



High performance electrodes in vanadium redox flow batteries through oxygen-enriched thermal activation



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HIGHLIGHTS

- Thermal activation of carbon paper electrodes enhances VRFB kinetic performance.
- Large increase in surface area is responsible for improved kinetic performance.
- Significant improvement in depth of charge is achieved.
- Charge/discharge cycling efficiency of 76% at 200 mA cm⁻² is realized.

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ABSTRACT

The roundtrip electrochemical energy efficiency is improved from 63% to 76% at a current density of 200 mA cm⁻² in an all-vanadium redox flow battery (VRFB) by utilizing modified carbon paper electrodes in the high-performance no-gap design. Heat treatment of the carbon paper electrodes in a 42% oxygen/58% nitrogen atmosphere increases the electrochemically wetted surface area from 0.24 to 51.22 m² g⁻¹, resulting in a 100–140 mV decrease in activation overpotential at operationally relevant current densities. An enriched oxygen environment decreases the amount of treatment time required to achieve high surface area. The increased efficiency and greater depth of discharge doubles the total usable energy stored in a fixed amount of electrolyte during operation at 200 mA cm⁻².

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1. Introduction

Redox flow batteries, initially researched by NASA in the 1970s, have risen to prominence as an energy storage technology and are an important factor in enabling wide-scale implementation of intermittent renewable energy sources on the grid [1]. Among them, the all-vanadium redox flow battery (VRFB) has drawn considerable attention; however, system costs are a barrier to

commercialization. The stack is estimated to account for roughly 30% of the total cost, and the vanadium-based electrolyte accounts for nearly 40% given conventional system operating parameters and design [2]. Recent studies have focused on improving electrode and membrane performance to increase power density and therefore decrease stack-associated costs [3–7]. These advancements also improve efficiency, which reduces electrolyte cost since more energy can be extracted per charged vanadium ion.

Activation overpotential as a result of sluggish electrode kinetics is one cause of efficiency loss in electrochemical systems. Electrode kinetic overpotential is a function of electrode surface area and surface chemistry [8,9]. Many studies have attempted to modify carbon or graphite felt surface chemistry through chemical [10–12]

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and thermal treatments [12–14]. In these investigations, increased activity of the electrode surface is generally attributed to enhanced oxygen content on the surface. However, the connection between oxygen content and electrode activity has not been conclusively verified.

Thermal treatments on graphite felts were first pioneered in VRFB systems by Sun and Skyllas-Kazacos [13]. In the current study, carbon paper electrodes were thermally treated under varied oxygen concentrations and then used in the high power density no-gap architecture [6]. This work demonstrates performance gains and associated system-level benefits that can be achieved by using enhanced carbon paper electrodes in a favorable architecture. The use of an enriched oxygen environment during treatment decreases the amount of time required for heat treatment, resulting in energy and cost savings during processing. Initial characterization results indicate that the large increase in surface area was responsible for the enhanced kinetic performance, rather than the addition of oxygen functionalities, as previous authors have suggested [10–14]. This implies that electrode modification studies must account for the change in surface area to complement analysis of the surface chemistry when attempting to explain any apparent change in electrode kinetics.

2. Experimental methods

2.1. Electrode preparation

Untreated SGL10AA carbon paper (SGL Group) was used as the baseline electrode material. Nine sets of the 10AA electrodes were heat treated in a tube furnace at 400 °C with oxygen concentrations of 0% (nitrogen), 21% (air), and 42% (enriched) balanced by nitrogen (Airgas) for 15, 30, and 45 h for each oxygen concentration. Prior to heat treatment, the electrodes were purged in the furnace with the treatment gas for 2 h. Selected electrodes were characterized to determine oxygen content, surface area, and wetted surface area with a PHI 3056 X-ray photoelectron spectrometer (XPS) with an Al K_{α} X-ray source (1486.6 eV) at 350 W, an Autosorb-iQ surface area analyzer (BET method), and electrochemical impedance spectroscopy, respectively [15]. Mass loss was determined by weighing samples before and after heat treatment.

