Extended Abstract

(For Ph.D. Open Seminar)

Optimizing Performance of a Vanadium Redox Flow Battery by Mechanical, Chemical and Operation Means

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Vanadium Redox Flow Batteries (VRFBs) have emerged as a promising solution for large-scale energy storage due to their scalability, long cycle life, and decoupled energy and power capabilities. However, optimizing their electrochemical performance, hydrodynamic behavior, and long-term stability requires careful design of flow fields, electrolyte formulation, and a deeper understanding of failure mechanism. In this context, our research focuses on three major aspects of VRFB-performance enhancement: (i) Design of new flow fields and modification of existing flow-fields, (ii) Additives in supporting electrolyte, and (iii) Identification and analysis of overshoots, and related performance-degradation mechanism.

Chapter 1. Introduction and research gap

This chapter presents the need for energy storage devices to enable renewable energy integration and, thus, to help in the decarbonization of various sectors. Various types of devices with their advantages and disadvantages are clearly delineated. A marked distinction of VRFB in various aspects over current technologies is presented. The construction of the device using its components, their working principles, commonly used materials, and electrochemical reactions occurring on electrodes are discussed. Performance analysis techniques applied in VRFB research, such as polarization curve measurements, electrochemical impedance spectroscopy (EIS), and efficiencies, are presented which form the basis for evaluating and improving the performance of the battery. Research gaps to improve the performance of the battery have been identified.

Chapter 2. Methodology

This chapter presents a detailed methodology used in the research on optimization of performance of the VRFB using newly designed and modified, using additive in the electrolyte flow fields, diagnosing and analyzing the degradation mechanism. All materials used in the experiments are clearly mentioned. Flow channels were designed and fabricated, and their performance was evaluated for flow behavior and pressure characteristics with and without porous electrodes. Electrochemical performance was examined in the 3-electrode systems and cell assemblies employing cyclic voltammetry (CV), polarization curves, and EIS measurements. Experimental data were analyzed and used for estimation of power density, internal resistances, and mass transfer resistance. Diagnostic studies were conducted for electrolyte leakage, and the effect of electrode thickness on overall efficiency of the battery.

Chapter 3. Design, development and performance analysis of modified split conventional serpentine flow field in VRFB

The chapter presents performance analysis of a scaled-up, modified split-conventional serpentine channel employing it in a VRFB. The channel is an upgraded version of previously presented split-serpentine channel of 10 cm^2 area, incorporating following changes:

(i) relocation inlet and outlet ports from corners to the center of the channel plate,
(ii) change in width of flow path, and
(iii) altering rectangular ribs to trapezoidal ones.

Hydrodynamic studies using water with and without electrode compression reveal a substantial reduction, up to 70%, in pressure drop with felt and 81% reduction without felt at a flow rate of 50 mL/min. This arises from decreased overall flow resistance in the MSCS channels. The channel also shows a superior electrochemical performance, achieving an *iR*-free peak power density, exceeding 700 mW/cm^2. The design is easy to engrave on the graphite plate using a computerized milling machine, offering simple, economic manufacturability, while enhancing the overall energy efficiency of the battery.

Chapter 4. Design, development, and performance analysis of Tesla valve inspired flow field

The chapter presents a Tesla valve-inspired serpentine (TVS) channel, which brings directional and asymmetrical flow characteristics. A comparative study of two intrinsic features, forward (TVS-F) and reverse (TVS-R) flows, of the channel, with and without felt electrodes against a conventional serpentine (CS) channel. The pressure drop for TVS-R is consistently higher than TVS-F, especially at higher flow rates. However, in the presence of felt electrodes, both TVS-F and TVS-R channels exhibited significantly reduced pressure drops compared to CS, against the findings of previous studies. Electrochemical studies through polarization curve measurements reveal that employing TVS-R in the VRFB, the highest peak power density (778 mW/cm^2) can be achieved, followed by TVS-F (685 mW/cm^2) and CS (678 mW/cm^2). EIS analysis confirmed lower impedance in the TVS-R design, suggesting improved accessibility of electroactive species in the porous spaces of the electrode and reduced internal resistance.

