Bismuth concentration influenced competition between electrochemical reactions in the all-vanadium redox flow battery

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HIGHLIGHTS

- Kinetics improved by three orders of magnitude with Bi additives in the VRFB.
- Bi selectively catalysed VRR over HER efficiently reduced the side reaction.
- Optimal peak kinetic enhancement with moderate Bi concentration.
- Reduced HER allows improved VRFB performance at high current density.

GRAPHICAL ABSTRACT

- Morphology change
- Hydrogen production level variation
- Increased electrode resistance along polarisation

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ABSTRACT

The current obstacles for all-vanadium redox flow batteries (VRFBs) include the sluggish reaction kinetics of electrode materials and the overlapping potential range of the hydrogen evolution reaction (HER) with the negative redox couple. Bismuth (Bi) additives have exhibited tremendous enhancement of battery performance; however, the performance plateaus with concentration of Bi and the catalytic mechanism remains inconclusive and controversial. Quantified kinetic values from three electrochemical methodologies, including modelling, show that the performance plateau with Bi concentration was related to the kinetics of the vanadium redox reaction (VRR) instead of dissolution of Bi, and VRR reaction rate was improved three orders of magnitude with the addition of Bi, with the highest VRR reaction rate observed for electrolyte with 750 ppm Bi additive. Additionally, a competing relationship between VRR and the HER was explored via electrochemical methodologies. It was further confirmed that Bi effectively selectively catalysed VRR over HER via in-situ mass spectrometry measurements during battery cycling, which allows for a higher battery charging cut-off potential of 1.7 V without electrolyte imbalance caused by water electrolysis, achieving 86% of the theoretical electrolyte capacity at 110 mA cm\(^{-2}\) with 750 ppm Bi. The full battery performance with 750 ppm Bi additive is among the best in the literature to date.

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1. Introduction

The global energy demand is ever-growing and, with the aim of a more sustainable future, traditional energy sources (carbon-intensive fossil fuels) are being gradually replaced by clean and renewable energy sources, such as solar, wind, and nuclear energy [1]. To offset the drawbacks of the temporal and intermittent nature of renewables and achieve the increased electrification demand of the transport and domestic sectors, the redox flow battery (RFB), having the ability to decouple the energy density and power output [2], has become one of the most promising stationary energy storage systems. Ever since the concept of redox flow batteries was developed from a redox-type fuel cell in 1971 and the foundation of rechargeable redox flow cells was demonstrated by NASA [3], researchers have aimed to push the battery performance to higher energy, power density, efficiency, and longer cycle life through investigation on RFB chemistries, materials, and systems.

Among various chemistries, all-vanadium redox flow batteries (VRFBs) are the most commercially established due to the reduced effect of crossover of redox materials, which dramatically extends the electrolyte lifespan. However, commercialisation of VRFBs is still hindered by the low electrochemical activity of current electrode materials, carbon/graphite felt and carbon paper [4], as well as high cost of vanadium. Via electro-catalytic studies, positive electrolyte couples (VO$^{2+/3+}$) have been improved by introducing oxygen functional groups to carbon-based electrode surfaces [5-7] and increasing electrode surface area with electrosyn nano-carbon fibres [8-11]. However, the negative electrolyte couple (V$^{3+/2+}$) is more problematic due to its overlapping potential with hydrogen evolution, along with a deterioration of oxygen functional groups under the reductive environment [12-14]. Because of the aforementioned reasons, the catalyst selection [15] for V$^{2+/3+}$ is constrained by the nature of its reductive chemistry and potential under operating conditions, where the quantitative effect of the catalyst on V$^{2+/3+}$ kinetics was possible to elucidate, due to its inner-sphere electron transfer [16] instead of outer-sphere electron transfer [12] for VO$^{2+/3+}$. As early as 2013, Li et al. [17] showed an impressive battery performance improvement by adding bismuth (Bi) into the electrolyte, which made Bi appeal to researchers as a replacement of unstable functional groups and noble metals. In this work, the authors proved Bi catalytic activity by the reduced redox peak potential separation on a glassy carbon electrode during cyclic voltammetry (CV). They credited this improvement to its suppressing the hydrogen evolution reaction (HER) and reducing the activation kinetic barrier for V$^{3+/2+}$. Following this study, Suarez et al. [18] found opposite evidence that bismuth promotes the HER reaction through comparing the generated current in the linear sweep voltammetry (LSV) instead of outer-sphere electron transfer [12] for VO$^{2+/3+}$. As early as 2013, Li et al. [17] showed an impressive battery performance improvement by adding bismuth (Bi) into the electrolyte, which made Bi appeal to researchers as a replacement of unstable functional groups and noble metals. In this work, the authors proved Bi catalytic activity by the reduced redox peak potential separation on a glassy carbon electrode during cyclic voltammetry (CV). They credited this improvement to its suppressing the hydrogen evolution reaction (HER) and reducing the activation kinetic barrier for V$^{3+/2+}$. Following this study, Suarez et al. [18] found opposite evidence that bismuth promotes the HER reaction through comparing the generated current in the linear sweep voltammetry (LSV). Therefore, they proposed a complex mechanism, where protons favour reacting with metallic bismuth into an unstable product bismuthine (BiH$_3$), which is a strong reducing agent that then reduces V$^{3+}$ to V$^{2+}$. Without direct mechanistic proof, this inference is also questionable as there is still a lack of direct or quantitative evidence. Contrary to this, Yu et al., in 2018 [19] also supposed that Bi suppresses hydrogen evolution, meaning that the small body of literature on this effect is still to be clarified.

