



In Situ Enhancement of Flow-through Porous Electrodes with Carbon Nanotubes via Flowing Deposition



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ABSTRACT

This study describes a novel flowing deposition method which can be used *in situ* on a fully assembled electrochemical cell to enhance the electrochemical active surface area of flow-through porous electrodes. As a test case, vanadium redox reaction rates are enhanced by flowing deposition of carbon nanotubes on carbon paper electrodes. The deposition is characterized using a recently developed analytical flow cell technique and shown to increase the electrochemical active surface area and therefore the exchange current for the limiting V^{2+}/V^{3+} reaction by over an order of magnitude. When applied to the anode of an assembled vanadium redox flow cell, the method nearly eliminates the overpotential associated with this reaction, thereby significantly improving the power output of the cell by up to 70% in the high voltage efficiency regime. As a surface area treatment, this flowing deposition method could be used to similarly enhance the energy conversion efficiency of many other electrochemical flow cells such as fuel cells, flow batteries and capacitive deionization cells.

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1. Introduction

In a bid to develop efficient and compact electrochemical energy conversion devices much attention has been devoted toward increasing the electrochemical surface area per unit volume of electrode. Whether for batteries, fuel cells, or capacitors, electrodes with nanoscopic features and porosity are necessary to achieve the highest energy and power densities [1,2]. Among the options available for conductive electrode materials, carbon continues to be principal due to its low cost, chemical resistance, and potentially high surface area [3]. As an inexpensive and abundant material, natural carbon has typically been processed into high surface area particles for electrochemical applications such as activated carbon for electrosorption [4,5] or carbon black as a catalyst support in fuel cells [6]. As a randomly aggregated electrode material these powders require some form of structural support which may interfere with the mass transport of reactants. In addition, amorphous natural carbon with a low degree of graphitization suffers from poor electrical conductivity which is exacerbated by high contact resistance between particles when packed too loosely [7]. A more synthetic approach to manufacturing carbon materials with large active surface area per unit volume

has involved pyrolysis of polymer precursors with a desired architecture and pore size distribution such as woven cloths, felts, papers, or foams [8,9]. Commercial vanadium redox flow batteries which do not require catalysts still rely upon graphite felt as electrodes with a recent trend toward more compact carbon papers made from pyrolyzed polyacrylonitrile (PAN) fibers [10,11]. Typically composed of micrometer sized fibers, these materials albeit fall short of the range needed to support the current densities required by modern energy applications. To attain the ideal nanometer scale pore size distribution while maintaining good electrical conductivity, many recent efforts have been made toward the development of carbon nanofoams [12,13]. With a well-connected carbon structure providing an unbroken electrical pathway, custom pore sizes can be achieved by a template process leading to potentially very high surface area [13,14]. Unfortunately these materials typically suffer from poor mechanical properties such as brittleness and micrometer-sized cracks which skew their overall pore size distribution [15].

One of the most common methods for increasing the active electrode area has been through the synthesis or deposition of high surface area nanomaterials onto a scaffold such as the powders, felts, and papers mentioned above [16]. In the case of metallic catalysts, electrodeposition has been used to synthesize an array of colourfully named nanoscale geometries with very high surface area such as onions and nanoflowers [17]. Most often these nanoparticles are deposited on supporting mesoscopic carbon

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powders and dispersed as inks for physical deposition. Depending on the design of the final cell and the reaction chemistry involved, these catalyst inks have been physically deposited with an array of methods including doctor-blading [18], immersion [19], spray coating [20], and inkjet printing [21]. Other methods of catalyst deposition such as sputtering and chemical and physical vapor deposition are unlikely to be adopted commercially due to their higher cost. More recently, synthesized carbon nanomaterials such as graphene and carbon nanotubes (CNTs) have received much interest as electrode materials and catalyst supports due to their exceptionally high surface area. In addition, their ordered graphitic structure endows them with high electrical conductivity and mechanical strength [22]. In the case of chemistries which do not rely on precious metal catalysts such as the vanadium redox battery, these nanomaterials have the potential to greatly increase the electrochemical active surface area (ESA) of a supporting carbon electrode such as graphite felt or carbon paper [23–31].

