IITB-Monash Research Academy

Indian Institute of Technology Bombay | MONASH University

An Indian-Australian research partnership

Project Title:	A safe and stable electrolyte system for high-energy aqueous rechargeable Zinc-manganese dioxide ($Zn-MnO_2$) batteries for cost-effective energy storage	
Project Number	**IMURA1041**	
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Research Clusters: / Research Themes:

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1	*Energy, Green Chem, Chemistry, Catalysis, Reaction Eng*	3	*Clean Energy*
		4	*Smart Materials*
		5	*Sustainable Societies*

The research problem

Lithium-ion batteries (LIBs) are the main commercial rechargeable batteries in the market due to their high energy density. However, the proliferation of electrical energy storage through LIBs has raised serious global concerns over the supply chain of battery raw materials, environmental and socio-economic impact, and their affordability. Rechargeable battery technologies, including lead-acid (Pb-acid), nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), redox flow-cells (RFCs), and LIBs, have found practical applications in various areas; however, these batteries suffer from issues such as low rates, hazardous constituents, and high costs that impede their applications in large-scale energy storage. For large-scale grid storage, a cost-effective, durable, high-power storage technology is critical for managing peak demands of most sustainable energy sources such as solar and wind energy for powering energy infrastructure.[1] Low-cost aqueous batteries using earth-abundant raw materials such as multivalent batteries (Zn, Ca, Mg, etc.) are promising alternatives.[2,3] Prior literature shows the average discharge plateaus (working voltage of battery) are in the range of 0.6–0.9 V for

Zn//V[4,10], 1.2–1.4V for Zn//Mn (alkaline electrolyte)[11], and 1.6–1.8V for Prussian blue analogues.[4] For these reasons, the specific energy of Zn batteries (70–140 Wh kg^{-1}) remains meaningfully lower than that of LIBs (180–230 Wh kg^{-1}). The use of manganese oxides (MnO_2) in rechargeable Zn-ion batteries (ZIBs) has attracted research attention due to the low cost, moderate discharge potentials, high rate performances, and a high theoretical capacity of about 308 mAh g^{-1}. However, these mechanisms use only one effective electron redox process of Mn^{4+}/Mn^{3+} in the applied cathode, limiting their capacities and output voltages. Therefore, the newly engineered acidic electrolyte Zn–Mn electrochemistry is an area of interest as it can help access higher valency electronic transitions. The variable valency of Mn (+2, +3, and +4) holds considerable potential for two-electron Mn^{4+}/Mn^{2+} reactions with a theoretical capacity of about 616 mAh g^{-1} and a high voltage of ~2V. Thus, aqueous Zn-MnO_2 batteries with the use of acid electrolytes with a theoretical voltage of ~2 V and a high energy density (~700 Wh kg^{-1}) may be achievable through leveraging the unique two-electron redox electrolysis reaction. This combined with the low-cost materials manufacturing and excellent safety make them promising batteries for large-scale grid storage.[2-4] However, poor cycle stability and low working voltages are the major limitations of aqueous Zn/MnO_2 batteries for grid storage. The alkaline electrolytes which are used primarily for the Zn-MnO_2 batteries have suffered from several fundamental problems such as the dissolution/precipitation, redox mechanism of zinc, passivation, shape change, dendrite growth, hydrogen evolution, the crossover of zincate to the cathode result in limitation of active material utilization, self-discharge, severe capacity fading, poor Coulombic efficiencies and possible sudden failure from short-circuits that limits its application in secondary batteries.[5] Recent studies show that neutral or mild acidic aqueous electrolytes are helpful to suppress the dendrite growth and enhance overall cell voltage, which helps to improve the electrochemical performance of aqueous Zn-MnO_2 batteries.[4,5] Although the neutral or mild acidic aqueous electrolytes are helpful to improve the electrochemical performance, the reaction mechanism of the MnO_2 cathode in acidic aqueous electrolytes remains controversial and is under debate which is an important aspect of this project that requires a thorough investigation. The charge/discharge mechanisms for MnO_2 reported by several studies show that the capacity of MnO_2 in acidic aqueous electrolytes can follow two processes: the reversible Zn^{2+} insertion/extraction or the reversible H^+ insertion/extraction process, which remain under investigation. These two possible mechanisms could be attributed to the difference in crystallographic polymorphs of MnO_2 (α, β, γ, δ, λ, and amorphous) or to the effect of the MnO_2 particle size controlling the ion insertion thermodynamics and kinetics of H^+ and Zn^{2+} which requires further investigation to understand fully.[8] To better understand the storage mechanism, we propose the use of *in-situ* synchrotron-based XRD and EXAFS experiments to investigate the MnO_2 cathode.[7] Based on the in-depth knowledge gained from in-situ synchrotron and electrochemical measurements, we will be better positioned to apply a strategy or a combination of strategies to modify the electrode materials for better electrochemical performance and efficiency of Zn/MnO_2 batteries.

