cycle. Similarly, a trend of energy efficiency decreased with an increase in the charge-discharge cycle and is

shown in Fig. 51b. Initially, the energy efficiency is recorded at ~56% and it decreases gradually to ~45% at the end of 50th cycle. Fig. 53 represents the real-time temperature distribution in the area of 25 cm² at the negative electrode during the charge and discharging process. It can be seen that the temperature distribution in the electrodes are non-uniform and concentrated more towards the edges of the electrode as shown in Fig. 53. The temperature distribution during the charge is slightly lower to the temperature distribution during discharge. This is because of the fluctuation in temperature caused by the variation of resistance and the heat absorption and release in chemical reaction during charge and discharge [41]. The temperature distribution in the electrodes is non-uniformly distributed with few hotspots at the edges of the electrodes as shown in fig. The charge takes place at low temperature and discharge takes place at high temperatures due to the nature of exothermic and endothermic reactions.

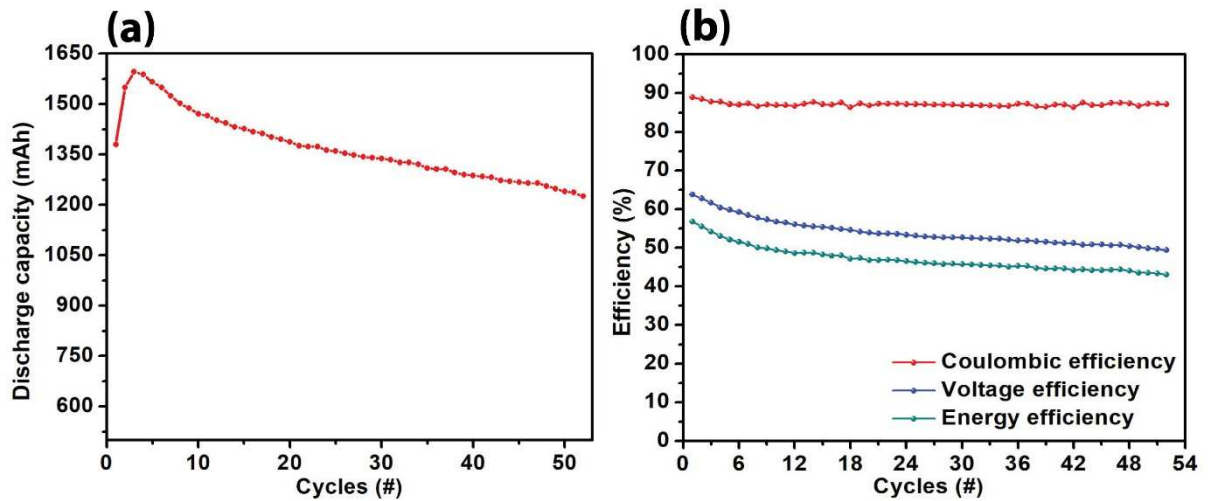


Fig. 51. Electrochemical performance in the full-cell configuration of VRFB at the negative side of the full cell at higher vanadium concentration. (a) discharge capacity vs. cycles, (b) Coulombic, Energy, and Voltaic efficiencies vs. cycles.

