

**Studies on oxides,  
phosphates, molybdates, and  
other sustainable materials  
for batteries and  
supercapacitors with  
electrochemical insights**

By

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*Thesis*

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## DECLARATION

### **A statement of the contribution made by the higher-doctorate candidate (Minakshi) to any work of joint authorship**

In the publications, where the candidate is the lead author, work has been completely formulated and carried out by him. Co-authors have contributed their areas of expertise. Those publications resulting from a Japanese university (listed #93-100) have not been submitted for any University degree/award.

The publications, in which he is the second or last author, indicate the first author is a post-doctoral fellow § (Ramkumar, Biswal, and Barmi) or master internship project fellow ++ (Divakaran, Watcharatharapong, Ash, Baral, Samal, Kandhasamy, Baskar, Verma, Kalidas, Babu, Pandey, and Minato). In this case, I devised the research program (through the ARC DP project and WA State Government funding) with their experimental work.

In the case of selected HDR student publications # (Delgado, Wickramaarachchi, Albohani, and Sharma) the work is initiated by the student, and as a Ph.D. supervisor, he mentored them and assisted in drafting a quality manuscript by providing critical comments.

Overall, the candidate certifies that none of the papers written together with any of his co-authors has been submitted for a qualification in any university, except the material from joint publications from his students stated above (listed # 1-4; 6, 10, 11, 25, and 40) were included in the student's Ph. D. thesis.

To the best of his knowledge, the thesis content does not contain any material previously published or written by another person except where due references are made in the contextual statement.

**Dr. Manickam Minakshi Sundaram**

**Date: 06/09/2023**

## LIST OF PUBLICATIONS

### Scholarly Book Chapter

- I. **M. Minakshi**, P. A. Schneider, and R. Ahuja “Suitable Electrode Materials for Hybrid Capacitors” Ch. 10, pp. 10-1, 2021. In *Next-Generation Materials for Batteries*. (Ed.) Rajeev Ahuja, AIP Publishing LLC AIP Publishing Melville, NY, USA. [https://doi.org/10.1063/9780735421684\\_010](https://doi.org/10.1063/9780735421684_010)
- II. **M. Minakshi**, P. A. Schneider, and M. Fichtner “Biowaste eggshells as efficient electrodes for energy storage” Ch 24, pp. 475 – 495, 2021. In *Valorization of Agri-Food Wastes and By-Products, Recent Trends, Innovations, and Sustainability Challenges*. (Ed.) Rajeev Bhat, Elsevier, Academic Press. <https://doi.org/10.1016/B978-0-12-824044-1.00047-7>.

### Refereed journal publications list

The ISI Impact Factor of journals for 2021 is given in brackets.

1. #K. Wickramaarachchi, and **M. Minakshi** “Consequences of electrodeposition parameters on the microstructure and electrochemical behavior of electrolytic manganese dioxide (EMD) for supercapacitor” *Ceramics International* **48** (2022) 19913. (4.5) <https://doi.org/10.1016/j.ceramint.2022.03.266>.
2. #P. Sharma, **M. Minakshi**, T. Watcharatharapong, S. Jungthawan, and R. Ahuja “Tuning the Nanoparticle Interfacial Properties and Stability of the Core-Shell Structure in Zn-doped NiMoO<sub>4</sub>@AWO<sub>4</sub>” *ACS Applied Materials Interfaces*, **13** (2021) 56116. (8.7) <https://doi.org/10.1021/acsami.1c16287>.
3. #WAMKP Wickramaarachchi, **M. Minakshi**, X. Gao, R. Dabare, KW. Wong “Hierarchical porous carbon from mango seed husk for electrochemical energy storage” *Chemical Engineering Journal Advances* **8** (2021) 100158. <https://doi.org/10.1016/j.cej.2021.100158>.
4. #K. Wickramaarachchi, **M. Minakshi**, D. J. Henry, and X. Gao “Alginate biopolymer effect on the electrodeposition of MnO<sub>2</sub> on electrodes for supercapacitors” *ACS Applied Energy Materials* **4** (7) (2021) 7040 (6.2) <https://doi.org/10.1021/acsaem.1c01111>.
5. ++A. M. Divakaran, **M. Minakshi**, P. A. Bahri, S. Paul, P. Kumari, A.M. Divakaran, and K. N. Manjunatha “Rational design on materials for developing next-generation lithium-ion batteries” *Progress in Solid State Materials* **62** (2021) 100298. <https://doi.org/10.1016/j.progsolidstchem.2020.100298>.
6. #P. Sharma, **M. Minakshi**, J. Whale, A. Jean-Fulcrand, G. Garnweitner “Effect of the anionic counterpart: Molybdate vs. tungstate in energy storage for pseudocapacitors applications” *Nanomaterials* **11** (2021) 580 (5.2) <https://doi.org/10.3390/nano11030580>.
7. **M. Minakshi**, and D. Appadoo “Traditional salt-in-water electrolyte vs. water-in-salt electrolyte with binary metal oxide for symmetric supercapacitors: Capacitive vs. faradaic” *Dalton Transactions* **49** (2020) 11743 (4.2). 10.1039/D0DT01871F.
8. ++B. Ash, V. S. Nalajala, A. K. Popuri, T. Subbaiah, and **M. Minakshi** “Perspectives on nickel hydroxide electrodes suitable for rechargeable batteries: Electrolytic vs. Chemical synthesis routes” *Nanomaterials* **10** (2020) 1879 (5.2)

- <https://doi.org/10.3390/nano10091878>.
9. §A. Biswal, P. K. Panda, A. N. Acharya, B. C. Tripathy, F. Alenazey, Z.-T. Jiang, and **M. Minakshi** “Tuning the morphology and redox behavior by varying the concentration of Fe in CoNiFe ternary oxide heterostructure for hybrid devices” *New Journal of Chemistry* **44** (2020) 9921. (3.0) 10.1039/D0NJ01486A.
  10. #P. Sharma, **M. Minakshi**, D. Singh, and R. Ahuja “Highly Energetic and Stable Gadolinium/Bismuth Molybdate with a Fast Reactive Species, Redox Mechanism of Aqueous Electrolyte” *ACS Applied Energy Materials* **3** (12) (2020) 12385 (6.2) <https://doi.org/10.1021/acsaem.0c02380>.
  11. #P. Sharma, **M. Minakshi**, T. Watcharatharapong, D. Laird, H. Euchner, and R. Ahuja “Zn Metal Atom Doping on the Surface Plane of One-Dimensional NiMoO<sub>4</sub> Nanorods with Improved Redox Chemistry” *ACS Applied Materials Interfaces*, **12** (2020) 44815. (8.7) <https://doi.org/10.1021/acsaem.0c13755>.
  12. ++A. M. Divakaran, D. Hamilton, K. N. Manjunatha, and **M. Minakshi** “Design, Development and Thermal Analysis of Reusable Li-ion Battery Module for Future Mobile and Stationary Applications” *Energies* **13**(6) (2020) 1477 (3.0). <https://doi.org/10.3390/en13061477>.
  13. §A. Biswal, P. Panda, Achutya Acharya, S. Mohapatra, N. Swain, B. Tripathy, Z. T. Jiang and **M. Minakshi** “Role of Additives in Electrochemical Deposition of Ternary Metal Oxide Microspheres for Supercapacitor Applications” *ACS Omega* **5** (2020) 3405. (3.2) <https://doi.org/10.1021/acsomega.9b03657>.
  14. **M. Minakshi**, David Mitchell, R T Jones, N C Pramanik, A. Jean-Fulcrand, and G. Garnweitner “A hybrid electrochemical energy storage device using sustainable electrode materials” *ChemistrySelect* **5** (2020) 1597. (2.3) <https://doi.org/10.1002/slct.201904553>.
  15. §A. Biswal, P. Panda, Z. T. Jiang, B. Tripathy, and **M. Minakshi** “Facile synthesis of a nanoporous sea sponge architecture in binary metal oxide” *Nanoscale Advances* **1** (2019) 1880. (4.95) 10.1039/C8NA00402A.
  16. **M. Minakshi**, S. Higley, C. Baur, D. R. G. Mitchell, R. T. Jones, and M. Fichtner “Calcined chicken eggshell electrode for battery and supercapacitor applications” *RSC Advances* **9** (2019) 26981. (3.0) 10.1039/C9RA04289J.
  17. **M. Minakshi**, D. R. G. Mitchell, C. Baur, J. Chable, A J. Barlow, and M. Fichtner, A. Banerjee, S. Chakraborty, and R. Ahuja “Phase evolution in calcium molybdate nanoparticles as a function of synthesis temperature and its electrochemical effect on energy storage” *Nanoscale Advances* **1** (2019) 565. (4.95) 10.1039/C8NA00156A.
  18. **M. Minakshi**, D. Mitchell, A.R. Munnangi, A. J. Barlow, and M. Fichtner “New insights into the electrochemistry of magnesium molybdate hierarchical architectures for high-performance sodium devices” *Nanoscale*, **10** (2018) 13277 (7.4) 10.1039/C8NR03824D
  19. **M. Minakshi**, H. Visbal, D. R. G. Mitchell, and M. Fichtner “Biowaste chicken eggshells to store energy” *Dalton Transactions* **47** (2018) 16828 (4.2) 10.1039/C8DT03252A.
  20. **M. Minakshi**, M. Barmi, D. Mitchell, A. J. Barlow, and M. Fichtner “Effect of oxidizer in the synthesis of NiO anchored nanostructure nickel molybdate for sodium-ion battery” *Materials Today Energy*, **10** (2018) 1-14 (7.3). <https://doi.org/10.1016/j.mtener.2018.08.004>.
  21. **M. Minakshi**, M. Barmi, and R. T. Jones “Rescaling metal molybdate nanostructures with biopolymer for energy storage having high capacitance with robust cycling

- stability” *Dalton Transactions* **46** (2017) 3588. (4.2) 10.1039/C7DT00139H.
22. **M. Minakshi**, T. Watcharatharapong, S. Chakraborty, and R. Ahuja “A combined theoretical and experimental approach of a new ternary metal oxide in molybdate composite for hybrid energy storage capacitors” *APL Materials* **6** (2018) 047701. (4.2) <https://doi.org/10.1063/1.4994750>.
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  24. **M. Minakshi** and D. R. G. Mitchell “Dispersion of Ni<sup>2+</sup> ions via acetate precursor in the preparation of NaNiPO<sub>4</sub> nanoparticles: effect of acetate vs. nitrate on the capacitive energy storage properties” *Dalton Transactions* **46** (2017) 13704. (4.2) 10.1039/C7DT02444D.
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  26. **M. Minakshi**, D. Mitchell, R. Jones, F. Alenazey, T. Watcharatharapong, S. Chakraborty and R. Ahuja “Synthesis, structural and electrochemical properties of sodium nickel phosphate for energy storage devices” *Nanoscale* **8** (2016) 11291. (7.7) 10.1039/C6NR01179A.
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  29. §M. Barmi and **M. Minakshi** “Tuning the redox properties of nanostructured CoMoO<sub>4</sub> electrode: Effects of surfactant contents and synthesis temperature” *ChemPlusChem* **81** (2016) 964 (3.0) <https://doi.org/10.1002/cplu.201600294>.
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  31. **M. Minakshi**, A. Biswal, D. Mitchell, R. Jones and C. Fernandez “Correlation among physical and electrochemical behaviour of nanostructured electrolytic manganese dioxide from leach liquor and synthetic for aqueous asymmetric capacitor” *Physical Chemistry Chemical Physics* **18** (2016) 4711. (4.20) 10.1039/C5CP07141K.
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  33. ++A. Baral, D. P. Das, **M. Minakshi**, M. K. Ghosh, and D. K. Padhi “Probing environmental remediation of RhB organic dye using α-MnO<sub>2</sub> under visible – light irradiation: structural, photocatalytic and mineralization studies” *ChemistrySelect* (2016) **1** (2016) 4277. (2.3) <https://doi.org/10.1002/slct.201600867>.
  34. §A. Biswal, B. C. Tripathy, and **M. Minakshi** “Probing the electrochemical properties of biopolymer modified EMD nanoflakes through electrodeposition for high-performance alkaline battery” *Dalton Transactions* **45** (2016) 5557. (4.2) 10.1039/C6DT00287K