We propose to study and explore aqueous gel electrolytes, which can help minimize the leakage issues faced by liquid electrolytes, provide physical flexibility, and inhibit the growth of zinc dendrites. Furthermore, gel electrolytes with limited free water can effectively suppress the dissolution of active materials, and the most important advantage is that separators are not required when the gel electrolytes are used.[8] Several research groups have verified the advantage of using gel electrolytes; reported literature by Zeng et al. demonstrated that the use of a PVA/$ZnCl_2$/$MnSO_4$ gel electrolyte to construct a flexible Zn-MnO_2 battery can retain more than 77.7% and 61.5% of its initial capacity after 300 and 1,000 cycles, respectively.[9] The limitations of gel electrolytes, i.e. the low ionic conductivity and poor mechanical strength, can be improved by adding graphene oxide (GO) as an additive to strengthen the ionic conductivity and mechanical strength of the gel electrolytes. We also plan to investigate different sources of carbons such as C-cloth, graphene, and graphite felt as different current collectors, including the different types of cell design approaches. Such innovative design and careful selection/optimization/engineering of the investigated electrolytes and MnO_2 structure could improve the cyclic stability of the as-developed Zn-MnO_2 cells. Therefore, it is important to understand the reaction mechanism of the electrodeposited MnO_2 in neutral or mildly acidic electrolytes, which represents a true mechanism for long-term cycling of MnO_2 cathodes. Investigating such electrode and electrolyte materials relies on the experience of the supervisory team,[3,7,12] and then modifying them in the context of the project can lead to dramatic improvement in the performances of aqueous rechargeable Zn-MnO_2 batteries for cost-effective energy storage.

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Project aims

This proposed research aims for the selection, optimization, engineering, fabrication, and advanced characterization of the investigated electrolytes and the structure of MnO_2 for cyclic stability in Zn-MnO_2 batteries. To reveal the correlation between the structural properties of the developed MnO_2 structure and the enhancement of electrochemical properties we propose the use of in-situ synchrotron-based X-ray advanced characterization techniques. We propose the implementation of gel electrolytes, which can help minimize the leakage issues faced by liquid electrolytes, provide physical flexibility, and inhibit the growth of zinc dendrites.

What is expected of the student when at IITB and when at Monash?

The PhD student needs to complete the coursework requirements of IITB in the first year of their PhD during their IITB stay. The student will work on material synthesis, in-situ synchrotron-based characterization, and fabrication of components of the electrochemical cells, which will provide an excellent opportunity for the PhD students to get trained and develop a fundamental understanding on Zn-MnO_2 battery technology. The substantial resources available to the PhD candidate include access to the Energy Lab at New Horizons Research Centre, Monash University, during their Monash stay, which will provide the core infrastructure for the synthesis/optimization/engineering/fabrication and advanced characterization of the investigated electrolytes and MnO_2 structure to improve the electrochemical performance of the Zn-MnO_2 batteries developed for this project.