2.2. Cell architecture

Single-cell flow batteries with 5 cm² of geometric active area were constructed with a serpentine flow field using the no-gap architecture [6]. Three layers of carbon paper compressed to ca. 70% of their original thickness were used in both sides of the cell. A Nafion[®] 117 membrane (DuPont) was utilized to maximize coulombic efficiency. For all testing, a flow rate of 90 mL min⁻¹ was provided by a dual-channel peristaltic pump (Cole–Parmer). Cell temperature was maintained at 30 °C.

2.3. Electrolyte solution

Electrolyte solutions consisting of 1 M vanadium ions in 5 M sulfuric acid were prepared from vanadium (IV) sulfate oxide hydrate (Alfa Aesar, 99.9%) and sulfuric acid (Alfa Aesar, ACS grade) in deionized water. Initial charging was performed with 100 mL catholyte and 50 mL anolyte. Upon reaching ca. 100% state of charge (SoC), one half of the catholyte solution was discarded to obtain a 1:1 ratio of charged catholyte and anolyte solutions. A nitrogen purge (Airgas, UHP) was used over both tanks of electrolyte to prevent oxidation of the vanadium species.

2.4. Electrochemical characterization

Polarization curves were obtained with alternating 30 s galvanostatic discharge and open-circuit steps with no recharge, resulting in a continuous decrease in SoC over the course of the curve. High-frequency resistance (HFR) measurements were taken during discharge steps to *iR*-correct the polarization curves. Two cycles at both 100 mA cm⁻² and 200 mA cm⁻² were carried out with the same electrolyte solution used for the polarization curves. Cutoff voltages of 1.7 and 0.6 V were used upon charge and discharge, respectively. HFR measurements were also taken during cycling and used to *iR*-correct the charge and discharge profiles. Electrochemical measurement and control and temperature control were carried out with a Scribner Associates 857 Redox Test System potentiostat.

3. Results and discussion

3.1. Polarization curves

With the passage of current, electrochemical systems deviate from their thermodynamic cell potential due to activation/kinetic, ohmic, and concentration polarizations. Polarization curves are a useful tool for resolving these sources of overpotential [16]. In this work, polarization curves were *iR*-corrected to remove the ohmic losses from the membrane, leaving ohmic losses in the liquid electrolyte and activation and concentration polarizations. While these contributors to polarization appear over all current densities, the activation overpotential dominates at lower current densities [17]. Given that there was no significant difference between polarization curves with and without recharge between discharge steps for low current densities (0–0.5 A cm⁻²), the concentration polarization is negligible in the low current density regime. Ohmic losses in the liquid electrolyte were assumed to be similar between different cell builds and are not discussed in the remainder of this work.

Treatment in nitrogen (0% oxygen) provides a moderate improvement in cell performance, while treatments in air (21% oxygen) and enriched (42%) oxygen provide a more marked improvement, as shown by the *iR*-corrected curves with the 15 h treated electrodes in Fig. 1(a). Similar trends were observed for both 30 and 45 h treated carbon papers. Fig. 1(b) shows the difference in *iR*-corrected voltage between each of the treated and untreated electrodes. The air and enriched oxygen treatments resulted in improvements of 100 mV over untreated carbon paper at a current density of 100 mA cm⁻² that asymptote to 140 mV at 0.5 A cm⁻². The pure nitrogen treatment showed a more modest boost of 40 mV that does not increase with current density beyond 40 mA cm⁻². Sharp gains in the low current density region of the polarization curve (0–0.5 A cm⁻²) with gains that level off at higher current densities (>0.5 A cm⁻²) indicate an improvement in the kinetic performance of the vanadium redox reactions on the electrode surface.

3.2. Electrode characterization

Both surface area and chemistry have an impact on reaction rates. The surface chemistry, probed with XPS, showed a small increase in oxygen content on the electrode, from 1% untreated to 2% with the enriched oxygen treated electrode. This change is much smaller than the increase from 4% to 20% observed by Sun and Skyllas-Kazacos on heat treated carbon felt [13]; however, carbon paper is a different material than felt and may be less susceptible to oxygen functionalization. The BET surface area of the 42% oxygen treated material was 21.0 m² g⁻¹, a significant gain over the

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