35. **M. Minakshi**, T. Watcharatharapong, S. Chakraborty, R. Ahuja, S. Duraisamy, P. R. Rao, and N. Munichandraiah “Synthesis, and crystal and electronic structure of sodium metal phosphate for use as a hybrid capacitor in non-aqueous electrolyte” *Dalton Transactions* **44** (2015) 201018. (4.2) 10.1039/C5DT03394B.
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37. §A. Biswal, B. C. Tripathy, **L. Li** and **M. Minakshi** “Electrodeposition of Pluronic F127 assisted rod-like EMD/carbon arrays for efficient energy storage” *Dalton Transactions* **44** (2015) 16446. (4.2). 10.1039/C5DT01975C.
38. §A. Biswal, B. C. Tripathy, K. Sanjay, T. Subbaiah and **M. Minakshi** “Electrolytic manganese dioxide (EMD): a perspective on worldwide production, reserves and its role in electrochemistry” *RSC Advances* **5** (2015) 58255. (3.8) 10.1039/C5RA05892A.
39. ++A. B. Baral, B. Dash, M. K. Gosh, T. Subbaiah, and **M. Minakshi** “Pathway of Sucrose Oxidation in Manganese (Pyrolusite) Nodule” *Industrial Engineering Chemistry Research* **54** (2015) 12233. (2.8) <https://doi.org/10.1021/acs.iecr.5b02881>.
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41. ++T. R. Penki, S. Shivakumara, **M. Minakshi**, and N. Munichandraiah “Porous flower-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructure: A high-performance anode material for lithium-ion batteries” *Electrochimica. Acta* **167** (2015) 330. (4.80) <https://doi.org/10.1016/j.electacta.2015.03.146>.
42. §B. Senthilkumar, R. K. Selvan, D. Meyrick and **M. Minakshi** “Synthesis and characterization of manganese molybdate for symmetric capacitor applications” *International Journal of Electrochemical Science* **10** (2015) 185. (2.0) [https://doi.org/10.1016/S1452-3981\(23\)04985-4](https://doi.org/10.1016/S1452-3981(23)04985-4).
43. §A. Biswal, B. C. Tripathy, T. Subbaiah, D. Meyrick and **M. Minakshi** “Dual effect of anionic surfactants in the electrodeposited MnO<sub>2</sub> trafficking redox ions for energy storage” *Journal of Electrochemical Society* **162** (2015) A30 (3.2) DOI 10.1149/2.0191501jes.
44. ++M. L. Verma, **M. Minakshi**, and N. K. Singh “Structural and electrochemical properties of nanocomposite polymer electrolytes for electrochemical devices” *Industrial Engineering Chemistry Research* **53** (2014) 14993 (2.8) <https://doi.org/10.1021/ie502615w>.
45. **M. Minakshi**, S. Duraisamy, P. Tirupathi Rao, S. Kandhasamy and N. Munichandraiah “Multi-component olivine for lithium-ion hybrid capacitor” *International Journal of Electrochemical Science* **9** (2014) 5974. (2.0) [https://doi.org/10.1016/S1452-3981\(23\)10863-7](https://doi.org/10.1016/S1452-3981(23)10863-7).
46. §A. Biswal, B. Tripathy, T. Subbaiah, D. Meyrick, M. Ionescu, and **M. Minakshi** “Effect of Non-ionic surfactants and its role in K intercalation in Electrolytic Manganese dioxide” *Metallurgical. Materials Transactions E* **1E** (2014) 227. <https://doi.org/10.1007/s40553-014-0022-9>
47. §S. Baskar, D. Meyrick, R. Kalaiselvan and **M. Minakshi** “Facile and large-scale combustion synthesis of  $\alpha$ -CoMoO<sub>4</sub>: Mimics the redox behavior of a battery in aqueous hybrid device” *Chemical Engineering Journal* **253** (2014) 502. (4.4) <https://doi.org/10.1016/j.cej.2014.05.068>.

48. ++M. L. Verma, **M. Minakshi** and N. K. Singh “Synthesis and Characterization of Solid Polymer Electrolyte based on Activated Carbon for Solid State Capacitor” *Electrochimica Acta* **137** (2014) 497. (4.50) <https://doi.org/10.1016/j.electacta.2014.06.039>.
49. **M. Minakshi**, D. E. Ralph, P. Singh, and C.-Y. Yin “New Insights into the electrochemical behavior of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) microparticles in strong aqueous basic electrolyte: formation of metallic iron” *Metallurgical and Materials Transactions A*. **45A** (2014) 2023. (2.3) <https://doi.org/10.1007/s11661-013-2128-6>.
50. **M. Minakshi**, D. Meyrick and D. Appadoo “Maricite (Na Mn<sub>1/3</sub>Ni<sub>1/3</sub>Co<sub>1/3</sub>PO<sub>4</sub>) / Activated Carbon: Hybrid Capacitor” *Energy & Fuels* **27** 3516. (2.73) <https://doi.org/10.1021/ef400333s>.
51. **M. Minakshi** and D. Meyrick “Electrochemical energy device for securing future renewable energy” *Electrochimica Acta* **101** (2013) 66. (4.80) <https://doi.org/10.1016/j.electacta.2013.02.075>.
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53. §B. Senthilkumar, K. Vijaya Sankar, R. Kalaiselvan, D. Meyrick and **M. Minakshi** “Nano  $\alpha$ -NiMoO<sub>4</sub> as a new electrode for electrochemical supercapacitors” *RSC Advances* **3** (2013) 352. (3.70) 10.1039/C2RA22743F.
54. ++G. Babu, K. Nallathamby, D. Meyrick and **M. Minakshi** “Carbonate anion controlled growth of LiCoPO<sub>4</sub>/C nanorods and its improved electrochemical behavior” *Electrochimica Acta* **101** (2013) 18 (4.80) <https://doi.org/10.1016/j.electacta.2012.09.115>.
55. **M. Minakshi** and D. Meyrick “Reversible sodiation in maricite Na Mn<sub>1/3</sub>Co<sub>1/3</sub>Ni<sub>1/3</sub>PO<sub>4</sub> for renewable energy storage” *J. Alloys & Compounds* **555** (2013) 10. (2.9) <https://doi.org/10.1016/j.jallcom.2012.11.203>.
56. **M. Minakshi** and D. Ralph “A novel sodium-ion rechargeable battery” *ECS Transactions* **45** (2013) 95. DOI 10.1149/04529.0095ecst.
57. **M. Minakshi** “Looking beyond lithium-ion technology: Aqueous NaOH battery” *Materials Science Engineering B* **177** (2012) 1788. (2.22) <https://doi.org/10.1016/j.mseb.2012.09.003>.
58. **M. Minakshi**, S. Kandhasamy and D. Meyrick “Synthetic strategies for better battery performance through advances in materials and chemistry: Olivine LiCo<sub>1/3</sub>Mn<sub>1/3</sub>Ni<sub>1/3</sub>PO<sub>4</sub>” *J. Alloys & Compounds* **544** (2012) 62. (2.9) <https://doi.org/10.1016/j.jallcom.2012.07.136>.
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61. **M. Minakshi** and S. Kandhasamy “Utilizing active multiple dopants (Co and Ni) in olivine LiMnPO<sub>4</sub>” *Current Opinion in Solid State and Material Science* **16** (2012) 163. (6.6) <https://doi.org/10.1016/j.cossms.2012.03.004>.
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64. **M. Minakshi** and P. Singh “Success and serendipity on achieving high energy density for rechargeable batteries” *Journal of Solid State Electrochemistry* **16** (2012) 2227. (2.44) <https://doi.org/10.1007/s10008-012-1655-1>.
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72. **M. Minakshi**, P. Singh, N. Sharma, M. Blackford, and M. Ionescu “Lithium extraction-insertion from/into  $\text{LiCoPO}_4$  in aqueous batteries” *Industrial Engineering Chemistry Research* **50** (2011) 1899 (1.89) <https://doi.org/10.1021/ie102267x>
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## CONTEXTUAL STATEMENT

### A Journey into the World of Electrochemical Energy Storage

The work for the higher doctorate (D. Sc.) thesis presents 102 laboratory-based research papers performed in electrochemical energy storage. Energy storage will be a critically important part of the transition to a low-emissions future. Out of 140 publications in the candidate's (Dr. Minakshi) career, 102 journal articles with details of authorship tabulated in Table 1 are included in his higher doctorate. The first author is the person who contributed most to the work, from conceptualization to realization and the writing of the manuscript. This higher doctorate, comprising several research publications, constitutes contributions published between 2000 and 2003 (pre-PhD); then 2007 and 2022 (post-PhD). The thesis focuses on physicochemical processes providing useful insights into oxide electrodes containing tetrahedral polyanions, cation substitutions in the octahedral site, the role of ex-situ additives, in-situ polymerization and its electrochemical activity, and subsequently how it influences the storage capability. The electrode materials comprising both cathode and anode play the most crucial role in the development of new energy storage devices.

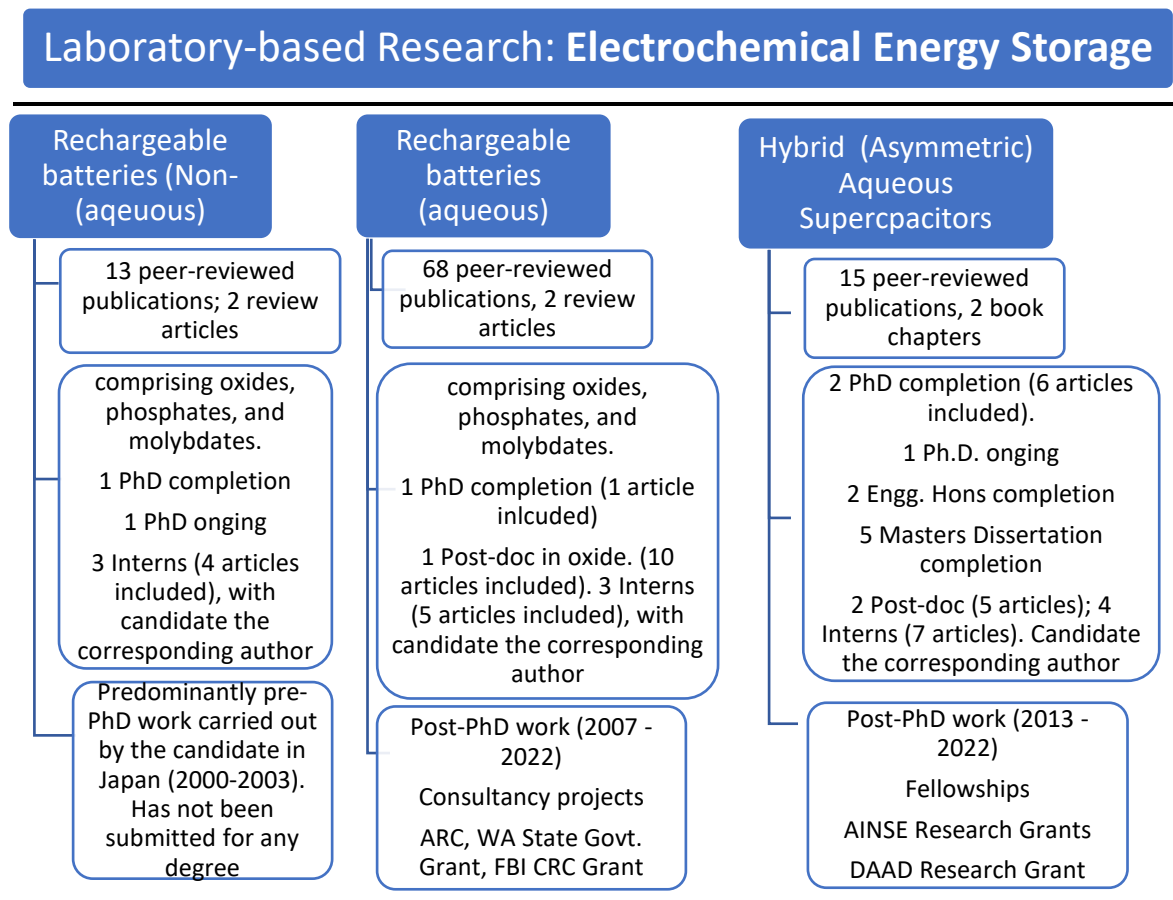
**Table 1** An overview of the candidate's research quality, and productivity in publications included

|                                | <b>Number of peer-reviewed journal articles (book chapters)</b> | <b>Sole author</b> | <b>First author</b> | <b>Corresponding author</b> | <b>Overall h-index Google Scholar/Scopus</b> |
|--------------------------------|---|--------------------|---------------------|-----------------------------|--|
| <b>Post-PhD</b><br>(2007-2022) | 92 (2)  | 6                  | 54                  | 89                          | 44/41  |
| <b>Pre-PhD</b><br>(2000-2003)  | 8 (0)   | 1                  | 8                   | 3                           | 3/3  |
| <b>Total</b>                   | <b>102</b>  | <b>7</b>           | <b>62</b>           | <b>92</b>                   | <b>43</b>                                    |

in the higher doctorate thesis

The thesis includes 96 original peer-reviewed research journal articles, 4 review articles, and 2 book chapters. Reflecting the division of the thesis, under the umbrella of electrochemical energy storage devices, into sections on non-aqueous rechargeable batteries; aqueous rechargeable batteries; and electrochemical asymmetric capacitors, they are assembled into **three themes**. The theme of non-aqueous batteries is supported by 15 papers (NA1 – NA15); in the theme of aqueous batteries having phosphates, oxides, and molybdate materials as electrodes are supported by 19 papers on phosphates (AP1 – AP19), 41 papers on oxides (AO1 – AO41), 10 papers on molybdates (AM1 – AM10), respectively. The theme of the hybrid capacitors is supported by 15 papers, and 2 book chapters (HC1 – HC17). Within each group, the candidate Dr. Minakshi has adopted a sequential order for including the papers in the respective sections.

