



Direct measurement of electrochemical reaction kinetics in flow-through porous electrodes



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ARTICLE INFO

Article history:

Received 7 April 2015

Received in revised form 30 April 2015

Accepted 30 April 2015

Available online 8 May 2015

Keywords:

Tafel

Kinetics

Flow-through porous electrode

Microfluidic

Flow cell

Vanadium

ABSTRACT

This work demonstrates the feasibility of measuring electrochemical reaction rates on common flow-through porous electrodes by traditional Tafel analysis. A customized microfluidic channel electrode was designed and demonstrated by measuring the intrinsic kinetics of the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ redox reactions in carbon paper electrodes under forced electrolyte flow. The exchange current density of the V^{2+}/V^{3+} reaction was found to be nearly two orders of magnitude slower than the VO^{2+}/VO_2^+ reaction, indicating that this may be the limiting reaction in vanadium redox flow batteries. The forced convection in this technique is found to generate reproducible exchange current densities which are consistently higher than for conventional electrochemical methods due to improved mass transport.

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1. Introduction

A commonly employed strategy to enhance effective rates of interfacial electrochemical reactions is to design and fabricate porous electrodes with high interfacial area between electronic and ionic conducting phases. Porous electrodes with nanoscopic feature sizes increase the electrochemical surface area (ESA) per unit electrode volume and thereby improve the voltage efficiency of electrochemical energy conversion.

Studying reaction rates on porous electrodes is not as straightforward however as on their planar counterparts. Traditional methods of studying reaction kinetics such as cyclic voltammetry are biased by the porosity, where a smaller peak to peak separation may falsely indicate improved kinetics if the semi-infinite diffusion criterion is ignored [1–3]. Tafel analysis by rotating disk method on porous electrodes has also been shown to lead to higher Tafel slopes particularly for electrodes with deeper pores [4]. Although rotation of the electrode increases convection and reactant replenishment at the surface of the electrode, this convection does not improve penetration of the reaction front into the depths of electrolyte-filled pores. Diffusion limitations, as accounted for in the transmission line model of De Levie [5,6], constrain the performance of porous electrodes. When the reaction penetration depth is much smaller than the thickness of the electrode in a 1D system, this diffusion limitation will lead to an exact doubling of the

Tafel slope [7]. One strategy to reduce diffusion limitations is to reduce the size of the electroactive area, as in the study with ultra-low catalyst loading by Zalitis et al. [8]. To overcome diffusion limitations in general, some researchers have proposed other indirect analytical methods of determining the reaction kinetics of porous materials independently from their morphology [9–11].

While some porous electrodes, such as those of traditional closed-cell batteries, have internal pore structure exclusively designed for diffusion of electroactive species, others are designed with open pores to permit convective flow of reactants. These ‘flow-through porous electrodes’ have long been considered for electrochemical uses such as the recovery of electropositive metals from industrial waste and oxidation of organic pollutants and surfactants [12]. These large scale applications typically utilize a packed or fluidized bed electrochemical reactor with electrodes composed of a layer of highly conductive non-porous particles supported by a current collector grid [13]. Several studies were performed in the 1960s and 1970s to quantify the polarization behavior and potential distribution in such electrodes [5,6,12–19]. Since then, other types of flow-through porous electrodes such as carbon felt have become a popular material and an integral part of redox flow batteries, a new class of batteries which rely on convective mass transport of externally stored reactants [20]. More recently, similar carbon paper electrodes have also been shown to considerably improve the performance of microfluidic co-laminar flow cells [21–24]. Growing interest in these technologies warrants more contemporary research into the polarization behavior of flow-through porous electrodes, which have been largely neglected in the literature, in favor of thin

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film diffusion based porous electrodes. Moreover, new low cost microfabrication techniques have made it possible for research groups to develop customized microfluidic analytical flow cells [21,25]. At the micro scale, flow is typically laminar and therefore amenable to analytical solution [26]. This allowed the Compton group to develop the concept of channel electrodes as an improvement over rotating disk methods for measuring polarization of planar electrodes [27]. Developing this idea further, the objective of the present work is to demonstrate the viability of using a customized microfluidic electrochemical cell for directly measuring the kinetics and general polarization behavior of accessible flow-through porous electrodes.

2. Methodology

2.1. Materials

The reactants used in this study are the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ redox couples first proposed by Skyllas-Kazacos et al. [28] for the all-vanadium redox flow battery and more recently employed in our co-laminar flow cells [29,30]. The reactants are prepared by charging a 1.7 M commercial grade vanadium stock solution in 4 M H_2SO_4 with a conventional flow battery to achieve a nearly even ratio of V^{2+}/V^{3+} or VO^{2+}/VO_2^+ . Initial concentrations are determined by permanganate titration [29]. The working electrode (WE) and counter electrode (CE) are both made from 180 μm thick Toray carbon paper (TGP-H 060) which is heat treated to increase hydrophilicity as explained in previous work [23]. The carbon paper surface area is measured to be $4 m^2 \cdot g^{-1}$ via mercury intrusion porosimetry which results in an estimated ESA of roughly $4 cm^2$ for the WE used in this study.¹