In our work, Bi was solubilized in the electrolyte in the ionized form before electrochemical testing, and then formed particles on the electrode surface through electrodeposition, where the reduction of Bi particles occurred simultaneously on the negative electrode side with the charging and catalysis process. This principle was first proposed by Li and colleagues [17], and it is worth noting that they found the enhancement of battery performance by Bi reached a maximum at 0.01 M (with increasing concentration from 0 M to 0.02 M). The optimal amount of Bi$^{3+}$ in the electrolyte was explained by the formation of agglomerated larger particles at the higher concentrations, which were dissolved in the flowing electrolyte and resulted in reduced catalytic surface area [17,20]. This highlighted dissolution of solid Bi as a potential concern; battery operational potential windows vary in the literature, with 1–1.55 V being the smallest window to avoid dissolution [21]. However, a study [22] on the bismuth deposition pattern using operando X-ray computed tomography indicated there was no obvious dissolution during the charging and discharging process, but another issue of uneven distribution of Bi deposition pattern was discovered. Therefore, higher flow rate and a pre-deposition step of Bi were suggested to achieve a better particle distribution [23]. To conclude, there are remaining unsolved questions around the nature of the Bi deposition and catalysis process of VRFB by Bi, including the influence on vanadium reaction rate (kinetics) by varying Bi concentrations, as well as the relationship between improved kinetics and battery performance.

VRFB performance in the literature does not simply linearly increase with Bi concentration, which questions the effect of deposited Bi, as a higher Bi concentration in the electrolyte should lead to more Bi deposited and hence more catalyst sites for the reactions. To understand the correlation between deposited Bi by different Bi concentrations and VRB kinetics, the experiments for kinetic study were designed with an excessive amount of dilute vanadium electrolyte with varied Bi additive concentration to provide a stable Bi concentration during the deposition process, then the VRB kinetics and side reaction of HER were studied with varied electrochemical approaches. The target of these three-electrode electrochemical studies was to isolate the VRR from other reactions and then enable quantification of VRR on the Bi metal surfaces with different starting Bi concentrations. The work here covers three electrochemical methodologies on glassy carbon electrodes (linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS)), as well as full-cell battery testing with carbon felt electrodes. LSV with Butler-Volmer (BVE) and Koutechy-Levich (KL) analysis was modified and applied to calculate the exchange current density ($I_0$), which was compared with the charge transfer resistance ($R_T$) by EIS and standard rate constant ($k_0$) by CV. With consideration of the complex reactions that occur on the electrode, the experimental LSV data was obtained on a simple electrode geometry (glassy carbon disk) and was then fitted with simulated data to achieve its constituent coefficient: exchange current density ($I_0$). Combined with an in-situ detection of hydrogen production on the commercial electrode with mass spectrometry, direct evidence for the onset potential of HER was obtained. Surface characterization of scanning electron microscopy (SEM) was applied to identify the morphology variation under the impact of polarization and Bi additive concentration. Five concentrations of Bi additives (0, 100, 500, 750 and 1000 ppm) were analysed, and the optimum concentration for improving VRR reaction rate was found to be 750 ppm for all three kinetic indicators ($I_0$ by LSV, $R_T$ by EIS and $k_0$ by CV), as well as in the battery performance with highest energy efficiency (EE) and least performance decay. This work quantitatively analysed the catalytic effect of Bi in this multiple electrochemical reaction system and found a non-linear relationship between Bi additive concentrations and kinetic rates of vanadium reaction. The Bi electrodeposition reaction was also studied by electrochemical methods coupled with ex-situ SEM imaging and in situ mass spectrometry to quantify the HER at varied polarization and Bi concentration. The effect of Bi on the HER was therefore verified with a direct proof for the first time in the literature. The results showed that the influence of Bi concentration on the electrocatalysis of the V$^{2+/3+}$ reaction rate can be attributed to change in morphology from 3D four-pointed stars into 1D nanorods with the increased Bi concentration. Finally, full cell tests combined with in-situ mass spectrometry indicate a successful reduction of HER by selective catalysis of VRR with Bi, which allowed for enlarging the battery operational potential window and achieved 86% of theoretical electrolyte capacity utilization under a high charge-discharge current density.
2. Experimental details

2.1. Electrochemical characterization

The electrochemical measurements were studied under room temperature in a three-electrode system, where a glassy carbon (GC) disk electrode (Pine Instruments, USA) with 0.1963 cm$^2$ surface area, a Pt mesh and an Ag/AgCl electrode were used as working, counter, and reference electrode, respectively. The Ag/AgCl reference electrode was measured against a hydrogen reference electrode (Gasketel) and the recorded potential of the potentiostat (Gamry Instruments, USA) was then corrected vs. normal hydrogen electrode (NHE). The GC electrode was prepared by polishing with 1, 0.3 and 0.05 μm alumina powder and then rinsing through ultrasonication in deionized water before testing. LSV, EIS and CV were studied in the 0.05 M VO$^{2+}$ electrolyte with different concentrations of Bi additives: 0, 100, 500, 750 and 1000 ppm. The vanadium electrolyte was prepared by diluting commercial vanadium electrolyte (1.6 M VO$^{2+}$/3 M sulfuric acid, Oxkem, UK) with 3 M sulfuric acid, where the concentration of sulfuric acid is the total sulfate. Then, bismuth chloride powder (reagent grade, >98%, Sigma-Aldrich, USA) was weighed based on target concentrations and solubilized in the vanadium electrolyte.