Expected outcomes

1. The expected outcome of this project is to make battery technology more environmentally sustainable and affordable to store energy from sunlight and wind.
2. The comprehensive study of the cyclability and electrochemical reaction mechanism of the aqueous Zn–MnO_2 battery will be the main objective of this project.
3. Development of an engineered gel electrolyte system that enables the high cell voltage and electrochemical performance of the electrolytic Zn–MnO_2 aqueous battery.

In summary, the scientific/learning perspective of this project will lead to the fundamental understanding of the aqueous Zn–MnO_2 battery system, the related physics, and chemistry of MnO_2 and other associated nanomaterials crystal structures, engineering of such electrode materials to suit the desired application of these materials in Zn–MnO_2 battery, the development of a novel electrolyte for high voltage and high-energy aqueous Zn–MnO_2 electrochemical energy storage system.

How will the project address the Goals of the above Themes?

1. A comprehensive study of the cyclability of the aqueous Zn–MnO_2 battery will be the main objective of this report.
2. The project will focus on constructing aqueous rechargeable Zn-MnO_2 test cells and prototypes. Aqueous batteries are gaining attention due to the use of low-cost earth-abundant materials and non-flammable electrolytes, which are the practical approach to augment safety concerns and reduce manufacturing costs.
3. An engineered gel electrolyte system that enables the high cell voltage and electrochemical performance of the electrolytic Zn–MnO_2 aqueous battery.
4. The prototype fabrication and electrochemical tests.
5. The study of the role of acidic electrolytes will be comprehensively discussed along with the working principle, electrochemical reaction mechanism, and post-service analysis to make rechargeable Zn-MnO_2 battery prototypes.
6. The role of crystallographic polymorphs of MnO_2 (α, β, γ, δ, λ, and amorphous) and the particle size in controlling the ion insertion thermodynamics and kinetics of H^+ and Zn^{2+} will investigate thoroughly by in-situ synchrotron-based experiments.

Potential RPCs from IITB and Monash

Prof. Nikhil Medhekar (Materials Science and Engineering, Monash), Prof. Douglas R. MacFarlane (School of Chemistry, Monash), Prof. Amartya Mukhopadhyay (Metallurgical Engineering and Materials Science, IIT Bombay) due to their expertise in materials science, electrolyte engineering, and the development of advanced battery technologies.

Capabilities and Degrees Required

The student should ideally have an essential degree in areas related to Materials Science (including chemistry or physics) and/or Materials/Metallurgical Engineering (including Ceramic/Polymer Engineering). Candidates possessing good experimental and analytical skills and critical thinking ability will be preferred. Candidates having a CPI of > 7/10 (or an overall % of 75%) in the qualifying examination/degree are likely to get preference. Similarly, candidates with previous research experience during the Master's program or as research/project associates might get priority.

Necessary Courses

1. EN 658 Electrochemical Energy Storage
2. EN 656 Chemistry for Energy Science
3. MM 684 X-Ray Diffraction and Electron Microscopy

Potential Collaborators

Prof. Douglas R. MacFarlane (School of Chemistry, Monash), Prof. Nikhil Medhekar (Materials Science and Engineering, Monash), Prof. Amartya Mukhopadhyay (Metallurgical Engineering and Materials Science, IIT Bombay), Prof. M. Aslam (Physics, IIT Bombay)

Select up to **(4)** keywords from the Academy's approved keyword list **(available at http://www.iitbmonash.org/becoming-a-research-supervisor/)** relating to this project to make it easier for the students to apply.

Energy, Energy Storage, Energy Materials;
Layered 2D materials (like graphene, MnO_2), Electrochemical-mechanical in-situ studies;
Nanotechnology, nanoscience;
Novel Batteries and Fuel Cells;
Modelling and Simulation