The candidate's laboratory-based research outcomes are in the following three themes below.



The final section body of work itemizes the publication details, from which the source has been extracted for the thesis.

- **Non-aqueous Battery (NA):** listed numbers 5, 8, 12, 28, 41, 52, 54, 93 – 100 (comprising 13 peer-reviewed journal articles; and 2 review articles #5 #8)
- **Aqueous battery Phosphate-based (AP):** listed numbers: #21, #24, #26, #35, #55, #56, #58, #59, #60, #61, #62, #63, #65, #67, #70 - #74 (comprising 18 peer-reviewed journal articles; and 1 review article #62)
- **Aqueous Battery Oxide-based (AO):** listed numbers #1, #4, #13, #15, #31, #32, #33, #34, #37, #38, #39, #40, #43, #44, #46, #48, 49, #51, #57, #64, #66, #68, #69, #75 - #92 (comprising 40 peer-reviewed journal articles; and 1 review article #38)
- **Aqueous Battery Molybdate-based (AM):** listed numbers #2, #7, #17, #18, #20, #22, #27, #42, #47, #53 (comprising 10 peer-reviewed journal articles)
- **Hybrid Capacitors (HC):** listed numbers # I, # II, #3, #6, #9, #10, #11, #14, #16, #19, #23, #25, #29, #30, #36, #45, #50 (comprising 15 peer-reviewed journal articles: and 2 book chapters #I, and #II)

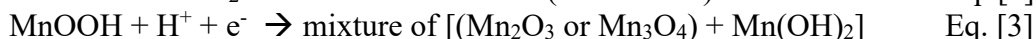
The thesis consists of five sections with an aim and objectives, an introduction to the body of work, and various electrode materials and electrolytes for energy storage applications. The candidate has contributed to the knowledge that resulted in 102 publications, detailed in sections 3-5, with a clear

focus on the core topic of the development of an affordable and safe energy storage system. The three themes are (1) Unfolding modified NASICON (sodium super ion conductors) type materials for lithium-ion batteries exhibiting three-dimensional diffusivity of Li<sup>+</sup> (or) Na<sup>+</sup> ions with high structural and thermal stability. Examining the role of conductive carbon black and their interaction with ion transport, are explored predominantly along with identifying suitable binder materials during pre-Ph.D. studies in Japan; (2) Development of new materials for safe rechargeable aqueous batteries, and mixing by additives for a long lifetime with high energy density; and (3) Establishment of hybrid devices with selected sustainable electrode materials coupled with oxides, phosphates, and molybdates during post-PhD studies at the Australian Institution.

## 1. Aim and Objectives of this Thesis

The higher doctorate thesis aims to coin a new mechanism associated with electrode materials and electrolytes that provides an alternative to the expensive and impractical power storage technologies used in the past and present. There is a critical need for a fundamental understanding of the reaction mechanisms associated with the storage processes in aqueous batteries and supercapacitors to enhance storage capacity. The candidate invented high-performance sustainable electrode materials, for instance, crushed chicken eggshells, and their inner shell membranes for batteries and supercapacitors applications. Likewise, carbonizing and activating a range of common livestock biowaste has been examined and reported in the thesis.

In this higher doctorate thesis, the candidate provides a narrative of experimental approaches that pave the way for an alternative energy future by removing global reliance on fossil fuels, replacing them with sustainable aqueous-based energy storage technology, reducing our environmental impact, and ensuring short and long-term energy supply. It has been reported in the domain through work on the solvent extraction of metals that saturated lithium/sodium hydroxide/chloride has high lithium/sodium and low free-water activity. Hence, lithium/sodium-containing (water-in-salt) electrolytes might be a potential candidate for an aqueous rechargeable battery. In principle, such a battery could have high power density and energy density since it contains a very conductive solution. The conductivity of an aqueous electrolyte is typically two orders of magnitude greater than the non-aqueous counterparts used in lithium-ion batteries. The candidate's Ph.D. thesis (in 2006) revolves around opening a new field of rechargeable alkaline batteries that utilize oxides and phosphates as the cathode material. The key objective of the higher doctorate thesis is to enhance the performance of energy storage technology by mapping modified olivine and binary transition metal oxide materials. These modifications have been achieved by incorporating suitable additives such as biodegradable redox polymer, titanium boride/sulfide (TiB<sub>2</sub>, TiS<sub>2</sub>), or bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) compound. The additives are included in a suitable proportion into the cathode of a similar ionic radius to the host manganese (Mn) as these may exert a structural stabilizing effect. The extensive studies made in post-PhD studies (funded by ARC Discovery Project; and WA State Government) indicated that the cell discharge mechanism in aqueous electrolytes involves both lithium (as shown in Eq. 1) and proton (H<sup>+</sup>) intercalation (as shown in Eqs. 2-3) into the cathode materials (typically electrolytic MnO<sub>2</sub>).



The MnOOH in the electrode undergoes a dissolution reaction that releases Mn<sup>3+</sup> ions into the electrolyte. The Mn<sup>3+</sup> species are further reduced to a soluble Mn<sup>2+</sup> that subsequently precipitates to form the end products shown in Eq. 3. Interestingly, the candidate found that the incorporation of additives in a suitable proportion into the manganese dioxide (MnO<sub>2</sub>) cathode retard this disproportionation reaction of Mn<sup>3+</sup> by keeping the Mn<sup>3+</sup> ions in the solution for a longer time i.e. during the discharge process and thereby prevent the formation of unwanted Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>, shown in Eq. 3. This leads to improved electrochemical performance in aqueous-based lithium battery in several key publications, which predominant work was carried out by the candidate and named as first-author and corresponding author. The Jahn-Teller effect may cause Mn<sup>2+</sup> dissolution leading to limited cycle life. One strategy is adding additives to the aqueous electrolyte to suppress Mn<sup>2+</sup> dissolution from the MnO<sub>2</sub> electrodes. The appropriate concentration of additive is needed to provide an equilibrium between the Mn<sup>2+</sup> dissolution and the re-oxidation. It has also been shown that using several additives and their synergistic effects helps mitigate this dissolution issue.

The candidate's other objective in the higher doctorate thesis is to demonstrate the synthesis protocol and the electrochemistry performance of oxide, phosphate, molybdate, and other sustainable materials. These materials could be used as cathodes/anodes in aqueous energy storage technologies including rechargeable batteries and supercapacitors. In olivine-type lithium nickel phosphate with the structural formula (LiNiPO<sub>4</sub>), it has been explored for the first time by the candidate that lithium ions can be electrochemically de-intercalated during the oxidation process leading to an amorphous NiPO<sub>4</sub> and a minor product of nickel (II) hydroxide (β-NiOOH). Before this study, the olivine family have not been considered for an aqueous system and was limited to non-aqueous batteries. While the sodium analog of triphylite (NaNiPO<sub>4</sub>) showed a high-performance energy density of 44 Wh kg<sup>-1</sup> in our studies which is attributed to the hierarchical structure of the porous NaNiPO<sub>4</sub> nanosheets, implying the structure is favorable to Na storage. The ternary molybdate using MMoO<sub>4</sub> (where M = Mn<sub>0.33</sub>Ni<sub>0.33</sub>Co<sub>0.33</sub>MoO<sub>4</sub>) cross-linked with biopolymer exhibited a narrow pore size distribution with a large surface area, which led to improved cycling stability of the device. The class of materials included here has the potential to undergo reversible intercalation of Li/Na in the host structure in the presence of lithium/sodium electrolytes. Therefore, synthesis strategies will be a prerequisite to a key understanding of the mechanism underpinning material development. The potential advantages of this type of intercalation mechanism in aqueous solutions are reversibility and the use of benign aqueous electrolytes with increased longevity. An [innovative saltwater-based battery](#) with the potential to change the world of sustainable energy was created at Murdoch University in 2012. This is one of the key contributions of post-Ph.D. work involving the candidate's specialist knowledge in physical, chemical, and materials sciences. In 2016, this work was recognized through the Murdoch University Vice Chancellor's Excellence in Research Award for Outstanding Research Development and published in the [media](#).

On the other hand, great efforts have been made both by the candidate and his group to find appropriate active materials for anodes in aqueous electrolytes. While studies by the candidate on various anodes e. g. Zn, Mg, and Sn have shown larger hydrated ionic radii, their multivalent nature provided an opportunity for enhanced specific discharge capacity closer to the conventional carbon anode (370 mA h g<sup>-1</sup>). One of his Ph. D, students demonstrated that the biomass-derived (typically mango-seed husk) activated carbon from H<sub>2</sub>SO<sub>4</sub> as an activating agent showed excellent electrochemical properties due to well-defined porous and surface functional features. Along with a post-doc, our work on biopolymers and eggshells, which has been cited more than 150 times,

stimulated intensive research in the utilization of both biopolymers and chicken eggshells as anodes in materials engineering and energy storage. We found that the N-doped carbon electrode derived from proteins (in chicken eggshells) possesses overall better performance than those electrodes obtained from N-containing polymers, such as polypyrrole and polyaniline. This is attributed due to the presence of active pyridine nitrogen after carbonizing the eggshells, and it is of the more valuable functional group. The work carried out by the candidate in a water-in-salt electrolyte system brought insights that with a lower concentration of free water molecules near the surface of the electrode material, the reaction kinetics of hydrogen evolution reaction on the anode material decreased.

## 2. Introduction

Energy has been identified as one of the most critical issues in this century. Global warming and climate change represent major challenges facing humanity in the 21<sup>st</sup> century that forced us to re-evaluate our society's dwindling supply of fossil fuels and biomass for energy. Fossil fuel energy resources such as oil, gas, and coal which are responsible for nearly 60% of global greenhouse emissions are currently used for electricity generation and transportation. Whereas electrical energy generated from renewable sources such as solar and wind to reduce fossil fuel consumption is more important today than ever before. The significance of the problem lies in the intermittent nature of the renewables. This intermittently generated power must be stored for use on demand. The lack of suitable energy storage technologies has plagued utility companies for a long time. Many energy storage systems have been proposed and developed, including pumped storage hydroelectricity, compressed air energy storage, and fly-wheel storage system. All the developed energy storage systems either require substantial construction of infrastructure or tend to be too expensive and environmentally unsafe.

Electrochemical energy storage in rechargeable batteries, supercapacitors, and fuel cells is the most promising solution to ensure a consistent energy supply. This electrochemical energy conversion from chemical energy to electrical energy by means of electrochemical reduction–oxidation (termed “redox”) reactions, is a promising route for storing energy in a clean and green process. The key to success will be a practically viable combination of renewable energy generation and reliable storage for load-leveling to withstand the gaps between production and consumption peaks. Integration of additional renewable capacity into power grids brings with it the risk of grid destabilization during such transients unless supply-leveling capacity is available. Battery storage is ideal for coping with such short-term power shortages due to its near-instantaneous response. Electrochemical energy storage devices such as rechargeable batteries and supercapacitors possess several desirable features, including, in many cases, environmentally benign operation, low maintenance, excellent efficiency, and cycling stability. Batteries such as lead-acid (Pb-acid) and nickel-metal hydride (Ni-MH) batteries have previously been of limited use in electric power systems due to their relatively small capacity and poor stability. Pb-acid batteries can last for up to a decade in standby mode but rapidly lose capacity when discharged deeply. These batteries employ highly toxic Pb and PbO<sub>2</sub> electrodes, and highly corrosive sulphuric acid as the electrolyte while providing meager energy density. This makes them unsuitable for large-scale renewable energy storage. Nickel–metal hydride (Ni-MH) has poor low-temperature capability and limited high-rate capability, but its higher energy density served to spur the development of the portable electronic device market. For more than two decades now, newer lithium battery technologies have been developed that can now provide significant utility-scale load-leveling capabilities. Li-ion batteries are finding application in this area, such as the 129 MWh Tesla facility recently commissioned at the Hornsdale wind farm in South Australia. The key issues

though are the very high cost, potential safety in the event of catastrophic battery failure, and insufficient long-term data about how such systems will behave under operating conditions – particularly when exposed to frequent deep discharges in widely varying ambient temperatures. Two important quantities for electrical energy storage devices are specific energy and specific power, and typical values are shown in the so-called “Ragone plot”. To meet these criteria, the development of lithium batteries required extensive development of cathode and anode materials. The chemical reactivity constraints also necessitated the development of suitable non-aqueous electrolytes. Therefore, optimized electrode materials and electrolytes described in Sections 3 – 5 are the keys to achieving the best electrochemical performance and low cost for a battery and supercapacitor system.