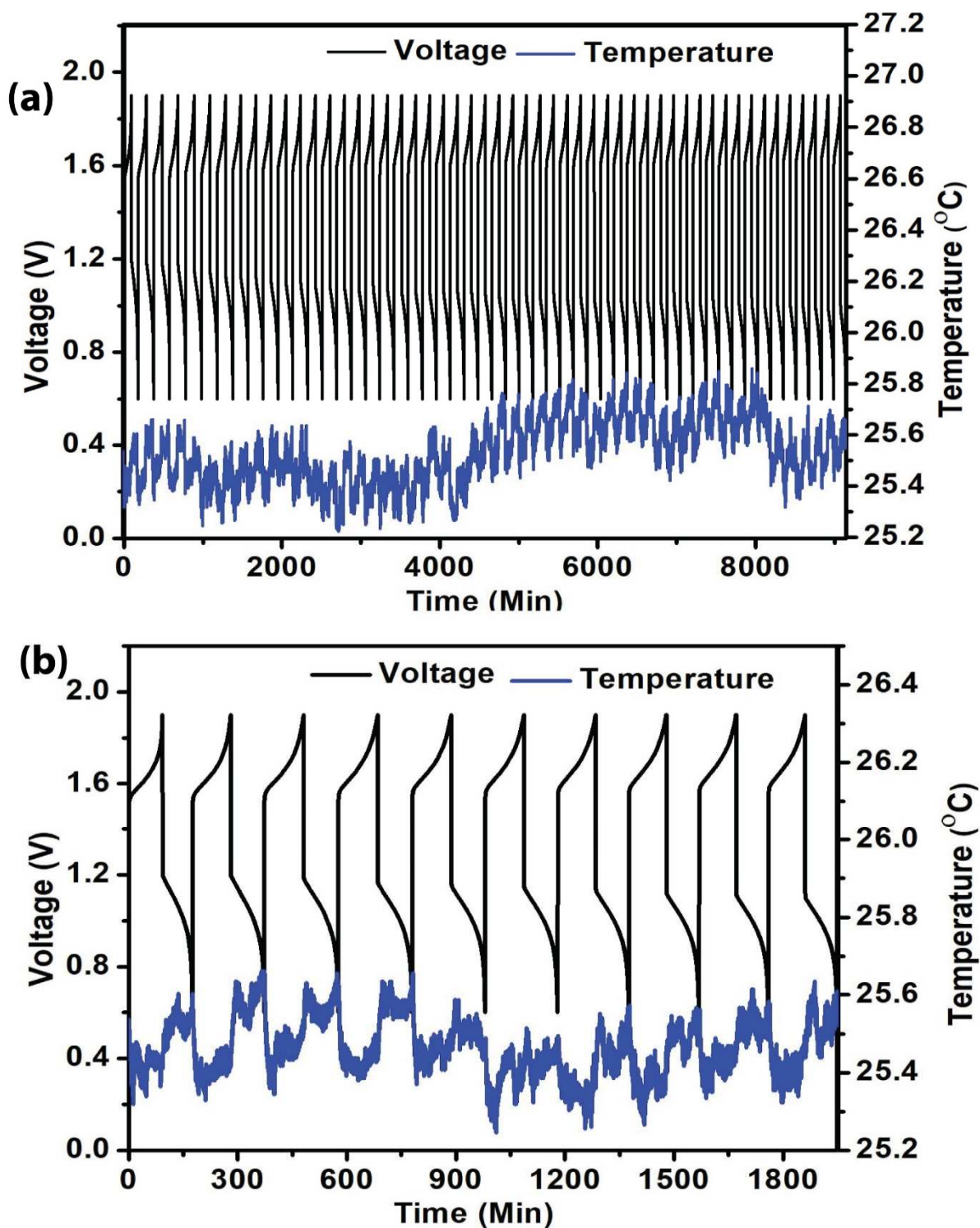


Fig. 52. Electrochemical performance in the full-cell configuration of VRFB at the negative side of the full cell at higher vanadium concentration. (a) Voltage and temperature vs. time plot at 40 mA cm^{-2} for 52 cycles, (b) Voltage and temperature vs. time plot at 40 mA cm^{-2} for first 10 cycles.