Chapter 5. Examination of roles of additives in supporting electrolyte

The chapter investigates the role of additives in improving the electrochemical performance of supporting electrolyte in the VRFB. Common supporting electrolyte used in sulfuric acid. Two additives: Methane sulfonic acid (MSA) and Trifluoro methane sulfonic acid (TFMSA), whose chemical structure closely resembles that of ionomer of Nafion membrane, commonly employed in the VRFB. Nine formulations using MSA or TFMSA and H_2SO_4 were prepared and their electrochemical characteristics were analyzed using cyclic voltammetry and in employing in the cell. Of all, a blend of 0.5 M H_2SO_4 and 1.0 M MSA illustrates superior electrochemical performance, offering over 81% higher peak power density compared to the least effective (0.5 M H_2SO_4 + 1.0 M TFMSA). These findings clearly indicate the role of additives in improving the performance of battery.

Chapter 6. Identification and analysis of performance degradation due to operational challenges of VRFB, and mitigation thereof

The chapter presents a detailed investigation of electrochemical overshoots during VRFB operation, aiming to diagnose system-level inefficiencies and degradation mechanism. The study highlights that asymmetric ion crossover, induced metal deposition, and electrolyte permeation through the graphite plate significantly influence the battery's stability and power output. Overshoots are linked to increased ohmic and charge transfer resistance, especially when electrolyte seepage occurs through the plates. Results show nearly two-fold increase in ohmic losses and 50% reduction in peak power output, with no effect on *iR*-free power density. Results also demonstrate the effect electrode-thickness on the performance: thicker electrodes lower diffusion limitations, though their influence in the ohmic regime is marginal.

Chapter 7. Conclusions and future scope

This research comprehensively addresses key challenges in vanadium redox flow batteries (VRFBs) through innovations in flow field design, additives in supporting electrolyte formulation, and analysis of degradation mechanisms. Modified flow channel, MSCS, and Tesla valve-inspired designs significantly reduce pressure drop in pumping the electrolyte and help in achieving enhanced peak power densities. The electrolyte formulations, particularly H_2SO_4-MSA blends, demonstrate significant improvements in redox activity and show compatibility with electrode materials. The study of electrochemical overshoots reveals critical failure pathways linked to ion crossover, metal deposition, and electrolyte leakage - offering insights for improving long-term stability.

Future scope of work, which includes exploring advanced manufacturing of complex flow fields for VRFB, long-term cyclic test of novel electrolyte systems, and integration of real-time monitoring tools for degradation diagnostics, is also delineated in the chapter. These directions will further the development of efficient, durable, and commercially viable VRFB systems for large-scale energy storage.

Manuscript prepared/ under preparation from the present work:

1. Scalable, trapezoid-ribbed, split-serpentine flow channel for enhancing energy efficiency of a vanadium redox flow battery. The Journal of Energy Storage **(Revision-1-Submitted)**
2. An electrochemical performance analysis on Tesla Valve inspired flow field geometry for vanadium redox flow battery. **(Prepared)**
3. Performance Analysis of Trifluoro-methyl Sulphuric Acid and Methyl-Sulphuric Acid as supporting electrolyte in VRFB. **(Prepared)**
4. In-depth evaluation and troubleshooting for VRFB: effects of electrode thickness, oxygen entrainment, and electrolyte leakage. **(Prepared)**
5. A novel two-step graphite felt treatment combining plasma activation and urea impregnation for vanadium redox flow battery **(under preparation)**
6. Electrochemical Performance of Stacked Vanadium Redox Flow Battery Cells with Split Serpentine Flow Channels **(under preparation)**

Patents

1. A structure for liquid electrolytic distribution for flow battery and a method thereof. Application No: **202411053407**
2. Bifunctional electrocatalyst for hydrogen production at industrial current density and process for preparing the same. Application No. **202511017168**