### **3. Electrode Materials and Electrolytes for Non-aqueous Energy Storage**

***Comprising 13 peer-reviewed journal papers and 2 review articles. Listed publications #5, #8, #12, #28, #41, #52, #54, #93 - #100; period 2000 – 2003; and 2012, 2021.***

This section demonstrates how the synergy between electrode materials and electrolytes for energy storage contributed to this field of research. Rechargeable batteries and supercapacitors, employ aqueous and non-aqueous electrolytes in either liquid or solid states. The safer approach to rechargeable lithium batteries is to replace lithium metal with either a graphite anode or lithium intercalation compound to give the term “Lithium-ion battery (LIB)”. Based on one of his previous studies (publications listed in #97) rechargeable lithium cells can be assembled with two different lithium intercalation host electrodes e. g. spinel structured oxides  $\text{LiMn}_2\text{O}_4$  cathode and  $\text{LiTi}_2\text{O}_4$  anode which are safer than the battery technology using pure Li metal termed “Lithium-battery”. The LIB battery also termed a “rocking-chair battery” uses an anode and a cathode, both of which can reversibly intercalate  $\text{Li}^+$  ions during charge/discharge cycles. Intercalation is the insertion of a guest Li atom into host spinel oxides, accompanied by only slight structural irreversible changes. Since Sony's commercialization of lithium-ion rechargeable batteries in 1990, lithium-ion batteries (LIBs) have been the standard electrical energy storage devices for small portable electronic devices. They are now even used for medium- to large-scale electrical energy storage for electric vehicles. This is mainly due to their combination of high power-to-weight ratios and sufficiently fast charging times. The typical design of a Li-ion battery comprises a crystalline lithium transition metal oxide (namely lithium cobalt oxide  $\text{LiCoO}_2$ ) cathode and graphite anode or lithium inserted compound e. g.  $\text{LiTiO}_2$ , separated by a liquid electrolyte made of an organic solvent. The traditional design has not changed significantly since its commercialization. Hence, LIBs are undoubtedly the most advanced rechargeable batteries in the market today.

During the candidate's pre-PhD in 2000, while working as a staff at a Japanese University (Nagaoka University of Technology), he published a body of work in peer-reviewed journal articles, comprising 8 papers between 2002-2003 (publications listed in #93 - #100), on rechargeable lithium-ion batteries. In all these 8 publications, the candidate was the first author and contributed (70% – 80%) to the conceptualization, research design, methodology, investigation, validation, and writing the original draft. The co-authorship (M. Takata) was his supervisor and contributed to funding acquisition, project administration, and the final proofreading of the article. In two papers, the co-author K. Minato (publications listed in #93, and #94) contributed to material synthesis and electrochemical data curation. The student KM did Honor's project back in 2001 under their supervision with a contribution to the individual publication of 20%.



The LIB is based on intercalation chemistry in non-aqueous electrolytes comprising 1M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in ethylene propylene carbonate (EC); and propylene carbonate (PC): dimethyl carbonate (1:1:3 vol.%). As thermodynamics was well established at that time, his publications have resulted in electrochemical requirements for the battery components. In 2000, the roles of acetylene black and binders as cathode mixtures were considered inert materials only serving the purpose of improving electronic conductivity and maintaining the strong connection between the electrode particles. However, his studies in those days have proved that this is not the case. The various amounts of carbon black in the cathode mixture determined the porosity and conductivity of the active material allowing the lithium ions to deeply penetrate the electrode. However, increasing the carbon black above the threshold resulted in a poor storage capacity (publication listed in #99). The high electronic conductivity achieved by the carbon black component in the cathode mixture with an optimized value while having a mixture of organic solvents with low electronic conductivity avoiding current leakage between electrodes resulted both in longevity and storage capacity of the Li-ion battery comprising phosphate electrodes. On the other hand, the careful selection of the cathode binder resulted in a remarkable improvement in battery performance. This article (publication listed in #96, cited 60 times) showed the commonly used fluorine-based binders are not inert materials but have a strong influence on electrochemical reactions. This contribution with a good number of citations indicates an advance to the existing knowledge by then. One aspect that has shown surprisingly great attention is the impact of the chosen cathode binder and its contact between the many phases such as active material, carbon conductive additive, choice of binder, and electrolyte that constitute a typical lithium battery cathode. The quality of interphase contacts possibly varies with the chosen binder chemistry during the charge and discharge process and affects the battery performance, which is of significance to the success of the lithium-ion batteries study. This study concluded that the capacity fade of electrodes is very sensitive to the choice of binder, carbon black, and composite materials. An excellent binder (e. g. PTFE) maintains the adhesion of the phosphate cathode to the current collector with good ionic contact and enhances the formation of a stable interface with the electrolyte.

One of the candidate's other publications also demonstrated that the energy of electron transfer depends on the Fermi levels of the Li anode and Phosphate cathode, which can be shifted by metal atom doping with appropriate synthesis conditions. With the aid of trivalent metal cations as dopants (such as niobium, chromium, manganese, and iron) the versatility of the host insertion NASICON compound otherwise sodium super ion conductor's framework has been shown (in publications listed #98, and #100) to modify allowing the lithium insertion/extraction reversibly. Two decades ago, the candidate's studies suggested that the synthesis of new materials and structures provides high storage capacity and high power rates, which are crucial to the development of energy storage systems. Overall, at that time, only a handful of successful crystal structure types were studied by the candidate, e.g. spinel  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiTi}_2\text{O}_4$ , and NASICON e.g.  $\text{Cr}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$ ,  $\text{TiNb}(\text{PO}_4)_3$ , etc. The transition metal phosphate cathode containing no lithium in its structure was initially (in the year 2000) considered a relatively new concept in the field of battery research and its community (publications listed in #95). The electrochemical insertion and reversible extraction of lithium into these host frameworks with the polyanion ( $\text{XO}_4$ ) ( $\text{X} = \text{P}$  and  $\text{S}$ ) and the presence of dopants (e. g. Nb; Mn; and Fe) have shown to be more tolerant to multiple cycles than the pristine  $\text{Cr}_2(\text{SO}_4)_3$ . The trivalent metal atom substitution in the octahedral sites and their battery behavior in terms of their difference in redox couples in the compounds having the same polyanion  $(\text{PO}_4)^{3-}$  determined the battery voltage and assisted the next generation of high-energy devices. His findings showed the use

of  $\text{LiMn}_2\text{O}_4$  cathodes in practical devices is limited (publication listed in #97) as they suffer from meager capacity retention due to Jahn-Teller distortion-induced metal dissolution. In the case of phosphates,  $\text{LiFePO}_4$ , intrinsic low electronic conductivity slows lithium-ion diffusion across the  $\text{Li/FePO}_4$  interphase while the NASICON structures showed potential interest for energy storage applications. The NASICON structures with metal atoms substituted Nb, and Ti with the appropriate amount of carbon black and cathode binder provide longer cycle life and useable voltage (publications listed in #93, and #94).

During the candidate's post-Ph. D recently, he has also continued to collaborate with and supervise many students in this area and to design an efficient and safe lithium system. He has made 6 publications as one of the authors and corresponding author. The numerical simulation and the cooling system design developed by the student (A. M. Divakaran, publication listed in #12) to dissipate the heat from the battery device for achieving higher performance got wider attention from the energy researchers, citing 50 times. Another work (A. M. Divakaran, publication listed #5) on rational cell and material design to promote the application of the evolving materials in practical lithium-ion batteries also received wider attention of 60 citations until now. Candidate Dr. Minakshi has contributed (25%) to the data validation, reviewing, and editing of the manuscript. In another publication, synthesis routes and their chemistry involved in the reaction mechanisms for producing nickel hydroxide electrodes by tuning the parameters are developed by a student (B. Ash, publication listed in #8) under the supervision of T. Subbaiah (co-author). This article provided insight into producing high-quality battery-grade nickel hydroxide. The collaborators (BA and TS) are metallurgists and the candidate's contribution (25%) to this work is by providing preliminary electrochemical data curation for nickel hydroxide and final proofreading the article. One of his post-docs R. Ramkumar, funded by ARC Discovery Project (Sole CI Candidate Dr. Minakshi) examined the binary transition metal oxide with a cobalt substitution in the tetrahedral site forming  $\text{CoMoO}_4$  for its use in energy storage and resulted in an article (publication listed in #28), cited 60 times. The role of polymers and cationic surfactants in the binary transition metal oxide has been explained in this article. The candidate mentored R. Ramkumar's project and his contributions (40%) to this article are formulating the methodology, reviewing and editing the original draft written by the post-doc, and funding acquisition. After this, during his visit to the Indian Institute of Science (IISc) in 2012 on an early career fellowship awarded by the Australian Academy of Science, he worked together with Professor N. Munichandraiah's group for 4 months. They jointly supervised the Ph. D. student (T. R. Penki, publication listed in #41) a project in anode material for battery applications. On a range of materials synthesized for T.R. Penki's Ph.D. project, the D. Sc. candidate has contributed (15%) to synthesizing the anode  $\text{Fe}_2\text{O}_3$  and reviewed the original draft of the manuscript (10%). The outcome of this article (cited 85 times) explained how the elegant synthesis method resulted in the porous nature of the material attributed to the high-rate capability. This article reported porous flower-like  $\alpha\text{-Fe}_2\text{O}_3$  nanostructures are found to be suitable for the anode in a lithium-ion battery having high reversibility of  $1060 \text{ mA h g}^{-1}$  at a specific current of  $50 \text{ mA g}^{-1}$ . Based on the reaction mechanism, the lithium insertion followed by a conversion reaction that involves the formation and decomposition of  $\text{Li}_2\text{O}$  accompanying the redox of metal nanoparticles looks to be feasible for cycling ability.

In the second phase of the candidate's fellowship, he spent a month time at the Central Electrochemical Research Institute (CECRI) in India and worked together with the principal scientist Dr. N. Kalaiselvi. They jointly supervised the student's project in carrying out the synthesis and battery characterization that resulted in two articles (N. Kalidas, the publication listed in #52; G.

Babu; the publication listed in #54). The role of fuel in combustion synthesis and its effect on the NASICON structure along with carbon coating on phosphate material has been demonstrated. The contribution to this work is around 25% each on interpreting the data and revising the original draft of the manuscript critically.

Overall, this phase of the research work on non-aqueous liquid electrolytes for batteries resulted in 15 publications, of which 8 publications are the candidate's first authorship and the rest are corresponding authors. This work emphasizes moving from "Lithium" to Lithium-ion" battery to safeguard the anode material during cell cycling. As a result, NASICON and other intercalation-type electrodes were proposed in organic carbonates as electrolyte solvents containing lithium salts. Although the choice of electrolytes in rechargeable batteries is of less consequence than the electrode materials, however, they are less tolerant to temperature, electrochemically unstable, and unsafe to use. The emergence of new electrode materials would be suited for the reformulation of non-aqueous electrolytes.

#### **4. Advanced Electrode Materials and Electrolytes for Aqueous Energy Storage *comprising 70 publications***

Although the traditional design of LIBs has not changed much since its commercialization, several design shortcomings have never been well resolved, most importantly, the need for organic electrolytes. These electrolytes, which were involved during pre-Ph.D, studies (discussed in Section 3) have several safety issues including flammability, toxicity, and electrochemical instability. The safety issues associated with limiting the range of temperatures under which they can be used make them less appealing for large-scale energy storage. If the temperature within the cells reaches the trigger temperature the whole system could generate uncontrollable heat which affects both the calendar life and safety aspects of the operating conditions. The usage of flammable organic electrolytes typically used 1M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in ethylene propylene carbonate (EC); and propylene carbonate (PC): dimethyl carbonate (1:1:3 vol.%). The thermal runaway hazard of reactive electrode materials is mainly attributed to the high safety risk of LIBs. Inherently safe lithium-ion batteries are only possible if the flammable liquid electrolyte is replaced by a non-flammable alternative. The search for less hazardous electrolytes is confounded by the many competing requirements necessary for an efficient power storage device. For example, solid-state electrolytes possess the desired stability but show low ionic conductivity and give rise to the growth of dendrites on the solid electrode surfaces during multiple charge-discharge cycles. All current-generation solid-state batteries exhibit very limited storage and durability. The research and development of non-flammable electrolytes were more critical to the increasing use of lithium-ion batteries of larger capacities in early 2000. The water-based electrolytes are non-flammable and environmentally friendly and have low production costs by avoiding stringent manufacturing conditions. In addition, the ionic conductivity of aqueous electrolytes ( $41 \text{ mS cm}^{-1}$ ) is significantly greater than that of the organic electrolytes ( $8 \text{ mS cm}^{-1}$ ), allowing higher discharge rates and lower voltage drops due to electrolyte impedance. The mechanism of lithium-ion transport is diffusion activated by concentration gradients of the electrode/electrolyte interface that determine the storage capacity. The aqueous cell designs can accommodate thick electrodes and the chemical potential in the solution increases with concentration.