2.2. In-situ mass spectrometry and ex-situ SEM

The three-electrode system described in the electrochemical characterization section was combined with in-situ mass spectrometry to monitor hydrogen production. In this case, the glassy carbon electrode was replaced with a heat-treated graphite felt as working electrode to increase the electrochemical surface area for more accurate gas analysis. Nitrogen gas was flowed through the system with a constant flow rate and the evolved gas was analysed by a quantitative gas analyser (QGA, Hiden analytical, UK). The monitored electrocatalysis gases were produced under controlled potentials in the vanadium electrolytes with different concentrations of Bi additive, where the potential steps were from −0.25 V to −0.6 V vs. NHE with 50 mV interval and holding for 20 min at each step.

The investigation of Bi electrodeposition process was conducted in the three-electrode system with glassy carbon electrode and potential holds at vanadium reaction potential (−0.3 V vs. NHE) for 30 min in the vanadium electrolyte containing various concentrations of Bi additives. Then surface characterization of the glassy carbon electrode with electrodeposited Bi particles was studied by SEM, which was performed with an EVO MA10 (ZEISS, Germany) and in secondary electron imaging mode at 10.00 kV.

2.3. Full cell battery testing

Current density and charge cut-off potential were studied in the full cell battery tests with varied concentrations of Bi additives. A custom built VRFB cell (GGM Engineering) was used for full cell cycling, which consists of a Nafion® 117 membrane, two gold plated copper current collectors, two graphite flow plates with interdigitated flow channel and two 3.45 mm thick PTFE spacers to deliver 25% compression of graphite felt (GFD 4.6 EA, SGL carbon, Germany) electrode, which is compressed to 75% of its original thickness. 20 ml of 1.6 M vanadium (50:50 of VO$^{2+}$/V$^{2+}$, Oxkem, UK) electrolyte was loaded on each side of the battery and circulated at a 20 ml min$^{-1}$ flow rate by a Watson-Marlow peristaltic pump.

The battery performance with heat treated graphite felt, which was pretreated in air at 400 °C for 30 h [7], and in the commercial electrolyte with 0, 100, 500, 750, and 1000 ppm Bi additives $I_f$ were compared on a Gamry Reference 3000 Potentiostat. The 50% state of charge (SoC) commercial electrolyte (1.6 M 50%:50% of V$^{2+}$/VO$^{2+}$) was first charged by reaching 1.60 V and then discharged to 0.85 V to get the initial electrolyte composition. Immediately following the first electrolyte balance step, the battery was continuously charge-discharge cycled with increasing current density (50, 80, 110, 140 mA cm$^{-2}$), and after that it was returned to 50 mA cm$^{-2}$ for comparison, where each current step was cycled for 4 times. Then its stability under high current density was analysed by cycling 80 times at 110 mA cm$^{-2}$, where the rate capability studies with varied Bi concentration used a constant current mode and with potential cut-off at 0.85 V for discharging and 1.6 V for charging. The investigation of charge cut-off potential used the same battery setup, after the electrolyte balance step, but the battery was charge-discharged with increased charging cut-off potentials of 1.6 V, 1.7 V and 1.8 V for 4 cycles for each potential step, followed by 20 cycles with a 1.8 V cut-off potential to compare battery stability. This protocol was repeated with varied Bi concentrations, where in-situ mass spectrometry was connected into the gas line of the negative electrolyte tank during the whole battery charge-discharging process to study the HER at varied cut-off potentials.

3. Results

3.1. Kinetic study of vanadium redox reaction

For a single reaction, open circle potential (OCP) is generally taken to be the equilibrium point of the system, due to no generation of Faradaic current in the circuit ($I$=0). At that point, the current due to the forward reaction ($I_f$) is equal to the current by the backward reaction ($I_b$), and the current value is defined as the exchange current, where $I_0 = I_f = I_b$. However, OCP for a system that contains multiple reactions only represents the balanced point for the system, not for individual reactions. When there is no Faradaic current flow for this multi-reaction system, it means the total forward current is equal to the total backward current generated by the multiple reactions, where $I_f = I_b$. At the redox potential range of V$^{2+}$/V$^{3+}$, bismuth reduction reaction occurs simultaneously. Because the vanadium reaction and in-situ Bi electrodeposition both contribute to the current, it is apparent that the $I_f$ for vanadium reaction cannot be determined at the OCP of this multi-reaction system in the presence of Bi$^{3+}$; therefore, the traditional methodology of calculation of $I_f$ through the BV equation is misleading and a particular model needs to be developed for this system with Bi additives.

3.1.1. Linear sweep voltammetry and multi-reaction mathematical model

Our designed model is needed in order to extract the true exchange current for VRR under the influence of Bi catalyst, and this model could also be generally applied for the kinetic evaluation of the redox flow battery system containing other types of electrolyte additives (e.g., Sb) that undergo deposition on the surface during the battery operation. Drawing upon BV theory and the model built by K-L on the rotating disk electrode (RDE) [24], the mathematical model for vanadium electrolyte containing Bi is specifically designed. The two major electrochemical reactions, bismuth redox reaction (BRR) and vanadium redox reaction (VRR), are taken into consideration to build this model, where the $E^0_{BRR}$ and $E^0_{VRR}$ are the standard potentials for bismuth redox reaction and vanadium redox reaction, respectively (in the electrochemical model, the Nernst equation has been used to calculate reversible potentials with the concentrations used in these experiments). For simplification, HER is not considered to contribute to the generated current here, as it is negligible around the vanadium reaction potential range compared to the other two reactions.