2.2. Design and fabrication

The microfluidic analytical flow cell is fabricated by soft lithography of poly(dimethylsiloxane) (PDMS) from a photoresist template as described elsewhere [31,32]. As depicted in Fig. 1, the cell consists of a single inlet and outlet with a uniform channel height of 150 μm to compress the electrodes and a channel width of 2 mm in the upstream WE section which gradually expands to a 4 mm width in the downstream CE section. The CE is sized to provide an order of magnitude larger ESA than the WE. Once the electrodes are placed within their respective grooves, the cell is capped by a glass slide and pressure sealed by a customized clamp. Contact is made with the electrodes which extend beyond the cell via copper clips. A saturated calomel reference electrode (RE) is positioned roughly 3 mm upstream from the WE with electrolytic contact made via a porous frit sealed into the PDMS channel. For better visualization of reactant conversion however quasi-reference electrodes are used based on silver and platinum foil for V^{2+}/V^{3+} and VO^{2+}/VO_2^+ respectively.

2.3. Half-cell characterization

The electrolyte is injected into the inlet by syringe pump and removed by a separate syringe pump at the outlet. The two pumps (Harvard Apparatus MA1 70-2209) are operated in unison at flow rates ranging from 2 to 2000 $\mu L \cdot min^{-1}$. All polarization measurements are made with a potentiostat (Gamry Reference 3000) operating at voltammetric scan rates slow enough to ensure steady state conditions. Electrochemical impedance spectroscopy (EIS) measurements are conducted at 10 mV perturbation from the open circuit potential (OCP) to determine the impedance of the WE and make post-run IR corrections. With IR correction, both the saturated calomel and quasi-reference methods generate identical polarization behavior for a given WE.

¹ It should be noted that the true surface area of carbon and that wetted by the electrolyte may differ markedly from this value.

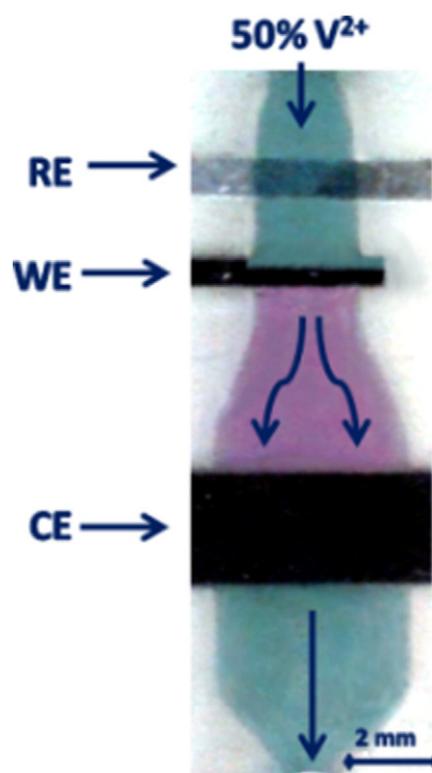


Fig. 1. Annotated image of the analytical flow cell in operation, showing complete reduction and oxidation of V^{2+}/V^{3+} in carbon paper working and counter electrodes, respectively.

3. Results and discussion

3.1. Validation

The stability of the system is first established within the experimental conditions. At negative pH, silver is stable at the negative potential of the V^{2+}/V^{3+} electrolyte whereas platinum is stable at the positive potential of the VO^{2+}/VO_2^+ electrolyte. This is observed by minimal drift (<10 mV) in the OCP of either solution over the course of several hours. The initial concentrations are verified by complete reactant conversion as in Fig. 1, which shows the complete reduction of green V^{3+} to purple V^{2+} . At a flow rate of $2 \mu L \cdot min^{-1}$ the anodic and cathodic limiting currents are averaged over the final 50 mV of the ± 300 mV overpotential range, producing 2.7 ± 0.2 mA and 2.8 ± 0.2 mA which correspond to full conversion of initial concentrations of 49% V^{2+} and 51% V^{3+} respectively from the total 1.7 M vanadium concentration. This demonstrates that all of the electrolyte injected into the flow-through cell can react without any flow bypassing the electrode and that no undesirable side reactions are occurring within the present potential range. The same validation was performed for the VO^{2+}/VO_2^+ solution, revealing initial concentrations of 54% and 46% respectively and no side-reactions within a ± 400 mV overpotential range.

3.2. Electrochemical kinetics

The Tafel curves in Fig. 2 demonstrate qualitatively the effect of flow rate on the polarization behavior of both redox reactions on the same WE. Above $400 \mu L \cdot min^{-1}$ there is little change in the polarization of the V^{2+}/V^{3+} reaction whereas the VO^{2+}/VO_2^+ polarization continues to change even beyond $1200 \mu L \cdot min^{-1}$, indicating that the V^{2+}/V^{3+} reaction is considerably slower than the VO^{2+}/VO_2^+ reaction. Although there is disagreement in the literature [33–35], most experimental studies with solutions that mimic those used in commercial flow battery systems have found that the VO^{2+}/VO_2^+ reaction is faster on carbon

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