#### **4.1. Aqueous Rechargeable Batteries Involving both Metallic and Non-metallic Charge Carriers**

Assessing the opportunity and mapping new materials for rechargeable aqueous battery systems formed the objective of the candidate's Ph. D work between 2003 – 2006, which is not the focus of his higher doctorate. Although the opportunities of aqueous energy storage have already been studied in his Ph. D, it remained rather unclear what the most critical “bottlenecks” in a typical practical composite electrode for this system. In 2007, aqueous energy storage was a relatively new system. Many challenges exist to rival the energy performance of non-aqueous LIBs, and the underlying reason is its narrow voltage window. Hydrogen and oxygen evolution reactions could occur on the two electrodes, limiting the voltage window to 1.5 V. Moreover, in 2012, there was increasing concern that lithium reserves around the world might be not sufficient to satisfy the demand for large-scale commercial applications in both electric vehicles and renewable energy storage. Therefore, a sodium-ion aqueous battery can be the key to solving this issue, because of the huge availability of sodium, its low price (\$ 0.5 vs. \$5 per kg for sodium and lithium carbonates), and the similarity of both Li and Na insertion chemistries. A decade ago, General Electric's molten state batteries were offered at a high temperature, where molten sodium and molten sulfur serve as anode and cathode respectively, and they have never found widespread use. An alternative strategic approach proposed by the candidate in 2012 was a sodium battery for a promising low-temperature energy storage device using sodium insertion on the cathode and zinc dissolution on the anode in an aqueous NaOH electrolyte. It has been shown in his publications that by carefully selecting sodium analog's high-energy electrode oxides and phosphate for cathodes, the energy density of sodium-ion batteries can be comparable to those of the electrodes reported for Li-ion counterparts.

During part of his post-PhD work, he worked toward the enhancement of the capacity in lithium and sodium aqueous systems, by applying five strategies. (1) Synthesized and studied the electrochemistry of phosphate and oxide materials as insertion electrodes and for their use as cathodes, (2) introduced additives to electrode materials since these additives act as “pillar” effect of structural water between the interlayers and weakened electrostatic interaction, further delaying the disproportionation reaction of metal cation in the aqueous electrolyte and showing much-improved storage capacity, (3) expanded the voltage window 1.5 V by using an alkaline electrolyte with different pH level, allowing for efficient charging of the positive electrode (4) used a “water-in-salt” electrolyte”, where an aqueous electrolyte dissolved with concentrated salt, minimizing the water activity suppresses hydrogen evolution reaction by enhancing the voltage window, and (5) adopted various earth-abundant charge carriers aqueous electrolytes e.g. lithium (Li), sodium (Na), potassium (K), and zinc (Zn) with different ionic radius 0.76; 0.95; 1.33, and 0.88 Å and hydrated radius 3.40, 2.76, 2.32, and 4.30 Å, respectively. These findings haven't been widely reported before in aqueous energy storage and from thereon generally been considered essential to enhance storage capacity as evidenced through numerous citations and research grants.

#### **4.2. Understanding Modified Cathode Materials and Electrolytes**

In this section of the thesis, cathode materials with an emphasis on polyanionic systems, such as phosphates, molybdates, and sulfates in the presence and absence of some additives along with the role of cations in electrolytes have been discussed. These materials have the potential to increase the electrochemical capacity and to be used as electrodes in batteries and supercapacitors.

#### **4.2.1. Synthesis of Metal Phosphates with Dopants**

**Comprising 10 peer-reviewed original papers; and 1 review article. Listed publications #58, #59, #61, #62, #63, #65, #70 - #74; period 2010 – 2012.**

The typical cathode material for an energy storage application should be qualified to be chemically stable in the electrolyte without undergoing any reactions and have electronic conductivity high to obtain good storage performance along with high-rate capabilities. The host compound should have good chemical potential against the anode to maximize the device voltage. The performance of the energy storage system depends on the structural and chemical properties of the phosphates used for the electrodes (publication listed in #62, cited 50 times; #71, cited 140 times).

Developing cost-effective electrode materials ranging from oxides, molybdates, phosphates, and sustainable eggshells to store large amounts of energy from wind turbines and solar farms is therefore an essential technology to help ensure that low-emission energy can be provided both cheaply and reliably. Therefore, implementing energy storage necessitates fundamental research on various electrode and electrolyte interactions to widen its voltage window and establish new battery chemistry for improved storage capacity, which has been achieved in the body of the work published in 11 peer-reviewed journal articles as a part of post-Ph.D. work. The outcome of several publications underpins their electrochemical oxidation and reduction of lithium in the host olivine structure. These publications are a part of the candidate's ARC DP funding outcome (sole CI) where he has provided a robust understanding of the lithium intercalation mechanism in aqueous solutions. Out of 11 articles, in 10 of those the candidate is the first author and corresponding author implying that he has contributed (around 70%) to conceptualization, research design, investigation, methodology, data curation, and original draft. The co-authors have contributed their areas of expertise. This is excepted for the publications listed (#58, #59, #61, and #62) where the co-authorship S. Kandhasamy, a master's internship student worked on this project under the candidate's supervision. SK contributed to data curation and informal analysis. The candidate's contribution to these articles with SK as co-author is 55%.

Phosphate-based electrode materials, especially the phospho-olivine's  $\text{LiMPO}_4$  (where  $M = \text{Fe, Mn, Co, and Ni}$ ) were recognized as attractive alternatives to oxide materials. The presence of  $(\text{PO}_4)^{3-}$  polyanions with a strong P-O covalent bond in the olivine-type structure provides a stable system when the electrode is fully charged. Hence, we have shown phospho-olivines of  $\text{LiMPO}_4$  as an attractive cathode material for aqueous energy storage. The olivine-type phosphate compounds  $\text{LiMPO}_4$  ( $M = \text{transition metal; Fe, Mn, Co or Ni}$ ) were synthesized and used as cathodes in an aqueous lithium hydroxide (LiOH) electrolyte, in a typical secondary aqueous battery system using a Zn (or) Carbon as an anode. It has been shown that the electrochemical oxidation of  $\text{LiCoPO}_4$  in an aqueous solution transforms to  $\text{CoPO}_4$  and it was anticipated that the other transition metal cations should follow a similar pattern. However, a potentially different reaction mechanism for deintercalation was observed for  $\text{LiFePO}_4$ ,  $\text{LiMnPO}_4$ , and  $\text{LiNiPO}_4$  cathodes reported in publications listed in #70 – #74.

The synthesized olivine powders in the laboratory provide a fundamental understanding of the intercalation chemistry of Li. The powders were obtained by the candidate using a simple one-step solid-state reaction method. The synthesized materials were verified with an X-ray diffraction pattern (XRD) which revealed that all the samples with the various transition metals used were invariably shown single-phase  $\text{LiMPO}_4$  (where  $M = \text{Fe, Mn, Co, and Ni}$ ; listed in #70 – #74) with an ordered olivine structure. A simple synthesis for  $\text{LiNiPO}_4$  and some of its analogs are developed in

this phase of the study, which has not been reported before for aqueous energy storage. The candidate's powder XRD patterns (lithium nickel phosphate and lithium cobalt nickel phosphates) have been selected for inclusion in the International Center for Diffraction Data (ICDD) powder XRD diffraction – release 2013. The synthesis was carried out in air at modest temperatures yielding products of high-purity compounds in a single phase. Investigation of the discharged/charged cathode materials using physical and spectroscopic techniques showed that the products formed are a mixture of two phases involving both charge carriers such as lithium ( $\text{Li}^+$ ) and proton ( $\text{H}^+$ ) intercalation. The insight into the nature of the phase change that transforms these olivine-type materials when charged has been a significant achievement. This article (publication listed in #71) had a significant impact of receiving 140 citations. The electrochemical oxidation of  $\text{LiNiPO}_4$  resulted in the formation of an amorphous de-lithiated  $\text{NiPO}_4$  and a minor product of  $\beta\text{-NiOOH}$ , (publication listed in #65). In the case of the analog, lithium manganese phosphate ( $\text{LiMnPO}_4$ ) electrode, the discharged products were  $\text{Li}_{1-x}\text{MnPO}_4$  and  $\text{MnOOH}$ . However, incorporating a  $\text{TiS}_2$  additive into the synthesized  $\text{LiMnPO}_4$  resulted in the suppression of both  $\text{MnOOH}$  formation and proton insertion. This improved the battery storage capacity to  $130 \text{ mA h g}^{-1}$  and its cycle life. Through this work (publication listed in #73), the correlation between additives and the suppression of proton insertion i. e. unwanted discharged products was identified. This resulted in a profound understanding of the relationship between the rate capability and the optimum level of suitable additives in cathode material for energy storage applications. For  $\text{LiFePO}_4$ , the reduction of the oxidized product of  $\text{LiFePO}_4$  produces a mixture of  $\text{LiFePO}_4$  and  $\text{Fe}_3\text{O}_4$ , suggesting the electrochemical behavior of olivine was different from those observed for non-aqueous electrolytes by having minor displacements such as  $\text{Fe}_3\text{O}_4$  phase limiting to  $65 \text{ mA h g}^{-1}$ . Alteration on the olivine-type phosphate cathode materials has been performed through metal ion doping, which resulted in novel lithium orthophosphate ( $\text{Li}(\text{Co}_{0.5}\text{Ni}_{0.5})\text{PO}_4$ ; and  $\text{Li}(\text{Mg}_{0.5}\text{Ni}_{0.5})\text{PO}_4$  (publications listed in #63, and #70, respectively). The refined lattice parameters indicate that  $\text{Li}(\text{Co}_{0.5}\text{Ni}_{0.5})\text{PO}_4$  and  $\text{Li}(\text{Mg}_{0.5}\text{Ni}_{0.5})\text{PO}_4$  had larger lattice parameters compared to the parent  $\text{LiNiPO}_4$  in accordance with the increase in ionic radius. These metal atom-substituted olivines resulted in reduced particle size with carbon (conductive) coating on the surface of lithium orthophosphate which improved the conductivity and specific capacity of the energy storage device. This was shown to be attributed to the improved kinetics of lithium diffusion when compared with pristine samples. The presence of carbon phase suppressed the growth of  $\text{Li}_3\text{PO}_4$  grains that enhanced the Mg substituted analog to become more conductive. The cell voltage and storage capacity of the studied olivine samples concluded that the battery performance with better capacity retention was increased in the order of  $\text{Ni} < \text{Fe} < \text{Mn} < \text{Co}$ . The candidate's frequent success in merit-based Synchrotron beam time grants from Australian Synchrotron and research grants to utilize the microscopy and depth profile analytical facilities at ANSTO through AINSE Ltd. led to several publications with Drs Blackford, Mitchell, Prince, Carter, and Ionescu (from ANSTO); and Appadoo, Martin (from Australian Synchrotron) as co-authors. Their role is to support a huge diversity of research projects and assist in the measurement and analysis of diffraction/infrared data associated with microscopy to understand the various structural motifs present, which influence energy storage materials. The concentration depth profiles, and electronic structure of the surface and near-surface region underpinned the chemical phenomenon that is responsible for the faradaic process.

#### 4.2.2. Sodium Analogue Phosphates

**Comprising 5 peer-reviewed journal papers. Listed publications #24, #26, #35, #55, #56; period 2010 – 2012.**

Among the phosphates, the olivine  $\text{LiMPO}_4$  ( $M = \text{Mn, Fe, Ni, or Co}$ ), has emerged as a promising class of cathode materials for Li-ion batteries using LiOH electrolyte. In particular, lithium iron phosphate,  $\text{LiFePO}_4$ , which has found widespread industrial application in non-aqueous electrolytes has also found some interest in aqueous media. Although numerous publications exist on olivine  $\text{LiFePO}_4$  about its significant electrochemical storage (discharge capacity) properties, the sodium equivalent ( $\text{NaFePO}_4$ ) has not been well characterized or documented in sodium cell applications by then. Most phosphates with the general formula  $\text{ABPO}_4$  ( $A$ : alkali cation;  $B$ : transition metal cation) crystallize forming either an olivine-, maricite- or zeolite-type structure. The structures of olivine and maricite are analogous, while that of zeolite shows some differences. When the size of the  $A$  alkali cation increases from Li, Na, to Cs the phosphates crystallize with the structures of olivine, maricite, and zeolite respectively. The typical  $\text{NaFePO}_4$  maricite phase is reported to be the thermodynamically favoured phase because it is obtained under high-temperature synthetic conditions. The maricite structure is similar to the olivine  $\text{LiFePO}_4$  with the difference being the occupation of the  $M(2)$  site by the alkali cation (Na), and the occupation of the  $M(1)$  site by the transition metal. A small number of early works reported that  $\text{NaFePO}_4$  is not viable as a cathode material, suggesting that the closed (no cationic channels), one-dimensional maricite framework results in entrapment of  $\text{Na}^+$ , thus preventing reversible electrochemical processes. To the best of the candidate's knowledge, no work has been reported by then on the maricite structure with metal atom substitutions ( $\text{NaMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{PO}_4$ ) (publications listed in ##35, #55, #56) in aqueous electrolytes. The substitution of mixed transition metal cations and novel materials processing by urea-assisted combustion technique have been reported to overcome the poor electronic conductivity of iron-containing olivine/maricite frameworks. The studies (publications listed in #35) on mixed sodium transition metal phosphate (maricite,  $\text{NaMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{PO}_4$ ) received 50 citations. The electrochemical reaction mechanism at the maricite electrode in NaOH electrolyte appears reversible, involving a faradaic process. The structural studies confirm that the  $\text{NaNiPO}_4$  compound exists in two different forms (triphylite and maricite), depending on the synthetic temperature (publication listed in #26). The as-prepared  $\text{NaNiPO}_4$  material forms nanosheets, while triphylite and maricite form nanorods and plates. The electrochemical properties of polycrystalline  $\text{NaNiPO}_4$  polymorphs, maricite, and triphylite, in which triphylite allows suitable pathways for insertion/de-insertion resulted in the promising cathode material. This publication has received 70 citations. The benefits of using acetate as an alternative to nitrate precursors are also explored (publication listed in #24) by using the  $\text{NaNiPO}_4$  nanoparticles as a cathode and the results indicated that metal acetates are homogeneously distributed compared with those nitrates. The synthetic steps and morphology of  $\text{NaNiPO}_4$ , using the highly conductive Ni cation in sodium analog, in an aqueous electrolyte developed an important novel energy storage cathode material based on an affordable, globally available element such as sodium. This new  $\text{NaNiPO}_4$ -based material is superior in storage performance and excellent cycling stability with a retention of 99% capacity up to 2000 cycles to that of lithium-based phosphate materials ( $\text{LiNiPO}_4$ ). A typical  $\text{MgMoO}_4$  as a cathode material in a sodium-ion battery produced a first discharge capacity of  $580 \text{ mA h g}^{-1}$ . Upon subsequent charging, the reversible capacity of  $300 \text{ mA h g}^{-1}$  is observed. This concludes that the Na-ion battery system can be a suitable choice in terms of electrochemical performance, safety, and raw material abundance.