$$\text{(Bismuth redox reaction)}: \text{Bi}^{3+} + 3e^- \rightarrow \text{Bi}, \quad E^0_{BRR} = 0.308 V \text{ vs. NHE}$$  
reaction 1

$$\text{(Vanadium redox reaction)}: \text{V}^{3+} + e^- \rightarrow \text{V}^{2+}, \quad E^0_{VRR} = -0.255 V \text{ vs. NHE}$$  
reaction 2
Therefore, the total measured current on RDE, $I_{\text{RDE}}$, takes the measured currents of two reactions, $I_{m,\text{BRR}}$ for bismuth reduction reaction (Reaction 1) and $I_{m,\text{VRR}}$ for vanadium redox reaction (Reaction 2) into account:

$$I_{\text{RDE}} = I_{m,\text{BRR}} + I_{m,\text{VRR}}$$

**Equation 1**

Steps to calculate measured current ($I_m$) of the RDE system for both reactions are identical, both applying the K-L equation. It is a representative model for construing the generated current from the electrochemical process and mass transport process on the RDE, where the $I_m$ is related to kinetic current ($I_k$) and the current by ion movement ($I_{MT}$).

$$I_m = \frac{1}{I_k} + \frac{1}{I_{MT}}$$

**Equation 2**

The $I_{MT}$ as the current associated with mass transport and linked with the rotation rate ($\omega$) and reactant bulk concentration ($C$), as shown in:

$$I_{MT} = 0.62nAFD^{2/3}D^{-1/6}C\omega^{1/3}$$

**Equation 3**

which contains constants of total electron number in half reaction ($n$), electrode surface area ($A$), Faraday constant ($F$) diffusion coefficient ($D$) and kinematic viscosity ($\nu$) and experimentally controlled variables of $\omega$ and $C$.

$I_k$ by the electrochemical reaction is calculated by the BV equation relating to overpotential ($\eta$), charge transfer coefficient ($\alpha$), gas constant ($R$), and temperature ($T$):

$$I_k = I_0 \left( \frac{C_{O_s}}{C_{O_b}} \exp \left( -\frac{n_k \alpha F \eta}{RT} \right) - \frac{C_{R_s}}{C_{R_b}} \exp \left( \frac{n_k (1 - \alpha) F \eta}{RT} \right) \right)$$

**Equation 4**

Where $C_{O_s}$ and $C_{O_b}$ are the oxidant concentrations on the electrode surface and in the bulk respectively, $C_{R_s}$ and $C_{R_b}$ are the reductant concentrations, and $n_k$ is the number of electrons transferred in the electrochemical reaction.

As aforementioned, the simulated total current, $I_{\text{RDE}}$ is a sum of two reactions, which are individually determined by their mass transport and kinetic processes. For the designed experimental conditions, the studied potential range is from $-0.1 \text{ V}$ to $-0.6 \text{ V}$, in which the overpotential ($\eta$) for bismuth reduction reaction (Reaction 1) is over $0.4 \text{ V}$. As $\eta$ is an exponential factor for $I_k$, the kinetic current at studied potential range is very large, making the term of $1/I_k$ in the K-L equation (Equation (2)) negligible. It is apparent that the limiting factor for bismuth reduction reaction is mass transport, which explains the first current plateau feature around $-0.15 \text{ V}$ shown in Fig. 1 (left)-region 1, as the mass transport current calculated via Equation (3), $I_{MT,\text{BRR}}$ is a fixed value at defined rotating speed, $\omega$ and reactant concentration, $C_{\text{Bi}}$.

Additional proof of the mass transport limited kinetics of Bi reduction is the reduced experimental value of $|I_{MT,\text{BRR}}|$ with decreasing $\omega$ (SI-...
Figure s2). In Fig. 1 (left)-region 1, there is a more complex situation for the electrolyte containing higher concentrations of Bi additive (500, 750, 1000 ppm), where the experimental data deviates from that predicted from the model. This phenomenon was also observed in the CV studies where a third reaction can be seen at the potential range from 0 V to −0.2 V with an onset potential around 0 V vs. NHE. This third reaction (Reaction 3) is thought to be the formation of bismuth hydrides (BiH₃), which has been reported in several previous studies [25,26], due to the metallic bismuth electrode surface. In a previous study on bismuth acting as a catalyst for the negative electrode, Suarez et al. [18] hypothesised that BiH₃ acts as a strong reductive agent, catalysing V⁰⁻¹ to V⁰⁻² instead of decomposing into H₂.

(Bismuth hydride reaction) \( \text{xH}^+ + \text{Bi} + \text{xe}^- \rightarrow \text{BiH}_x, \ E_{\text{BiH}_x} \sim 0 \text{ V vs. NHE} \)

Reaction 3

The next region (region 2) as shown in Fig. 1 (left) is dominated by the vanadium redox couple. The exponential feature is caused by \( I_{\text{VRR}} \) as the kinetic current is the limiting factor at the potential range close to its standard reaction potential, \( E_{\text{VRR}}^0 \) and at the high rotation rate. With the proposed mathematical model, the exchange current of vanadium redox reaction, \( I_{\text{VRR}} \) becomes the only undefined value. Therefore, an iterative method to fit the experimental data is used to obtain the value of \( I_{\text{VRR}} \). Then the exchange current is normalised to the exchange current density, \( I_{\text{VRR}} \) with the electrode surface area, \( A \).