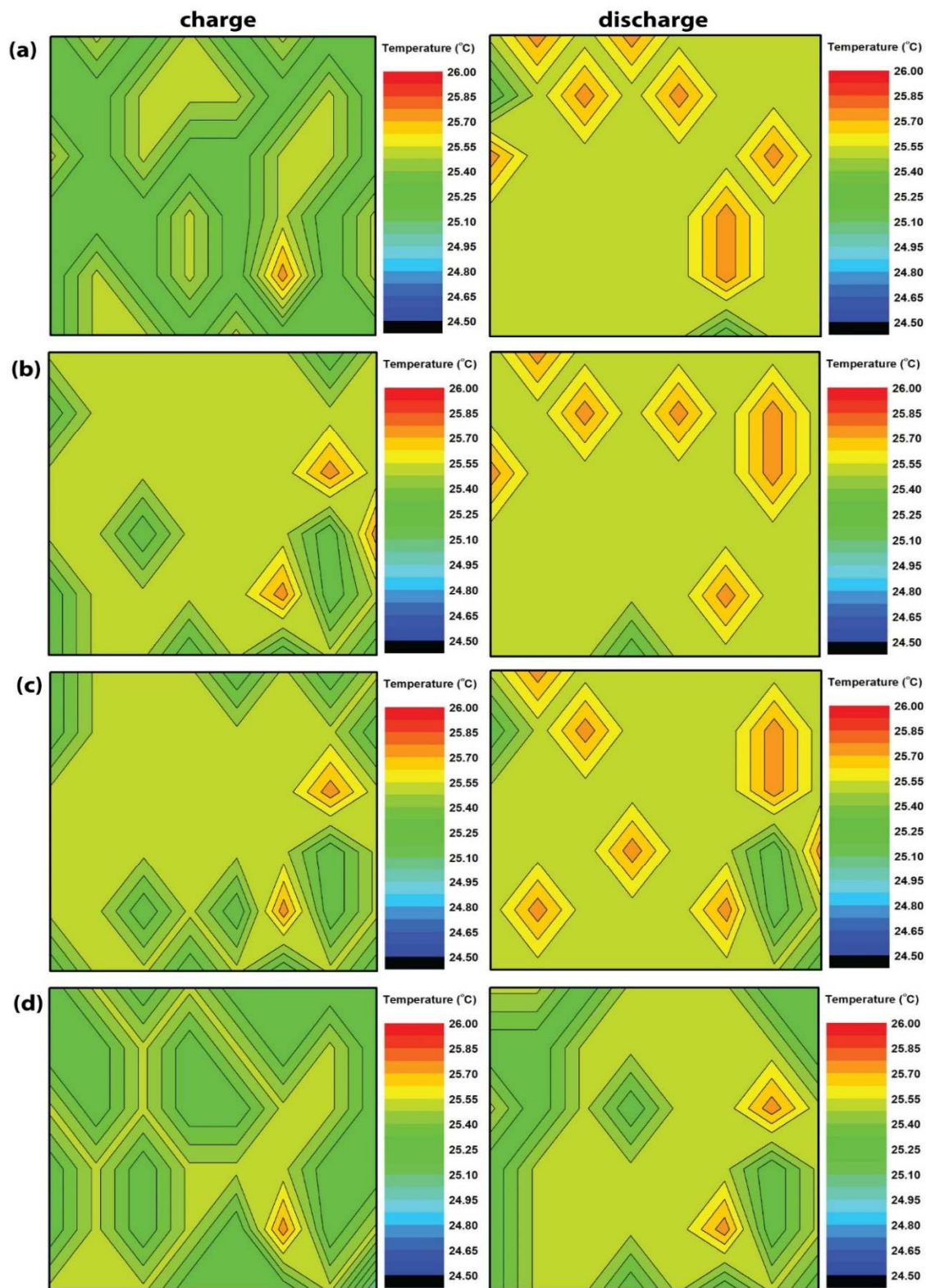


Fig. 53. Temperature contours at charge and discharge at higher vanadium concentration. (a) 1st cycle, (b) 3rd cycle, (c) 5th cycle, (d) 7th cycle.