The outcome of the sodium analog material resulted in 5 peer-reviewed journal articles as a part of post-Ph.D. work, in which the candidate is the first author and corresponding author for all the articles. This implies that the candidate has contributed (around 70%) significantly to conceptualization, research design, investigation, methodology, data curation, and the original draft. Notably, the co-authors have contributed their areas of expertise in terms of computer simulation to derive the electronic properties of these novel phosphates. These publications are part of the State of WA funding for the Center for Research into Energy for Sustainable Energy (CREST) funding outcome (Sole CI Dr. Minakshi).

**4.2.3. Role of Chelating Agents in Metal Atom Substituted Phosphates**  
**Comprising 3 peer-reviewed journal papers. Listed publications #21, #60, #67; period 2012 & 2017.**

As discussed in the earlier sections (4.2.1), synthesis strategy is the primary factor influencing the storage capacity of the metal atom-substituted phosphate materials. The chosen sol-gel synthesis method is shown to be promising in the presence of chelating agents, resulting in better rate performance and longevity of the cell compared to that of ceramic synthesis. It has also been explored that the choice of chelating agents determines the particle size and morphology of the obtained products. A range of chelating agents like a weak organic acid (Citric acid - CA), emulsifier (Triethanolamine - TEA), and non-ionic surfactant (Polyvinylpyrrolidone - PVP) was employed in sol-gel wet chemical synthesis of olivine phosphates (publications listed in #60, #67). Although a variety of organic solvents and polymers are available as chelating agents, CA was widely used as a chelating agent due to its carboxylic group that led to a homogeneous precursor gel with finer particle size. However, the degradation of CA during synthesis leaves randomly coated residual carbon over the cathode that did not show any superior quality in terms of electrochemical performance to that of the uncoated cathode  $\text{LiCo}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3}\text{PO}_4$ . In this context, chelating agents such as TEA and PVP have been explored and shown to have different properties. One of the unique properties of TEA is the presence of nitrogen atoms which act as a fuel in producing internal heat and performing a combustion reaction. The resultant heat accelerates remarkably the decomposition of the remaining constituents resulting in smaller particle sizes with higher crystallinity. In the case of PVP, its uniquely strong pyrrolidine ring (with nitrogen and carbon atoms) decomposes and forms a new organic trap over the material that increases the conductivity of the phosphate families. Hence, the physicochemical properties of synthesized powders strongly depend on the chelating agent used in the sol-gel method. This prompted us to investigate (publication listed in #60) the range of chelating agents and to determine their role in achieving a higher energy density battery and compare those with the traditional synthesis methods. The sol-gel synthesis employed in preparing an olivine electrode using metal acetate precursors with poly(N-vinylpyrrolidone) (PVP) as a chelating agent (article #67) influenced the particle size and the homogeneity. This approach yielded a single-phase olivine phosphate at a considerably lower temperature and shortened heating time, compared to that of the conventional solid-state reaction. The combination of multiple chelating agents (TEA + PVP) was shown to improve the electrochemical properties of the synthesized cathode. In another article, a novel combustion method was employed to synthesize the material at a lower temperature to attain a preferred crystal lattice for lithium-ion intercalation and extraction. The amount of defect has been reduced by a low concentration of Co and Mg dopants, choosing a suitable synthesis method and optimized reaction conditions. The lattice defects owing to metal ion doping and its influence in improving the cathode performance of the olivine phosphates (publications listed in #60, #67), and lithium-free oxide materials are quite crucial. Using biopolymer glutamic acid as a complexing agent



for synthesizing phosphate electrodes facilitates the electrostatic interaction between carboxylate ions and Ni cations (publication listed #21). This enhances the adsorption reaction of the metal molybdate structure during the electrochemical process. The development of a facile synthetic method described in key publications to give the required degree of purity and homogeneity of the product is certainly a most important technical achievement made during post-Ph. D. studies. The publication listed in #67 was cited around 55 times.

For the listed 3 articles, the candidate is the corresponding author for all, however, he is the first author for only one of the publications (#21). The first authorship, S. Kandhasamy, in the other two publications (#60, and #67) is a master's internship student who worked on this project under the candidate's supervision formulated the chelating agents and investigated the material. The candidate's contribution to the first author's article is 70%, and the last/corresponding author's contribution in publications listed #60, and #67 is 55%.

#### ***4.2.4. Metal Oxides with ex-situ Suitable Additives***

***Comprising 14 peer-reviewed journal papers. Listed publications #66, #68, #69, #77, #79, #80, #81, #83, #87 - #92; period 2007 - 2012.***

In parallel with the above efforts to map modified electrode materials described in Sections 4.2.1. – 4.2.3, two approaches have been made to exploring new materials chemistries for improved storage capacity. First, building on the previous knowledge during Ph. D. studies on oxide ( $\text{MnO}_2$ ,  $\text{TiO}_2$ ) electrodes with structural instability, the candidate introduced metal oxide ex-situ additives e.g.  $\text{Bi}_2\text{O}_3$ ,  $\text{B}_4\text{C}$ ,  $\text{CeO}_2$ ,  $\text{TiS}_2$ , and  $\text{TiB}_2$  (publications listed in #77, #79, #80, #81, 83, #87 - #92; each article devoted to additives cited at least 40 times) with physical mixing that would provide a modified local environment with a weakened interaction between metal-oxygen frameworks to facilitate ion transport inside the  $\text{MnO}_2$  oxide bulk material. Small amounts of additives in the  $\text{MnO}_2$  cathode improve the discharge capacity by stabilizing the structure of  $\text{MnO}_2$  while preventing the formation of unwanted discharged products and suppressing the proton insertion mechanism (publication listed in #87, cited 50 times). Nevertheless, increasing the additive content above the optimal amount causes a decrease in the cell voltage and the discharge capacity. The appropriate concentration of additive is needed to provide an equilibrium between the  $\text{Mn}^{2+}$  dissolution and the re-oxidation. The synergistic effect of multiple additives in different proportions in the oxide cathode material led to enhanced storage behavior. It is shown that these foreign cations (additives such as  $\text{TiB}_2$  or  $\text{TiS}_2$  in the presence and absence of  $\text{Bi}_2\text{O}_3$ ) stabilized the oxide  $\text{MnO}_2$  structure upon multiple cycling and the synergistic effect between the two additives enhanced the rechargeability of the battery system. The  $\text{MnO}_2$  aqueous cell containing multiple additives (publication listed in #66) performed well providing a good storage capacity ( $215 \text{ mA h g}^{-1}$  or  $270 \text{ Wh Kg}^{-1}$ ) and capacity retention of just 8% loss after hundreds of consecutive cycles. This class of modified  $\text{MnO}_2$  may be of interest for high-energy density and safer batteries for applications such as electric vehicles etc. However, the long-term cycling of the oxide material concludes it is suitable for renewable energy storage applications. Another set of additives (alkaline earth oxides i.e. barium oxide ( $\text{BaO}$ ), magnesium oxide ( $\text{MgO}$ ), and calcium oxide ( $\text{CaO}$ ) trialed in  $\text{MnO}_2$  have resulted in further improved capacity retention and cycle performance (publications listed in #66, #68, and #69). The set of additives based on alkaline earth oxides resulted in a patent cooperation treaty (PCT) patent application in 2011. The  $\text{MgO}$  or  $\text{BaO}$  added  $\text{MnO}_2$  was found to result in significantly improved initial discharge capacity of 196 and  $265 \text{ mA h g}^{-1}$  respectively compared to the additive-free cell which shows just  $145 \text{ mA h g}^{-1}$ . This demonstrates that alkaline-earth oxides have influences on the electrochemical behavior of the  $\text{MnO}_2$

cathode but not in a similar mechanism observed for a range of other additives (mentioned earlier – synergistic effect of multiple additives; TiB<sub>2</sub>; TiS<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>; publication listed in #66) in that the formation of non-electroactive forms of manganese (MnOOH, Mn<sub>2</sub>O<sub>3</sub>, and Mn<sub>3</sub>O<sub>4</sub>) are suppressed. Surprisingly, in the alkaline earth oxide-modified cathodes, the structural patterns obtained from the X-ray diffraction technique of the discharged product showed (publications listed in #68, and #69). these non-electroactive forms of manganese still exist. This demonstrates that a stable crystalline structure has been achieved for alkaline-earth-modified MnO<sub>2</sub> that suits the longevity of the battery. On a different approach, a unique synthetic method to carbon coat the MnO<sub>2</sub> particles using polyvinylpyrrolidone (PVP) as a source has been carried out in one of the candidate's publications. The polymer, PVP, has excellent wetting properties that make it good as an encapsulation on MnO<sub>2</sub> particles. PVP as a polymer can form a conducting matrix and acts as a backbone in the cathode material. This polymer coating on the host MnO<sub>2</sub> shown to enhance the conductivity and lithium intercalation mechanism during discharge but unfortunately reduces the working voltage of the MnO<sub>2</sub> cathode during synthesis. It is the candidate's opinion that the aqueous Li-ion approach based on oxide cathodes described in this section (4.2.4) of the higher doctorate work shows promise and needs to be included in the hunt for both portable and large-scale energy storage applications.

The outcome of the additives in different proportions into the MnO<sub>2</sub> cathode material resulted in 14 peer-reviewed journal articles as a part of post-Ph.D. work, in which the candidate is the first author and corresponding author for all the articles. This implies that the candidate has contributed (around 75%) significantly to conceptualization, research design, investigation, methodology, data curation, and the original draft. The co-authors have contributed their areas of expertise in terms of providing access to ANSTO facilities through the Scientists Dr. Blackford, and Dr. Mitchell., and proofreading the articles by providing critical comments These publications are a part of AINSE funding (Sole CI Dr. Minakshi) to utilize the facility at ANSTO and the State of WA funding for the Center for Research into Energy for Sustainable Energy (CREST) funding outcome (Sole CI Dr. Minakshi).

#### **4.2.5. High-Quality Electrolytic MnO<sub>2</sub>**

***Comprising 13 peer-reviewed original papers, and 1 review article. Listed publications #1, #4, #13, #15, #31, #32, #33, #34, #37, #38, #39, #40, #43, #46; period 2014 - 2022.***

Among the oxide cathode materials, electrolytic manganese dioxide (EMD-MnO<sub>2</sub>) has been widely considered a promising electrode in energy storage applications due to its low cost and environmental friendliness. EMD is the critical component of the cathode material in modern alkaline, lithium, and sodium batteries including electrochemical capacitors, photocatalysts, and hydrogen production (publication listed in #33, #34, #39, and #40). In addition, several crystal structures exist for MnO<sub>2</sub> due to the presence of Mn in multiple oxidation states. The difference in the crystal structure lies in the arrangement of the Mn<sup>4+</sup> within the octahedral sites. The intense interest in manganese dioxide for energy applications is driven by this material's low cost and non-toxicity when compared with nickel and cobalt oxides. In our publications listed in #1, it is evidenced that the EMD-MnO<sub>2</sub> on the surface of the lead anode relies on the electrodeposition parameters (e.g., current density, deposition time, thickness, and morphology) and alterations made in the electrolytic bath, which enhances the storage behavior (publications listed in #4, #13, #34). Our outcomes suggest the significance of the strategic design of the electrodeposited MnO<sub>2</sub> for improving storage characteristics.