The high value of \( J_{\text{VRR}} \) (7.9 mA cm⁻²@100 ppm Bi, 39.9 mA cm⁻²@500 ppm Bi, 50.4 mA cm⁻²@500 ppm Bi and 49.8 mA cm⁻²@1000 ppm Bi) derived in this system with the presence of Bi ions confirms that the kinetics of the vanadium redox couple are effectively catalysed by Bi, which improves the exchange current density of glassy carbon (\( J_{\text{VRR}} = 2 \sim 3 \times 10^{-3} \text{ mA cm}^{-2} \)) [16] by at least three orders of magnitude. Another apparent observation is the \( J_{\text{VRR}} \) increases with increasing \( C_{\text{Bi}} \) and then plateaus after 750 ppm Bi, which could explain the battery performance limitation with increasing \( C_{\text{Bi}} \) in the literature [17,20].

In region 3, at high overpotentials, experimental data and simulated data both agree a second plateau feature for low \( C_{\text{Bi}} \) (100 ppm), which is due to the mass transport limitation of vanadium. However, for the high \( C_{\text{Bi}} \) (500, 750 and 1000 ppm) systems, the experimental data shows deviation from this second plateau, with the deviation increasing with increasing overpotential, indicating a fourth dominating reaction occurs on the electrode with an onset potential around −0.47 V vs. NHE. As hydrogen evolution is not considered in this model, this deviation of the experimental data from the model is most likely caused by HER, which is confirmed in the following section with in-situ mass spectrometry.

(Hydrogen evolution reaction) \( \text{2H}^+ + \text{2e}^- \rightarrow \text{H}_2, E_{\text{HER}} = -0.47 \text{ V vs. NHE} \)

Reaction 4

To understand the variables’ impact on the current, the simulated data with different values of the variables α, \( I_{\text{VRR}} \), \( E_{\text{VRR}} \), and \( C_{\text{Bi}} \) are presented in Fig. 1 (right), where \( E_{\text{VRR}} \) is the vanadium reaction potential with specified reactant concentrations (which vary through the state of charge of the battery, the highest value of \( E_{\text{VRR}} \) being at 100% SoC) and temperature. A trend can be concluded that the higher values of \( I_{\text{VRR}} \) and \( E_{\text{VRR}} \) have an earlier onset potential and a steeper slope. Therefore, higher values of \( I_{\text{VRR}} \) and \( E_{\text{VRR}} \) are expected to have a better battery performance due to lower overpotential under a higher operating current density. The influence of α is more complex, where increased α shows a steeper gradient in region 2, but a retarded onset potential. It is generally considered that alpha represents the symmetry of the transition state during catalysis, and that a charge transfer coefficient (α) value of 0.5 represents a symmetric transition state that equally favours the forward and reverse redox reactions. Even if it is assumed that Bi does not contribute to the catalysis of the VRR, increasing bismuth concentration, \( C_{\text{Bi}} \) still increases the negative current due to the bismuth reduction reaction, but it has no impact on the onset potential and slope.

This is highlighted by the fact that the simulated LSV data differs from the experimental data with varied Bi concentrations, as we have not accounted for the catalytic action of Bi on VRR in the model (simulated LSV data). Therefore, it can be elucidated that the improved slope, which is directly related to \( I_{\text{VRR}} \) and onset potential of VRR are the result of bismuth catalytic activity.

3.1.2. Electrochemical impedance spectroscopy

Apart from the exchange current density derived from the BV equation, charge transfer resistance (\( R_c \)) from EIS at the OCP has been applied in many studies for \( I_0 \) calculation [16]. Klaus [27] defined the charge transfer resistance to be proportional to the overpotential (η) and current (I) as the equilibrium point is approached (η→0 and I→0), where η and I exhibit a linear relationship and obey Ohm’s law. With formula derivations (Equation ii-vii in SI-section 1.2), exchange current \( I_0 \) can also be calculated by \( R_c \) with a relationship of:

\[ I_0 (by \ R_c) = \frac{RT}{nF R_c(\eta=0)} \]

However, this methodology is inapplicable here because of the multi-reaction system when Bi additives are used, as explained in the LSV model. EIS was conducted at different polarization and additive concentration, where Nyquist representations of the EIS result for electrolyte containing 1000 ppm and 0 ppm Bi³⁺ are shown in Fig. 2 (a) and (b). Other Bi concentrations have a similar trend to 1000 ppm Bi (Figure s3). The Nyquist plots (showing the imaginary and real contributions to impedance) exhibit two typical features: a semi-circular arc at the high frequency region, which is attributed to the Faradaic reaction, and a line with 45° angle at the low frequency region, related to the mass transfer process. An equivalent electrical circuit model (Fig. 2, d) with a constant-phase element (CPE) and infinite Warburg diffusion behaviour is used to fit the Nyquist plots, where \( R_c \) for electrolytes containing various \( C_{\text{Bi}} \) were found to reduce from OCV to around −0.3 V vs. NHE, and then increase after further negative polarization (Fig. 2, e).

There was an unusual trend of \( R_c \) under polarization observed for all the electrolyte containing Bi³⁺ (an example is given for 1000 ppm Bi in Fig. 2 (a)), where the lowest \( R_c \) was found nearby the formal potentials and a peak of \( R_c \) (Fig. 2e) was formed along the direction of polarization potentials. It is believed this phenomenon is caused by the mass transport limitation during the potentiostatic EIS without rotating (electrode was not rotated to obtain stable EIS), as the reaction rate increased with polarization until a point that the reaction rate became higher than the diffusion rate, which caused reduced surface concentration of reactant and hence increased \( R_c \). This diffusion limitation also increases as the EIS is performed at increasingly negative potentials, due to the local concentration of V³⁺ becoming diminished with increasing drive for VRR, hence why the size of this arc increases at higher negative overpotential, beyond around −0.28 V. This mass transport limitation for the charge transfer process was only evident with the dramatically accelerated VRR kinetics with Bi additives; the vanadium only electrolyte and sulfuric acid background, with three orders of magnitude higher \( R_c \), were not affected (Fig. 2b and c).