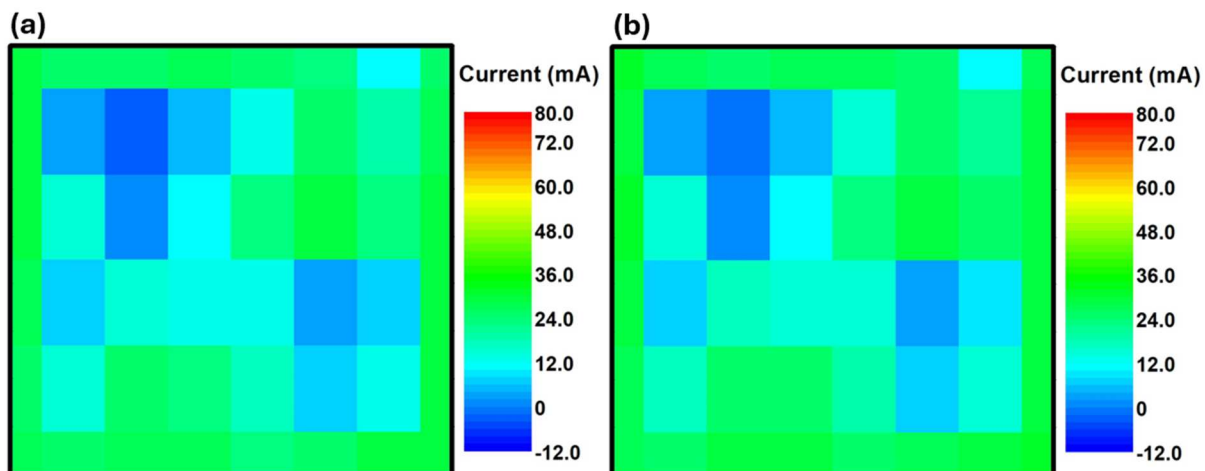


Fig. 54. Real-time current distribution of electrochemical cell at anode at temperature 25°C, flow rate 100 ml min⁻¹ and 1.5 M Vanadium concentration: (a) current contour plot at 60 mA cm⁻² charge, (b) current contour plot at 60 mA cm⁻² discharge

CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1 Conclusions

The study analyzed the real-time distribution of temperature and current of the single stack full-cell for the vanadium redox flow battery using the operando technique. The temperature distribution at the bipolar plate, in contact with electrolyte flow and graphite felt during the charge and discharge processes, was analyzed with varying current densities from 60 to 90 mA cm⁻², flow rates from 50 to 100 mL min⁻¹, and operating temperatures for the cell and tank ranging from 25 to 30 °C. Our investigation showed that the temperature at the negative electrode rises during charging and falls during discharging. The operando temperature profile exhibits analogous patterns to the voltage profile throughout the charge-discharge operation. Unexpectedly, the operando temperature profile at the positive electrode differs from that at the negative electrode under analogous experimental charge-discharge conditions. The temperature diminishes at the positive electrode during charging and escalates during discharging. Consequently, the profile is contrary to the negative electrode. Furthermore, the negative electrode undergoes greater temperature fluctuations during galvanostatic cycling compared to the positive electrode under analogous experimental conditions. It also observed a slight increase or decrease in temperature at the cell's electrodes with varying applied current densities during charge-discharge cycles. A two-dimensional representation of temperature distribution on the surfaces of the cell's electrodes (negative and positive) demonstrates greater homogeneity at a flow rate of 100 mL min⁻¹ compared to 50 mL min⁻¹. Our work reveals that

homogeneous temperature distribution, coupled with an elevated flow velocity, significantly enhances the electrochemical performance of advanced VRFBs, particularly in terms of discharge capacity. The current density distribution in both electrodes is more uniform at elevated electrolyte flow rates compared to lower flow rates, where the distribution is more concentrated at the edges. The same pattern of temperature distribution is also analyzed at higher vanadium concentration.

We firmly assert that our comprehensive analysis of the cell's real-time temperature distribution during galvanostatic cycling can facilitate the advancement of vanadium-based redox flow batteries and may be crucial in preventing the precipitation of vanadium active species during operation by optimizing electrolyte flow rate and current density. The findings indicate that enhanced engineering and design are necessary to optimize the electrolyte flow field, ensuring that the bipolar plates achieve uniform temperature distribution throughout battery operation to reduce electrochemical performance degradation. The time fluctuation in temperature distribution can elucidate the electrochemical processes occurring during the charging and discharging of both sides of the RFB. They can also be utilized to devise effective thermal management solutions.

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6.2 Future Recommendations

- To analyse the temperature distribution in the cell and the electrodes under the same experimental conditions at higher temperatures.
- The thickness of the bipolar plate can be reduced for more accuracy in the temperature distribution results.
- The temperature distribution can be analysed using different flow field designs, such as interdigitated, parallel, and zig-zag flow fields.
- Stabilising agents can be used to improve the efficiency of the cell and minimize the hydrogen and oxygen evolution.
- The reduction of the electrolyte can be done using various reducing agents such as L-Ascorbic acid and Citric acid to minimize the quantity and time for reduction.

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