Numerous reports are available regarding the synthesis of  $\gamma$ -MnO<sub>2</sub> from various manganese ores and its role in energy storage applications, while the possibility of producing EMD from low-grade and secondary manganese resources has not been fully explored. Production of EMD from a range of sources will be necessary to meet future escalating demand. Therefore, with collaborative work from one of the candidate's post-docs (A. Biswal), we have identified a different approach to electro-synthesize EMD from purified manganese sulfate solution obtained from low-grade manganese ore (publication listed in #31, cited 45 times and #38, cited 125 times). EMD synthesized in most of the previous studies was produced as a self-standing electrode for electrochemical applications. The self-standing method largely retards the scalability of the material utilized to develop commercial applications. In contrast, EMD material synthesized by our team comprising post-doc (A. Biswal, 2016) and Ph.D. student (K. Wickramaarachchi, 2022) was deposited in bulk providing the opportunity for scalable material production. The primary focus of our studies was the role of surfactants that influence the MnO<sub>2</sub> microstructure as additives to the electrolytic bath. Adsorption of the surfactants on the MnO<sub>2</sub> surface not only affects the kinetics of the electron the transfer through blocking of active sites but also affects the electrostatic interactions between electroactive species in the electrolytic bath. Consequently, the addition of organic surfactants to the electrolytic bath was shown to affect the morphology, perhaps crystal structure, and mechanical properties of electrochemically deposited MnO<sub>2</sub>. These additives led to altered electrochemical behavior that resulted in high storage capacity meeting the suitability for energy storage devices (publications listed in #4, #37, #43). EMD prepared in the presence of cetyltrimethylammonium bromide (CTAB) or sodium n-dodecylbenzene sulfonate (SDBS) has been reported by our team earlier (publication listed in #43) and found suitable for battery applications with lower storage capacity. The electrodeposited material produced in the absence of any additive had a rough and nodular surface while in the presence of additive in the bath a smooth surface has been demonstrated. The presence of surfactants also significantly altered the morphology and crystal orientation in the cathodes.

In the next phase of this work, the use of the non-ionic surfactants e. g. Triton X-100 and Tween-20, and quaternary ammonium-based surfactants on EMD produced from a secondary source was examined and found to improve storage capacity (publications listed in #43, and #46). The outcomes of this work concluded that surfactants reach the critical micelle concentration value, which controls the disproportionation and hydrolysis reactions of the Mn<sup>2+</sup> ions at the electrode-electrolyte interface. With their hydrophobic chains, surfactants also helped extend the operating voltage of the cathode due to hydrophobic thin films incorporated in the electrode, which shifts the water electrolysis region. The influence of surfactants in the electrodeposited MnO<sub>2</sub> material and its concentration and chain length led to improved microstructure (microspheres to nanosheets) in contact with the electrolyte delivering larger storage capacity. In another study, both the non-ionic Pluronic surfactant (50 mg dm<sup>-3</sup>) and the activated carbon (5 g dm<sup>-3</sup>) were added together in the electrolytic bath during the electrodeposition process and found the resultant EMD exhibits a high specific capacity and excellent cycling stability (publication listed in #37). This study illustrates the synergistic effect of the optimal ratio of surfactant to carbon powder-produced rod-like arrays exhibiting a larger surface area, which facilitates ion transport for better energy storage. The effects of surfactants and polymer as additives upon the structure and morphology of EMD cathodes were reported with particular emphasis on the microstructure and morphology in the cathodes influencing the electrochemical properties. High concentrations of additives are seen to be detrimental in electrolytic MnO<sub>2</sub> as the pitting corrosion of the stainless-steel blanks can become excessive.

Alternatively, employing ternary metal oxides such as cobalt–nickel–copper (Co–Ni–Cu) mixed oxides, in which varying the Cu concentration could increase the electrical conductivity, change in morphology, and electrochemical performance (publication listed in #32, #15). The role of ternary oxides is seen as complementary. Interestingly, the Ni and Co possess high redox activity, but their storage capability decayed after multiple cycles due to their phase transformation. To solve this, the addition of copper acts as a pillaring effect to stabilize the structure. The various physicochemical analyses reported by our team in the body of work (publication listed in #32, #15) clarify the presence of additives/dopants in the final product and their role in the charge and discharge processes. Such an understanding paved the way to identifying the critical structure and energy storage parameters that could stabilize the desired amounts of additives/dopants during the synthesis and faradaic reactions resulting in improved energy density of the battery. Second, I have explored how the alkalinity of the electrolyte improves the storage and reversibility of oxide electrodes. The published body of work (publications listed in #1, #43, and #46) in this area suggested a proliferation in an understanding of the formation of interphase contacts and structural effects on the battery electrode materials. Moreover, controlling the interaction between the nature of cations and anions of the aqueous electrolyte and electrode structures allowed for the design of new electrodes with improved storage capacity, and energy density, comparable to those of non-aqueous LIB counterparts, but safer, cost-effective, and more environmentally friendly. The modified electrolytic manganese dioxide ( $\text{MnO}_2$ ) studied in this post-PhD work as a cathode for rechargeable batteries and sodium nickel phosphate ( $\text{LiNiPO}_4$ ) detailed in Section 4.2.1 as a cathode showed good potential for large-scale stationary applications.

For the listed 14 articles, the candidate is the corresponding author and co-author for all except #31. The Ph.D. students are the first authors in the three articles (publications listed in #1, #4, and #40) who graduated in 2022 namely K. Wickramaarachchi, and D. Delgado in 2016. They worked on the EMD project under the supervision of the candidate. As a Ph.D. supervisor, the candidate mentored them and assisted in formulating the methodology and investigating the material with extensive analysis. The candidate's contribution to these articles is 40% by validating the data and assisting in drafting a quality manuscript suitable for publication. Another first author named A. Biswal (listed in #13, #15, #32, #34, #37, #38, #43, #46) is a post-doc funded by Murdoch University and as a supervisor, the candidate mentored his project and assisted in writing quality publications, and funding acquisition. The contribution to his articles is 40%. The other first author is Baral (listed in #33, and #39), who worked under the supervision of Drs T. Subbaiah & M. Ghosh (co-author), which is the candidate's collaborator. The collaborators are metallurgists and the candidate's contribution (20%) to this work is by providing some discussions on the interpretation of data relating to electrochemical, XRD, and SEM studies on  $\text{MnO}_2$  and proofreading the article.

#### **4.2.6. Metal Molybdates (Binary transition metal oxides) nanomaterials**

**Comprising 8 peer-reviewed original papers. Listed publications #2, #17, #18, #22, #27, #42, #47, #53; period 2013 - 2022.**

Another unique class of transition metal molybdate (such as  $M\text{MoO}_4$  framework;  $M = \text{Ni, Mn, Mg, Ca, and Co}$ ) developed during post-PhD work offers reversible redox chemistry, multiple oxidation states, thermal stability, and high storage capacity. We mapped mixed metal oxides as potential electrode because the single transition metal oxides like EMD are poor conductors and requires additives to be included in the bath (discussed in the previous section 4.2.5). This makes metal molybdates attractive as electrodes in energy storage applications. While the hydrothermal,

solvothermal, and solid-state reactions are widely used to synthesize metal molybdates, we have introduced solution combustion synthesis to produce nanoarchitecture (publication listed in #47; cited 50 times). This involves a fast and self-sustained redox reaction between urea as fuel and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) as an oxidant in the presence of metal cations (Ni and Mo in the case of  $\text{NiMoO}_4$ ). The role of fuel and oxidant strongly affects the combustion process and resulting material and its storage properties. The nanoparticles of nickel molybdate can be simply achieved by varying the concentration of oxidant while keeping the fuel concentration constant (publication listed in #53; cited 185 times). The high fuel content reduces the active sites at the surface, while the optimized fuel content gives the highest active sites, which are valuable information for a wider community.

Research on the molybdate structural framework ( $\text{MMoO}_4$ ) of the various metal cations ( $M = \text{Ni, Mn, Mg, Ca, and Co}$ ) has been reported in his body of work (publication listed in #17, #18, #42, and #53) showing their potential in energy storage materials. Among the metal cations in the molybdate framework, nickel molybdate crystallized in  $\text{NiMoO}_4$  structure with the presence of dopants exhibited great interest due to their high redox potential, low cost, low toxicity, and environmental friendliness (publications listed in #2). Cobalt molybdates are another favorable candidate for supercapacitors as it possesses fast reversible redox reaction but is less electrochemically active (publications listed in #22). Among molybdates, alkaline earth-based molybdate systems are much more important functional materials because of their unique intrinsic properties which were not explored yet for energy storage devices (publications listed in #17, and #18). The  $\text{MgMoO}_4$  (listed in #18) nanoplates with hierarchical architecture are strong anode candidates among the available conventional hard carbon materials of sodium-ion batteries. This is mainly due to their excellent cyclability, reversibility, and rate capability. It delivered a specific discharge capacity of  $590 \text{ mA h g}^{-1}$ . This work attracted 55 citations. In the case of Ca alkaline earth cation,  $\text{CaMoO}_4$  (listed in #17) involves electron transfer in the Ca redox couple, with the ability of  $\text{OH}^-$  to be reversibly intercalated into  $\text{Ca}_3\text{O}_4$  for improved charge storage (forming  $\text{CaOOH}$ ) which is attributed to pseudocapacitance.  $\text{CaMoO}_4$  prepared at  $300 \text{ }^\circ\text{C}$  is suitable to act as both the anode and cathode. However, the available storage is three times larger in the negative region. This contrasts with  $\text{CoMoO}_4$ ,  $\text{MgMoO}_4$ , and  $\text{NiMoO}_4$  electrodes tested for energy storage in aqueous  $2 \text{ M NaOH}$  solutions, for which the potential window is limited to a maximum of  $0.7 \text{ V}$ . The work on  $\text{CaMoO}_4$  (#17) has attracted a cover page of the journal, *Nanoscale Advances* (2019). Moreover, substituting various metal cations in the molybdate framework and introducing various functional groups allows for tuning the redox activity in the host biodegradable polymer e. g. chitosan (publication listed in #27). However, the stated redox species show low electronic conductivity and are easily dissolved in the electrolyte. To solve these issues, the redox species such as quinone/chitosan and molybdate can be cross-linked to a conducting polymer forming a conducting redox polymer (publications listed in #27, cited 65 times).

Redox polymers can mimic oxidation-reduction behavior with a storage performance loss of about 5% after multiple cycles. Such biopolymer composites are interesting potential hosts for reversible  $\text{Li}^+/\text{Na}^+$  ions intercalation. They originate from many unsuccessful experiments of  $\text{Li}^+/\text{Na}^+$  ion insertion into well-known layered oxide and olivine phosphate hosts. The replacement of oxygen and phosphorous by molybdenum as the anionic element in the polymer backbone may increase the intensity of attractive interactions between the intercalated  $\text{Li}^+/\text{Na}^+$  ions and the anionic framework of the host, thus reducing the diffusion barriers. Molybdate hosts also enhance the energy density to  $70 \text{ Wh Kg}^{-1}$ . The galvanostatic polymerization of polyaniline (PANI) on the  $\text{NiMoO}_4$  substrate in the presence of  $0.5 \text{ M p-toluenesulfonic acid}$  resulted in chitosan cross-linked with PANI/ $\text{NiMoO}_4$ . Polyaniline is one of the widely investigated conducting polymers, due to its inherent stability, a wide range of electronic properties, and affinity to biomolecules. The various oxidation states of PANI are

beneficial since different pH ranges can be made use of to tune the redox species. The growth, shape, and size of the conducting polymers have been shown to be controlled by optimizing the current density and time of polymerization. The obtained fibrous morphology of glutaraldehyde encapsulated PANI/NiMoO<sub>4</sub> composite enables excellent cross-linking between the metal molybdate and biopolymer, thus enhancing the storage capability of the molybdate material (publication listed in #28). Although conducting polymer-based electrodes is widely reported for energy storage but biopolymer cross-linked metal molybdates tuning the redox reactions of the NiMoO<sub>4</sub> electrode seems to be relatively new.