3.1.3. Cyclic voltammetry

In addition to the exchange current density (\( J_{\text{VRR}} \)) and charge transfer resistance (\( R_c \)) calculated by BV and EIS methods, reaction rate constant (\( k_0 \)) is a useful metric to compare kinetics as \( k_0 \) is independent of the reactant concentration. CV has been applied to investigate vanadium couples’ kinetics (\( \text{V}^{2+}/\text{V}^{3+} \)) and calculate \( k_0 \) as early as 1985 [28]. In the majority of work on electrode catalysts for VRFB during recent years, CV has been used to demonstrate a catalytic activity with an embellished electrode surface [11,23]. Unfortunately, most studies stopped at comparison of the peak potential separation, \( E_P - E_0 \) and peak current, \( I_p \). With CV studies, \( k_0 \) can be measured with assistance of Equation (6) for an irreversible reaction, where the intercept from the
plot of $E_P - E'_0$ against $\ln I_p$ can be used to calculate the magnitude of $k_0$. A detailed derivation of Equation (6) from the Nernst and Cottrell equations can be found in SI-section 3.

$$I_p = 0.227nAFC_O\alpha k_0\exp\left(-\frac{m\alpha F}{RT}(E_p - E'_0)\right)$$

Equation 6

In Fig. 3 (a), CVs of 100 ppm Bi at varied scan rates exhibit a standard curve shape with one reduction peak around $-0.35$ V and one oxidation peak around $-0.15$ V, centred at $-0.325$ V. On the contrary, CVs with 1000 ppm Bi additive, displayed in Fig. 3 (d), feature two reduction peaks: one smaller peak observed around $-0.1$ V and another larger peak around $-0.4$ V, which corresponds to the formation of BiH$_x$ [18] and vanadium (III) reduction, respectively. The single anodic peak around $-0.15$ V corresponds to vanadium (II) oxidation, which is centred with the vanadium reduction peak at $-0.286$ V. Comparing the CVs of electrolytes containing different $C_Bi$ (500 and 750 ppm in SI, Figure s4 and s5), Table 1 shows that higher concentration of Bi additive shifts the
Table 1

<table>
<thead>
<tr>
<th>C_{Bi} (ppm)</th>
<th>J_{VRR} (mA cm(^{-2}))</th>
<th>R_{ct} (Ω)</th>
<th>E_{0} (V)</th>
<th>k_{0} (cm s(^{-1}))</th>
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<td>50.4</td>
<td>5.2</td>
<td>-0.298</td>
<td>2.76 × 10^-2</td>
</tr>
<tr>
<td>1000</td>
<td>49.8</td>
<td>6.4</td>
<td>-0.286</td>
<td>2.71 × 10^-2</td>
</tr>
</tbody>
</table>

Notes: J_{VRR}, R_{ct}, E_{0} and k_{0} are exchange current density, charge transfer resistance, formal potential, and kinetic coefficient.

vanadium reaction to a more positive potential (−0.286 V@1000 ppm > −0.298 V@500 ppm > −0.302 V@500 ppm > −0.322 V@100 ppm). There is a linear relationship between vanadium redox peak current (I_{p}) and √scan rate for all CVs containing Bi additive, indicating a diffusion-controlled process. Additionally, the intercept from the linear plot of E_{p} = E_{0} against ln I_{p} suggests the rate constants, k_{0} for 100, 500, 750, 1000 ppm Bi are 0.38 × 10^-2, 2.62 × 10^-2, 2.76 × 10^-2 and 2.71 × 10^-2 cm s\(^{-1}\) respectively, all enhanced by roughly three orders of magnitude compared to glassy carbon without the presence of Bi (1.70 × 10^-5 cm s\(^{-1}\) at pH = 0) [26].

The evaluated terms from different methods (exchange current density (J_{0\_VRR}), charge transfer resistance (R_{ct}) from EIS and rate constant (k_{0}) from CV) all agree that Bi additives improve the kinetics of the bare glassy carbon by one thousand times and the enhancement effect peaks when C_{Bi} = 750 ppm. Most research work [29,30] on catalysts do not distinguish the catalytic activity from the increased surface area by the catalyst; however, it is worth noting the improved kinetics include both effect of increased surface area and catalytic activity by deposited Bi as geometric surface area of glassy carbon (0.1963 cm\(^{-2}\)) is used to calculate all parameters. Though these two factors were hard to deconvolute with the electrochemical methodologies used in this work, the reduced peak voltage separation in CVs by the graphite felt with Bi (SI-Figure, s12) indicates a consistent improvement contributed by Bi catalysis on both the low surface area glassy carbon electrode and the high surface area graphite felt. As the increase in surface area is relatively far greater for the glassy carbon than the graphite felt, the fact that addition of Bi has a similar effect on the kinetics of the reactions in both systems, implies that it is not solely down to an increase in surface area from the deposited Bi. The strong agreement of results from different kinetic studies validated the model proposed in the LSV simulation work, as well as providing the first quantitative demonstration in the literature [32-34].

