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1. **Project details**
   a. *Title*: ***Towards Designing High Performance Rechargeable Zinc Ion Aqueous Batteries***
   b. *Institute*: Centre for Nano and Material Sciences, JAIN (Deemed to be University)

2. **Aim / Objectives:**

The primary objective of the research is to develop suitable cathode materials or positive electrodes to host zinc ions in aqueous based electrolytes. Towards this the project aimed to develop vanadium oxide-based cathode.

The initial objectives

- Development of functional nanocomposites as cathode: here the goal is to explore graphene and Mxene based nanocomposites of structurally modified different vanadium oxides of the type $M_xV_yO_z$, nH_2O (where M= doped/pre-inserted alkali or transition metal ions) with expanded layer spacing as high-performance cathode for reversible Zn2+ ion (de)intercalation.
- Study of structure and property relationship: here the goal is to understand the effect of doping, crystallinity, surface area of the metal oxide on the reversible Zn2+ ion storage and optimize the ratio of the metal oxide to graphene or Mxene to realize the favourable synergistic interaction towards improved cathode performance.
- Deep understanding of the underlying Zn2+ storage mechanism for different cathodes.
- Development of high energy high power and long cycling aqueous Zinc ion battery prototype with performance optimized cathode coupled with electrodeposited zinc anode.

However, during the project progress, we understood the practical constraints of Vanadium based cathode for commercial applications, so we additionally focused on developing alternative cathodes. We explored manganese oxide, high entropy Prussian blue analogs, sulfur and biomass derived engineered carbon as cathode or positive electrode for aqueous zinc ion batteries/capacitors.

3. Executive Summary (*One page*):

Over the past two years, this project has taken a broad yet integrated approach to advancing aqueous zinc-ion–based energy storage systems, with the clear goal of developing technologies that are safe, affordable, sustainable, and practically deployable. Moving beyond incremental material improvements, the work combines rational materials design, green synthesis strategies, device engineering, and mechanistic insights to tackle some of the most persistent challenges facing aqueous zinc-ion batteries/capacitors. Furthermore, while our primary objective was to fabricate cathode capable of hosting zinc ions, we also explored side by side task specifically modified electrodes for Li-ion and electrolyte for supercapacitors application as extended objectives.

A major part of the effort focused on cathode materials capable of reversibly accommodating Zn^{2+} ions without rapid capacity loss. In this context, zinc-doped $V_{10}O_{24}\cdot 12H_2O$ was explored for the first time as a cathode for aqueous zinc-ion batteries. Zinc doping showed to improve the electronic conductivity, reduce charge transfer resistance and provide structural stability to the vanadium oxide leading to an enhanced capacity and cycling stability.

However, although vanadium itself is a critical/strategic metal, also the nominal voltage with vanadium oxide cathode is limited to <0.8V. Further we explored MnO2 based composites as AZIB electrode, where we synthesis deep eutectic solvent mediated brown seaweed derived carbonaceous composites of β-MnO2 as a high performance AZIB electrode. Although the obtained capacity is somewhat lower than the engineered vanadium oxide cathode, the Zn//MnO2 cell showed a high nominal voltage of ~1.45 V, leading to enhanced energy density.

Furthermore, Prussian blue analogues are considered as promising cathodes for hosting Zn2+ ions. However, the structural dissolution of PBAs is the major challenge behind their feasible applications as AZIB cathode. Herein we introduced high configurational entropy into PBAs analogues by replacing the N coordinated metal centre with Fe, Mn, Ni, Zn and Mg. The high entropy PBAs showed an enhanced capacity and performance rate compared to PBAs.

Along with intercalation-based cathode, we also explored conversion-based cathode with elemental sulfur entrapped in porous and defect rich laser induced graphene (LIG) as cathode and metallic zinc electrodeposited onto LIG as anode and demonstrate an aqueous Zn-S battery in plane. The process does not use any binder or conductive additive and can be completed in less than 2 hours. While the electrochemical performance is comparatively lower than the conventional coin cell configuration, the interdigitated cell design allows for customizable form factors and offers a platform accessible to optical and spectroscopic techniques, facilitating future operando and ex situ studies for continuous development of this emerging technology.

Furthermore, we explored biomass-derived engineered carbon as a high-performance capacitive electrode for reversible Zn-ion storage. A dual-modification strategy was employed to generate micropore-rich carbon with pore sizes ranging from 0.86–1.5 nm, along with a high specific surface area. This pore matches the size of hydrated zinc ion for monolayer confinement. This led to a high capacity and excellent stability with >95% capacity retention over half a million cycles.

