a) Title of the project:

EVALUATION OF MANGANESE–TUNGSTEN REDOX FLOW BATTERY

b) Name of the College & Department:

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d) Keywords:

Grid-connected energy storage system, Renewable energy, Electrochemical energy conversion and storage devices, Redox flow battery, Non-vanadium redox flow batteries

e) Introduction/background :

The manganese-tungsten redox flow battery is an innovative approach to address the concerns associated with the current reliance on vanadium-based redox flow batteries (RFBs). Being scarce, costly, and toxic, Vanadium has prompted researchers to explore alternative materials for RFBs. Transition metals like iron, chromium, manganese, and nonmetallic materials such as organic compounds and polymers are being actively investigated as potential alternatives. Among these alternatives, the iron-tungsten flow battery has gained attention for its potential in large-scale energy storage applications, showing promising performance in recent studies. One possible modification to the iron-tungsten flow battery chemistry involves substituting manganese for iron in the battery's electrodes. Manganese, being a transition metal with electrochemical behaviour similar to iron, can also be comfortable with tungsten. This substitution has the potential to enhance the energy density, cycle life, and rate capability of the battery. An important advantage of manganese is its abundant availability, making it a cost-effective alternative to iron. This exploration could potentially result in significant performance improvements. The development of the manganese-tungsten redox flow battery holds promise for overcoming the limitations associated with vanadium-based systems. By leveraging the electrochemical properties and alloy formation capabilities of manganese and tungsten, this battery technology offers a potential solution to vanadium's scarcity, cost, and toxicity concerns. Through continued research and experimentation, the manganese-tungsten redox flow battery has the potential to emerge as a sustainable and efficient alternative for large-scale energy storage applications.

f) Objectives:

In the present study, we propose to evaluate the manganese (Mn^{2+}/Mn^{3+}) and tungsten (PTA^{3-}) redox electrolytes for redox flow battery (RFB) for storing renewable energy. It is expected that the use of Mn^{2+}/Mn^{3+} and PTA^{3-} provides higher cell potential in comparison with already investigated iron-tungsten RFB. The following objectives were carried out:

1. Electrochemical characterization (cyclic voltammetry, open circuit potential, electrochemical impedance spectroscopy, and rotating disk electrode voltammetry) for individual redox electrolytes.
2. Evaluation of RFB performance for charge/discharge behaviour, cell potential, and energy density.
3. Study the effect of redox electrolytes concentration and flow rate on RFB's performance.

g) Methodology:

The preparation of positive and negative electrolytes involves several steps. Manganese salt was dissolved in a 0.5 M H_2SO_4 supporting electrolyte for the positive electrolyte. On the other hand, the negative electrolyte was prepared by dissolving tungsten salt in a 0.5 M H_2SO_4 supporting electrolyte. Nafion 211 proton exchange membrane was used as a separator and prior to its use, it was subjected to the pre-treatment to remove any impurities present. Breifly, the membrane is boiled in an aqueous solution containing 3 % (w/w) hydrogen peroxide and 0.5 M H_2SO_4 in DI water. After the pre-treatment, the membrane is washed with DI water and stored in DI water for further use. For the electrochemical characterization experiments, a standard three-electrode configuration was used. A polished glassy carbon (GC) rotating disk electrode serves as the working electrode, while a platinum wire electrode used as the counter electrode. A saturated Hg/Hg_2SO4 reference electrode was used, whose actual potential was measured against an in-house fabricated RHE (reversible hydrogen electrode) in 0.5 M H_2SO_4. Cyclic voltammetry is performed in a five-neck volumetric flask to measure the electrode potential of positive and negative electrolytes. Important parameters such as diffusion coefficient (D_0), transfer coefficient (α), Tafel slope, and kinetic rate constant (k_o) for both half-cell reactions are determined using rotating disk electrode voltammetry. A specific battery setup was used to characterize the manganese-tungsten redox flow battery. The setup includes stainless steel current collectors, graphite plates with a serpentine flow field, porous graphite felt as the electrode surface, and a Nafion 211 membrane as the proton-conducting membrane.

Two peristaltic pumps and electrolyte storage tanks with tubing arrangement are used. The Manganese-Tungsten redox flow battery's schematic is presented in Figure 1.

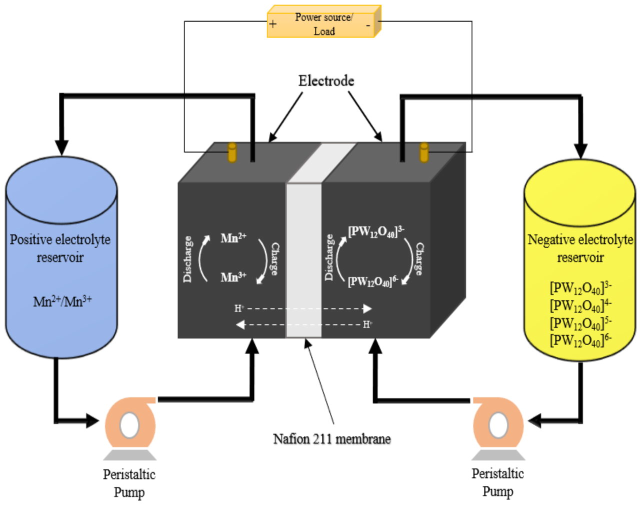

Figure 1. Schematic of the manganese-tungsten redox flow battery with charging and discharging reactions.

h) Results and Conclusions:

This study evaluates manganese–tungsten RFB, where the negative electrolyte was tungsten and the positive electrolyte was manganous sulphate monohydrate. Experiments were conducted where the charge/discharge capacity, Coulumbic efficiency, and specific capacity were studied. Along with these studies, basic electrochemical studies have also been performed, including cyclic voltammetry and rotating disk electrode voltammetry. Based on the conducted studies, the following conclusions can be drawn:

1. From cyclic voltammetry experiments, the formal potential of Mn^{2+}/Mn^{3+} was 1.48 V vs RHE in 0.2 M of concentration, and the formal potential of PTA^{3-} was - 0.41, - 0.07 and 0.20 V vs RHE for the three distinct peaks for a concentration of 0.05 M.
2. A Coulombic efficiency of 66.67 % was achieved with a specific capacity of 41.67 mAh/L for a 150 mL/min flow rate with a concentration of 0.2 M Mn^{2+} and 0.05 M PTA^{3-}.
3. A maximum capacity of 1560.41 mAh/L were seen for the flow rate of 150 mL/min with a concentration of 0.2 M Mn^{2+} and 0.05 M PTA^{3-}.

The charge-discharge characteristics of the manganese-tungsten redox flow battery are depicted in Figure 2, illustrating the electrochemical behavior of the system during the cycling process.

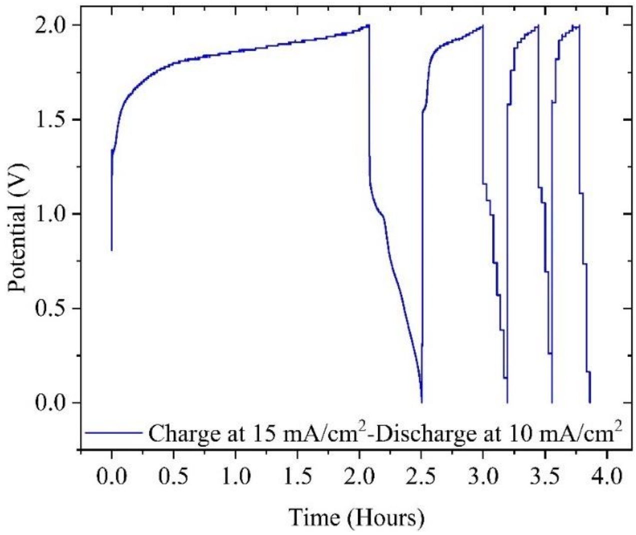

Figure 2: First four charge/discharge cycles at a current density of 15 mA/cm^2 for charging and 10 mA/cm^2 for discharging at a flowrate of 150 mL/min with a concentration of 0.05 M PTA^{3-}

Despite having low capacity and Coulombic efficiency, the RFB comes with a major advantage in terms of higher potential; also, the electrolytes used here are better than conventional RFB, such as vanadium redox flow batteries. Significant improvement in the performance of the manganese–tungsten redox flow battery can be made by avoiding oxidation of phosphotungstic acid through constant argon purging. Further research can be done to increase the overall performance of the battery.

i) What is the innovation in the project

The project's innovation lies in the pioneering development and exploration of the manganese-tungsten redox flow battery as a novel alternative to existing vanadium-based redox flow batteries. the project aims to address the limitations associated with vanadium, such as scarcity, cost, and toxicity. One key distinction is the significant difference in standard electrode potential between the two systems. The manganese-tungsten redox flow battery exhibits a higher standard electrode potential of 1.87 V, whereas the vanadium battery has a standard electrode potential of 1.26 V. In practical applications, the manganese-tungsten battery has achieved electrode potentials ranging from 1.1 V to 1.25 V. The project's aim is to thoroughly evaluate the performance and characteristics of the manganese-tungsten redox flow battery. By conducting comprehensive studies and analyses, the project seeks to assess the battery's charge/discharge behavior, coulombic efficiency, capacity, and stability. Through this evaluation, a deeper understanding of the manganese-tungsten battery's capabilities and limitations can be gained. The project aims to investigate the potential advantages and drawbacks of the manganese-tungsten system compared to the traditional vanadium-based approach. Ultimately, this evaluation will contribute to the advancement of redox flow battery technology by exploring alternative materials and improving the efficiency, cost-effectiveness, and sustainability of large-scale energy storage systems.

j) Scope for future work:

The performance of the manganese-tungsten redox flow battery can be further enhanced. Firstly, efforts can be directed towards optimizing the electrolyte composition and concentration. Fine-tuning the concentrations of manganese and tungsten can potentially improve the charge/discharge capacity, Coulombic efficiency, and specific capacity of the battery. Additionally, investigating the use of alternative supporting electrolytes or additives may offer opportunities to enhance the electrochemical performance and stability of the system. Moreover, the electrode materials and design can be optimized to improve the overall efficiency and durability of the battery. Exploring different electrode architectures, such as nanostructured or composite materials, could facilitate faster charge transfer kinetics and increase the active surface area, resulting in improved performance. Additionally, coating or modifying the electrodes with suitable catalysts can enhance the electrochemical reactions and minimize side reactions, leading to increased efficiency and long cycle life. The study can also be expanded to explore the effect of operating parameters such as flow rate and temperature on the performance of the manganese-tungsten redox flow battery. Investigating the influence of flow rate on the charge/discharge capacity, energy efficiency, and overall stability can provide valuable insights into the system's optimal operation conditions. Similarly, examining the temperature dependence of the battery's performance can help identify suitable temperature ranges for achieving optimal energy conversion and storage.