3.2. Bismuth reduction reaction and hydrogen evolution reaction

The deposition of bismuth via the reduction reaction on the working electrode was studied by ex-situ scanning electron microscopy (SEM) imaging of glassy carbon after holding at the V\(^2+\)/V\(^3+\) reversible potential (−0.3 V vs. NHE) for 5 min in the vanadium electrolyte containing various concentrations of Bi additives. As shown in the SEM images in Fig. 5, there is a distinct difference between the morphologies of electrodeposited Bi in the electrolyte containing 100 ppm and 1000 ppm Bi, where the former displays a regular four-pointed star morphology and the latter produces nanorods. The 1D nanorod shape is also found in electrolyte containing 500 and 750 ppm Bi (SI-Figure s6), and the tunable morphologies were reported in previous works [35-37] on the electrodeposition of Bi. The SEM images with EDS confirm the formation of Bi particles on the electrode under vanadium battery working potential, where surfaces of the Bi nanoparticles were partially oxidised in all concentrations and the electrolyte with 100 ppm Bi has a higher degree of oxidation indicated by EDS. Apparently, the concentration variation of Bi additives into the electrolyte effects both morphology and chemistry of electrodeposited Bi particles. It was speculated that the morphology and chemistry variations are related to the kinetics changes with increasing Bi concentration.
In-situ mass spectrometry was applied to monitor the hydrogen evolution reaction in the potential range of interest. Hydrogen production was detected from −0.25 V to −0.6 V vs. NHE on the commercial heat-treated graphite felt for electrolyte containing varied concentrations of 0, 100, 500, 750 and 1000 ppm Bi. The data in the bar chart of hydrogen production levels in Fig. 5 (e) were detected in-situ with stepwise holding voltages and represent the average values of hydrogen produced holding at certain voltage within 10 min, where the values and standard deviations can be found in SI-Table s3. Until −0.3 V, hydrogen production in electrolyte without Bi (0 ppm) remains constant, and then dramatically increases after −0.3 V, which suggests the onset potential for commercial electrolyte (0 ppm Bi) on graphite felt is ~ −0.3 V vs. NHE. Conversely, hydrogen production for electrolytes containing Bi is low until a more negative potential of −0.45 V vs. NHE, which confirms the conclusion of delayed onset potential in the presence of Bi in the LSV simulation model. The slightly increased HER at higher concentration of Bi after −0.45 V vs. NHE was due to the reduced concentration of V3+, where HER starts to participate in the electrochemical process and increased with increasing surface area of higher Cmp. With LSV and CV studies on higher V concentration (0.2 M) shown in Fig. 4 and SI-Figure s11, there is no current attributable to HER at region 3 of LSVs and CVs. All findings support a competing relationship of VRR and HER occurring on the Bi surface, when a higher concentration of V is available for the VRR; the contribution to the current from HER is negligible for the same amount of Bi additive in solution. To conclude, it is apparent that the side reaction of HER was effectively reduced by Bi by selective catalysis of the VRR not only through retarding the onset potential, but also reducing the reaction rate with increasing overpotential. Previous studies [17-19] investigated the Bi kinetic mechanism with traditional electrochemical approaches without considering the complexity of the multi-reaction model presented here and without direct proof of Bi suppression of the HER, resulting in uncertain conclusions to date.

3.3. Battery performance

The concentration of electrolyte additive (Bi) under varied current densities and charging cut-off potentials are both analysed in the full battery performances. For the study of the battery with different concentrations of Bi, VRFBs were cycled under different current densities to assess rate capability, followed by stability testing consisting of 100 cycles at 110 mA cm−2 current density. The sole variable of full cell analysis was the concentration of Bi additive. Detailed discussion of the battery performance is given in section s5 and Figure s7 (SI), where the battery with 750 ppm Bi additive showed the best performance in coulombic efficiency (CE), potential efficiency (VE), energy efficiency (EE), capacity and in the stability test, with the factors of improved vanadium reaction rate and side reaction (HER) reduction attributed to this performance. The theoretical capacity was calculated based on assumption of 100% SOC charge and discharge by an equation listed in SI (equation xxvii). Microwave plasma-atomic emission spectrometry (MP-AES) was also applied to detect the Bi concentration in the electrolyte during the stability tests, where no Bi was detected in the electrolyte (Table s1) suggesting a full deposition without subsequent dissolution of Bi during the battery cycles, which agrees with the conclusion of the operando X-ray computed tomography study [22]. It is possible that there is dissolution occurring that leads to redeposition in other areas of the electrode, or in different morphologies; however, the investigation of this is out of the scope to this paper and should be considered for future work. Nevertheless, it is clear that significant amounts of Bi are not redissolving into the electrolyte here. Therefore, we can conclude that the limitation on enhancement of performance of Bi at 750 ppm is due to the catalytic effect on VRR and competition with the HER at higher Bi concentrations, contrary to previous works suggesting that the limitation of enhancement was due to Bi dissolution [17].