We further developed a water-in-salt hybrid electrolyte which showed a wide electrochemical stability window >2.6 V and allowed stable cell operation over a wide temperature range of -40˚C - +60˚C. The electrochemical performance was demonstrated in planer symmetric supercapacitor with MnO_2 and V_5O_{12} as electrode.
Utilizing the project funding we have published a total of 12 research articles and 3 more are under preparation.

4. Scope for further work

The project opened several new research directions. Rechargeable Zn-ion batteries can be a game changer for grid scale energy storage. While our initial data are very promising, and can be potentially used as an electrode material, the prototype fabrication requires few other considerations leaving a significant room for future research and innovation before the technology can be commercialized. Following are the potential research direction for individual work carried out under this RSOP project.

- Dissolution of MnO_2 in aqueous electrolytes remains a primary cause of capacity fading. Although the addition of $MnSO_4$ to the electrolyte can partially offset this loss by replenishing Mn^{2+} species, effective mitigation ultimately requires appropriate structural modification of MnO2 together with cathode-level engineering to suppress material dissolution.
- Zinc corrosion and dendrite formation is the main challenge against AZIB technology commercialization. Anode interfacial engineering with suitable electrolyte additive is the key to protecting the metallic zinc anode. Our future objective is to protect the zinc anode from corrosion and dendrite formation via electrolyte additive constructed interfacial engineering.
- Our initial results with HEPBAs are highly promising towards stabilizing the PBA framework against structural breakdown. However, the elemental compositions of HEPBAs must be optimized. Also, the conductivity of the HEPBAs must be improved to improve the performance rate.
- Our dual-modification strategy for producing porous carbon from biomass shows strong promise; however, its general applicability must be validated across diverse biomass precursors with varying cellulose and lignocellulosic compositions. Also we are optimizing the all-weather applicability of the fabricated zinc ion capacitor with modified electrolyte comprising antifreezing molecularly crowding agent as electrolyte additives.
- The miniaturized flexible zinc-sulfur prototype has a limited capacity at this stage, which can be significantly improved via controlling the sulfur oxidation via scribing assisted melt infiltration of sulfur into the LIG matrix in control atmosphere. Further electrolyte engineering is important to stabilize the zinc anode, particularly where stoichiometric or near stoichiometric zinc is used.

5. Benefits visualized

The scientific outcome of the work carried out (direct and extended objectives) under the project addresses important bottlenecks in aqueous based energy storage systems in terms of fabricating high-performance electrodes/engineered electrolytes and device engineering to suit applications in grid scale to personal portable electronics. The project follows scalable and cost-efficient materials synthesis approach, aqueous based non flammable engineered electrolytes and overall innovative strategies from materials engineering to device/prototype fabrication.

The project establishes simple and scalable strategies for the fabrication of high performance AZIB cathode, including metal-ion doping in vanadium oxides, entropy-engineered Prussian blue analogues, and MnO_2–carbon composites. These approaches improve electronic conductivity, structural stability, and electrochemical performance, helping to overcome some of the existing bottlenecks in AZIB development.

The project also promotes green synthesis and waste to wealth transition via utilizing biomass-derived carbon from brown seaweed and engineered porous carbon structures and deep eutectic solvent assisted synthesis of MnO_2 composites. Further, the dual-modification strategy developed for biomass derived carbon materials for zinc ion storage is highly promising in terms of scalability, cost efficiency and performance. The ability to sustain more than half a million charge–discharge cycles with over 95% capacitance retention highlights the robustness and long-term viability of this approach. Such approaches reduce reliance on expensive or environmentally hazards materials, making zinc-based energy storage technologies more economically viable and environmentally benign.

Further, the project is benefited from the development of innovative and scalable device architectures, particularly the binder-free planar Zn–S battery fabricated using laser-induced graphene as sulfur host and as template for electroplating of zinc. This approach enables rapid manufacturing, customizable device architecture, and compatibility with spectroscopic techniques for operando studies, thereby facilitating future mechanistic understanding and technological optimization.

In addition, the development of a water-in-salt hybrid electrolyte with a wide electrochemical stability window and excellent temperature tolerance significantly expands the operational range of aqueous energy storage devices. The ability to operate reliably from −40 °C to +60 °C makes these systems particularly attractive for deployment in all climate condition, from the top of mount Everest to the death vally.

Finally, the project has generated 12 published articles, and several additional manuscripts in preparation contributed significantly to knowledge generation and research dissemination. Overall, the measurable outputs significantly strengthen the scientific foundation of aqueous zinc-based energy storage research and support future technological advancements in safe, sustainable, and affordable aqueous based energy storage systems.