In this study a novel method is described for increasing the ESA of flow-through porous electrodes while addressing the issue of cost reduction. In its present incarnation, the invention consists of *in situ* flowing deposition of carbon nanotubes (CNT) onto a carbon paper scaffold which increases the surface area available for electrochemical reactions [32]. With few steps and no added chemicals or solvents this method provides a simple and environmentally benign way of increasing the performance of electrochemical cells based on flow-through porous electrodes. In the current example, the performance improvement related to the increased surface area is quantified via half-cell electrochemical impedance spectroscopy (EIS) in addition to standard Tafel analysis with the use of an analytical flow cell technique. The deposition method is also demonstrated *in situ* by enhancing the performance of a previously assembled full electrochemical cell for discharge of vanadium redox reactants. The flowing deposition of CNTs is used to increase the surface area of the anode of the cell to offset the slower intrinsic kinetics of the V^{2+}/V^{3+} reaction in particular. The deposition aims to effectively eliminate the kinetic overpotential associated with this reaction in terms of overall device performance.

2. Methodology

2.1. Device fabrication

Assessing the kinetic performance of compact high surface area electrodes which are inherently porous has repeatedly been shown to be prone to error [33–37]. Porosity and surface roughness introduce artificial effects which cannot easily be extracted from polarization data, making it difficult to evaluate both the nanomaterials and deposition methods being used [38,39]. A recent study released by our group has suggested a new analytical flow cell technique for quantifying the kinetics of flow through porous electrodes in particular [40]. This technique uses a customized microfluidic channel to force reactants through the electrode at rates high enough to compensate for diffusion limitations. The analytical flow cell has already proven useful for determining which vanadium half-cell reaction is limiting on carbon paper electrodes and the effect of electro-oxidation on the rate of the V^{2+}/V^{3+} reaction in particular [41].

In the present work, the previously published three electrode analytical flow cell depicted in Fig. 1a is used for half-cell ESA characterization and initial analysis of the flow deposition method [40]. Additionally, for the purpose of demonstrating *in situ* deposition in a full electrochemical cell, the previously published co-laminar flow cell (CLFC) depicted in Fig. 1b is used [42]. This new class of electrochemical cell is based on membraneless co-laminar flow to achieve reactant separation and has been extensively reviewed elsewhere [43,44]. The microfluidic channels for these cells are fabricated by soft lithography of poly (dimethylsiloxane) (PDMS) from a photoresist template. The analytical flow 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 active section of the WE is therefore 2 mm wide, with a flow-through depth of 0.5 mm. The CE is sized with a flow-through depth of 4 mm 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

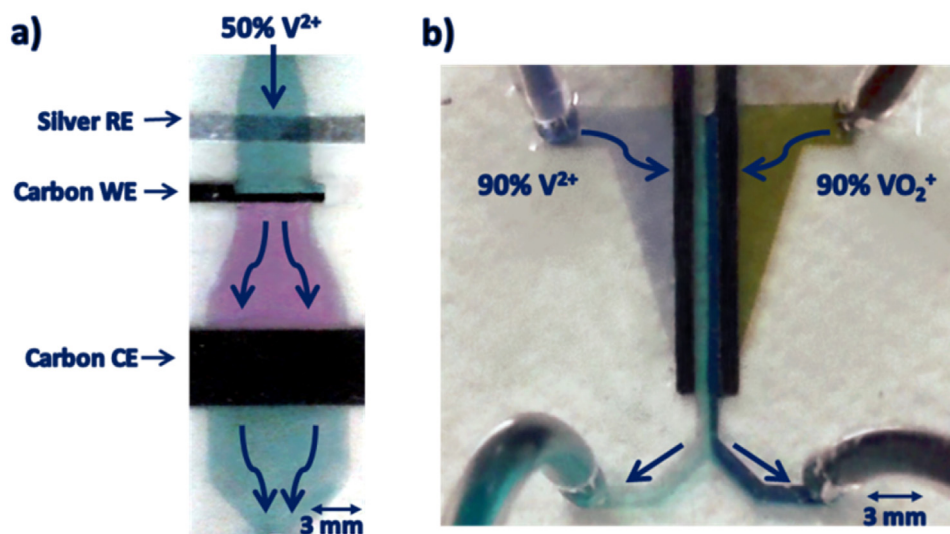


Fig. 1. Annotated live images of a) the analytical flow cell during complete oxidation of 50% V^{2+} on the upstream working electrode and subsequent complete reduction on the downstream counter electrode [40] and b) the co-laminar flow cell discharging 90% vanadium reactants. The colour changes observed are indicative of the different vanadium ion oxidation states and hence show effective reactant conversion in each flow-through porous electrode [42].

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