Another focus was the charging cut-off potential, which is limited by the potential window of water electrolysis due to the side reactions of hydrogen and oxygen production when charging to higher potentials. To validate the impact on HER by Bi, VRFBs with different concentration of Bi additives were charged to 1.6 V, followed by higher charging cut-off potentials of 1.7 V and 1.8 V, and were compared at the current density of 110 mA cm−2. An in-situ mass spectrometer was connected to the VRFB system to detect the hydrogen level variation of VRFBs during charge-discharge and the variable Bi concentration and charging cut-off potential. Fig. 6 (a) to (f) represents the charge-discharge potential curves (left axis, black) and hydrogen production level (right axis, coloured) of VRFB with 0, 100, 500, 750 and 1000 ppm Bi additives, respectively. For the battery without Bi additive (0 ppm), increased hydrogen levels were found when charged to 1.7 V and severe water electrolysis was detected when charged to 1.8 V; after adding Bi into the system, the HER of VRFBs charged to 1.7 V and 1.8 V was effectively reduced, where 100 ppm Bi showed the most effective impact for CE; however, this is not reflected in the overall battery performance due to the insufficient catalyst surface area produced by 100 ppm Bi. As studied in section 3.2, increased hydrogen evolution rate for the commercial graphite felt was found after −0.4 V vs. NHE, which correlates to the theoretical value of 1.6 V for the full cell (the detailed simulation methodology is included in the SI, section s6 and Figure s8). This
Fig. 6. Real time monitoring of hydrogen production levels (right y-axis, coloured) during battery charging cycles (left y-axis, black) of electrolytes containing varied Bi concentrations: (a) 0 ppm, (b) 100 ppm, (c) 500 ppm, (d) 750 ppm, and (e) 1000 ppm; battery performances with different operational procedures and electrolyte additive concentrations were compared in (f) CE, (g) VE, (h) EE, (i) percentage of theoretical electrolyte capacities with standard deviation (blocks) and (j) stability during 20 cycles with cut-off potential of 0.85–1.8 V with capacity retention.
explains the severe HER of VRFB without Bi additives charged to 1.7 V and 1.8 V. To understand how the side reaction affects the battery performance, the produced hydrogen level was converted into current density using an approximate methodology shown in SI-section 8, where hydrogen levels ranging from 200 ppm to 1000 ppm could be converted into 0.264 mA–1.32 mA in current and 0.048%–0.24% in coulombic ratio wasted by side reaction, respectively. With Bi additives, the hydrogen production level was controlled below 200 ppm meaning the side reaction impact on CE was lower than 0.048%.

The battery performances with varied concentration of Bi additive and charging cut-off potentials were evaluated in CE, VE, EE and % of theoretical electrolyte capacity in Fig. 6 (f) to (i), respectively. For the VRFB performances with varied charging cut-off potentials, Bi additive dramatically improved both VE and EE, as found in the Bi concentration study with varied current densities, where 750 ppm performed the best. For the CE, which is mostly affected by the side reactions, the VRFB with Bi additive has a lower value compared to the VRFB without Bi when charging potential was cut-off at 1.6 V; this is probably due to the side reaction of bismuth hydrides. For the CE of VRFBs with 1.7 V and 1.8 V cut-off potential, a dramatic drop in CE was seen in the battery without Bi, due to HER side reactions. On the other hand, Bi additives effectively prevented the sharp decline of CE when charging to the higher potential, thanks to its impact on HER. It is worth noting that the electrolyte utilisation was doubly enhanced by adding Bi additives and then by charging to a higher potential; 86% utilisation of electrolyte capacity was achieved with 750 ppm Bi at the high current density (110 mA cm−2), an improvement of 22% utilisation over the VRFB without Bi charged to 1.6 V. Battery stability was also improved by Bi additives at 1.8 V cut-off potential, where 46% capacity loss was reduced to 10% by adding Bi, as shown in Fig. 6 (j). To conclude, the electrodeposited Bi catalyst successfully catalysed VRR, which enlarged the VRFB operation potential window and further improved electrolyte utilisation with higher capacity retention.

4. Conclusions

Electrocatalytic activity and mechanisms of bismuth towards V2+/V3+ were evaluated through three electrochemical methodologies, where the electrochemical models are adjusted for this specific multi-reactivation process. The kinetic parameters: exchange current density, charge transfer resistance and rate constant, obtained from the three approaches are in accordance with each other, providing strong evidence for bismuth being an efficient kinetic enhancer with three orders of magnitude improvement on vanadium redox reaction (V2+/V3+). A peak kinetic enhancement of VRR was found in the system with 750 ppm Bi, which explained the plateau performance in full-cell VRFB testing with increasing Bi concentration from the perspective of electrochemical reaction rate. The non-linear improvement on the VRB with Bi additive concentrations was believed to be the consequence of the unique selective catalysis mechanism of Bi on VRR over HER, where a competing environment was created on the Bi surface and increasing vanadium concentration was found to further suppress the HER. Following the kinetic study, the in-situ hydrogen detection on a three-electrode cell and full battery performance supplied further evidence of this competing electrochemical process between VRR and HER. Thanks to the selective catalysis by Bi, the battery could be stably cycled to 1.7 V and even 1.8 V, where the battery with 750 ppm Bi exhibited the highest performance and achieved the highest electrolyte capacity utilization with 86% of the theoretical electrolyte capacity at a high current density of 110 mA cm−2.

This work provides extensive electrochemical studies and evidence for Bi being a promising and stable catalyst that reduces the polarisation loss under high charge-discharge current density and capacity loss by selective catalysis of VRR over the side reaction. More dedicated research approaches would be required for understanding the catalysis mechanism at the atomic and electronic level. With better understanding, upgrading the performance of industrial scale of VRFB by Bi could be envisaged in the future, and could help to offset the capital costs associated with VRFB systems and improve the operating power.

CRediT authorship contribution statement

Yue Wen: Methodology, Software, Validation, Formal analysis, Investigation, Writing – original draft, Visualization. Tobias P. Neville: Methodology, Software, Writing – review & editing. Ana Jorge Sobrido: Methodology, Writing – review & editing. Paul R. Shearing: Resources, Writing – review & editing. Dan J.L. Brett: Resources, Writing – review & editing. Rhodri Jervis: Conceptualization, Methodology, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A Supplementary data

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References