A conducting redox polymer consists of a biodegradable chitosan backbone, a redox-active group that can store charge, and a linker connecting the redox group to the backbone. Biopolymer chitosan, produced by enzymatic deacetylation of chitin, is selective to the sorption of metal ions. We demonstrated that chitosan does not take sorption of alkali and alkali earth metal ions, but it collects transition metals like cobalt/molybdenum metal ions from an aqueous solution. By functionalizing a conducting polymer with redox-active materials, polymers that are both conducting and redox-active can be obtained. Moreover, we showed that (publication listed in #27) chitosan reacted with glutaraldehyde forms a cross-linked gel, into which molybdate nanoparticle powder can be incorporated. The chitosan-glutaraldehyde cross-linking influences the degree of amorphosity in the composite, decreasing the particle size and promoting the formation of cluster-like particles. The interaction between the crystalline nanoparticulate phase and the mixed amorphous regions is reported to produce interesting behavior in electrochemical reactions involving both Faradaic and non-Faradaic processes which, in turn, influence the storage capability. This published work provided insights into the behavior of an interpenetrating polymer network between a biopolymer, such as chitosan, and a nanoparticulate phase (transition metal molybdate), which contains a molybdenum anion framework. The metal molybdate is synthesized using a solution-combustion method and these nanoparticles are subsequently embedded in the cross-linked chitosan network. This leads to a material with improved energy storage performance compared with metal molybdate or conducting polymer alone. The outcome of this article demonstrating an effective strategy of crosslinking metal ions in the polymeric structure, facilitating surface redox chemistry, and improving electrochemical performance was well received by his peers in the field and received several citations. Biopolymer-derived electrode materials exhibited excellent electrochemical properties having functional groups, together with water-based electrolytes could provide safe, inexpensive sustainable alternatives to inorganic electrode materials. In the subsequent publications (listed in #28, and #36), chitosan cross-linked with different amounts of glutaraldehyde was optimized for preparing the chitosan cross-linked CoMoO<sub>4</sub> electrode. The molybdate moiety has been proven to be a potential host for accommodating the chitosan molecule. It is concluded that the chitosan gel will adhere to the molybdate moiety of CoMoO<sub>4</sub> strongly and will increase the capacitance four-fold compared with the chitosan-free material. This concept was widely acknowledged by researchers through numerous citations.

For the listed 8 articles, the candidate is the corresponding author and co-author for many articles except the MgMoO<sub>4</sub>, CaMoO<sub>4</sub>, and one of the ternary oxides (listed in #17, #18, and #22), where the candidate is the first author. The first author in the publication listed in #2 is Ph.D. student P. Sharma worked on the molybdate project and graduated in 2022. As a Ph.D. supervisor, the candidate mentored her and assisted in formulating the methodology and investigating the material with extensive analysis. His contribution to these articles is 40% by validating the data and assisting in drafting a quality manuscript suitable for publication. Another first author named R. Ramkumar is a post-doc funded by Murdoch University and as a supervisor, the candidate mentored her project and assisted in writing quality publications (listed in #27). His contribution to her articles was 40%, as the post-doc is new to supercapacitors The other first author named S. Baskar (publication listed

in #42, #47, and #53), was a Ph. D internship student who worked on this project under the joint supervision of Dr's. Minakshi, Meyrick, and Kalaiselvan. SB contributed to data curation and formal analysis with validation. The candidate's contribution to these articles is 40% by contributing to funding acquisition, visualization, review, and final editing of the manuscript.

**4.2.7. Anode Materials for Next-Generation Aqueous Zn/Li-ion Batteries**  
**Comprising 6 peer-reviewed journal papers. Listed publications #20, #49, #51, #75, #76, #78; period 2010 - 2015.**

Aqueous Zn batteries are one of the most promising battery systems due to the stable metallic Zn anode with a high theoretical capacity of  $820 \text{ mA h g}^{-1}$ . Non-carbonaceous and carbonaceous materials have been largely investigated as anodes to replace metallic lithium. The use of alloy electrodes led to large volume changes during alloying and de-alloying processes. Graphite has been used as an anode material for energy storage systems because of its high efficiency and safety. However, graphite has a limited storage capacity of  $370 \text{ mA h g}^{-1}$  and discharge-charge rate capability. To address this issue, the development of alternative anode materials with excellent features is important.

The traditional Zn anode has low electrode potential and high hydrogen over potential making it a very suitable negative material for use in an aqueous energy storage system. However, the main issue with the Zn anode materials is the formation of dendrites, which is quite a common issue in aqueous energy storage. The Zn dendrite formation depends on several factors including electrolyte type, pH of the electrolyte solution, morphology of the Zn anode, and collector material. We found that while using zinc in a saturated (water-in-salt) LiOH electrolyte, zincate ions ( $\text{Zn}(\text{OH})_4^{2-}$ ) decompose to form ZnO deposits during the continued cycling (publications listed in #75, and #78). The solubility of this deposit is, unfortunately, so high, leading to eventually placate the effectiveness of the remaining zinc, thus reducing zinc utilization and reducing the cell's overall efficiency. The accumulation of uneven ZnO deposits causes premature cell failure. In other words, the battery performance is limited primarily not by the  $\text{MnO}_2$  cathode, but to a greater extent by the Zn anode. Another drawback of using a Zn anode is Zn tends to become incorporated into the  $\text{MnO}_2$  crystal structure forming hetaerolite ( $\text{ZnO.Mn}_2\text{O}_3$ ) that deteriorates the cycling ability. This problem is mitigated when using Sn as an anode (publication listed in #76). Many studies exist on the formation of dendrites in zinc anodes, but most efforts seem to focus on changing the electrolyte's pH to mitigate dendrite formation. Developing other approaches to control dendrite formation in Zn anodes may allow us to optimize the electrolyte without less worry about dendrite formation. The candidate has focused on Zn anodes using foils, and nanostructured powdered morphology to improve material utilization and improve electrolyte permeability, while also improving Zn stability. This concept of using porous zinc has received great attention and this article has been cited 65 times.

Another new strategy that the candidate made during his post-PhD for an aqueous rechargeable battery is a new anode with improved battery rechargeability while overcoming the cycle-life limiting phenomenon characteristic of zinc (Zn) anode. The approach is the effect of replacing Zn with tin (Sn) anode and potassium hydroxide (KOH) with lithium hydroxide (LiOH) electrolyte in the existing technology (publication listed in #76). An alkaline zinc-manganese dioxide ( $\text{Zn-MnO}_2$ ) battery with LiOH electrolyte may not be a new concept by itself, but all the prior commercially available systems use KOH as an electrolyte that limits the battery as non-rechargeable.

The concept employed here uses a metallic Sn anode, an aqueous LiOH electrolyte, and a MnO<sub>2</sub> cathode.

Anode tin can store twice (992 mA h g<sup>-1</sup>) as much lithium as zinc (412 mA h g<sup>-1</sup>) and its reversibility is high. The chemical stability of Sn in our aqueous electrolyte is found to be stable, unlike the solid-electrolyte interphase (SEI) layer that limits the cycling as what is observed for lithium-ion batteries using Sn anode in non-aqueous electrolyte. This improved the utilization efficiency of the Sn anode which is generally seen as low for traditional Zn due to the formation of passivated products on the Zn anode preventing the metal beneath from undergoing further electron transfer. Interestingly, we also found the surface area of planar (foil) and porous (powder) Zn and Sn electrodes in a battery is critical to redox reactions. One of the major factors that govern anode (Zn or Sn) mass utilization, and thus the specific energy density of a battery, is its surface area. A higher surface area per unit volume for a given amount of Zn/Sn decreases the current density and is found an increase the electrode rate capability and active material utilization (publications listed in #51, and #76). The outcome of the work published in #51 addresses that the cycling stability issue using Zn anode must be alleviated by adding redox additives in the electrolyte to suppress the dendrite formation or the concentration of the electrolyte must be studied.

Alternatively, research activities on various metal oxides have been widely examined and reported as promising anode materials for battery systems because of their favorable chemical and physical properties, and iron oxides deliver a high capacity of around 1000 mA h g<sup>-1</sup>. Among the transition metal oxides, nanostructured hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) that enhances the rate performance and cycling stability in the aqueous battery is reported by the candidate. The outcome of the work indicated that factors such as optimum crystallinity, porosity, and surface area determined the battery performance (publications listed in #49). The discharge capacity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> anode observed in this study is 250 mA h g<sup>-1</sup> and the performance is comparable to that reported for non-aqueous lithium-ion batteries (discussed in section 3, the publication listed in #49). However, in the presence of a strongly alkaline aqueous electrolyte, the hematite phase was reduced to metallic Fe after delivering a higher reversible discharge capacity of 335 mA h g<sup>-1</sup>. The production of the Fe phase retards the reversibility.

Nickel molybdate (NiMoO<sub>4</sub>), in which Mo possesses multiple oxidation states, with improved electrical conductivity associated with Mo exhibits excellent electrochemical performance originating from Ni. In one of the publications, the candidate identified NiMoO<sub>4</sub> as an alternative insertion anode for sodium-ion batteries (publications listed in #20). It is explored that the electrochemical reactions, involving both insertion and conversion reactions, during the initial cycle and subsequent cycle. The electrode exhibits an initial discharge capacity of 665 mA h g<sup>-1</sup> and a reversible charge capacity of 365 mA h g<sup>-1</sup>, respectively, corresponding to the initial coulombic efficiency of 54%. Materials Today, Elsevier (Oct. 2018) put out a [short news story](#) on Na-ion battery material published with Dr. Minakshi's mentor Prof. Fichtner at KIT, Germany.

The outcome of the anode material resulted in 6 peer-reviewed journal articles as a part of post-Ph.D. work, in which the candidate is the first author and corresponding author for all the articles. This implies that the candidate has contributed (around 70%) significantly to conceptualization, research design, investigation, methodology, data curation, and the original draft. However, the co-authors have contributed their areas of expertise and assisted in collecting microscopic images, etc. One of the publications (listed # 20) is a part of his visit to Karlsruhe Institute of Technology (KIT),



Germany. The candidate took a visiting research paid position at KIT (Fellow Dr. Minakshi) for 4 months and worked in Professor Max Fichtner's laboratory.

#### ***4.2.8. Aqueous (Water-in-salt) Electrolyte: Beyond Lithium***

***Comprising 9 peer-reviewed journal papers. Listed publications #7, #44, #48, #57, #64, #82, #84, #85, #86; period 2008 - 2021.***

Aqueous rechargeable batteries feature  $H^+$ ,  $Li^+$ , and  $Na^+$  ions (from the respective LiOH, and NaOH electrolytes) shuttling between anodes and cathodes upon charge/discharge, whereas both  $H^+$  and  $Li^+/Na^+$  follow the classical topotactic insertion chemistry at the corresponding electrodes (publication listed in #82). In one of his publications (listed in #85), they found the hydrogen evolution reaction at the Zinc anode can lead to low coulombic efficiency, poor cycling stability, and safety concerns. To avoid this, the candidate has postulated the electrochemical stability window of aqueous electrodes from a thermodynamic point of view. The interaction between  $MnO_2$  and charge carriers (e.g.  $OH^-$ ,  $SO_4^{2-}$ ) showed encouraging results for  $OH^-$  based surface adsorption (non-faradaic) and discouraged the  $SO_4^{2-}$  based insertion (faradaic) that impedes the rechargeability (publications listed in #84, #85, and #86). It has also been explored that proton insertion dominates the capacity contribution for Zn- $MnO_2$  battery using mild electrolytes "salt-in-water" electrolytes (pH = 5). At a higher pH value "water-in-salt" electrolyte with a wide electrochemical stability window, the cation insertion is found to be dominant (publications listed in #7). Compared to the widely reported electrode materials, the role of aqueous electrolytes playing the role of "blood" in a battery has received much less attention. Therefore, understanding the fundamental working mechanism of aqueous electrolytes can help us to design better aqueous batteries (publication listed in #64). The research funding secured by the candidate from AINSE Ltd. to access the surface analysis facilities at ANSTO assisted us in qualitatively assessing the intercalation mechanism in aqueous systems. This paved the way to develop a method for producing electrochemically stable aqueous electrolytes.

Further to this, the candidate has coined an aqueous sodium energy storage using sodium hydroxide electrolyte (NaOH) with additional storage capacity. The demand for LIBs as a major power source is increasing steeply (demand will grow by 200% by 2025), however, lithium is rare (98% of the total reserves are in Chile, Argentina, China, and Australia), expensive, and it is used in LiOH electrolytes. Lithium is the lightest metallic element with a very low redox potential (-3.04 V vs. SHE) that enables high voltage and high energy density. It has a small ionic radius allowing "easy" diffusion into and out of host compounds, resulting in excellent reversibility. However, there are serious concerns associated with its safety, high cost, and availability, globally lithium reserves are in remote areas that will deplete in time and are not sufficient to address global needs. Manganese and iron are both abundant in Earth's crust relative to lithium, cathodes based on these elements could be advantageous for large-scale energy storage applications. Developing an alternative approach to supporting these technologies is therefore crucial. The abundance of sodium will prove that Na-ion battery (NIB) will be potentially very low cost; with a redox potential (-2.71 V vs. standard hydrogen electrode (SHE) highly suitable for battery applications and presents an appealing option for lithium replacement. Hence, sodium-ion batteries are potentially very attractive alternatives to lithium-ion batteries (publication listed in #57).

The influence of concentrations and anions/cations on the electrolytes has been studied, requiring electrodes with increased tunnel size and interlayer spacing to accommodate sodiation/desodiation. Regarding the cathode,  $MnO_2$  with good interlayer spacing has been used, while additives have been

added at appropriate amounts into the MnO<sub>2</sub> surface is shown to potentially increase the capacity and redox potentials to ensure higher Na<sup>+</sup> storage. In one of the candidate's publications in 2012 (listed in #57), he examined the performance of manganese dioxide (MnO<sub>2</sub>) in NaOH electrolytes and compared it with other alkaline electrolytes (like KOH and LiOH). The ionic volume of Na<sup>+</sup> is 2.5 times larger than that of Li<sup>+</sup>, so host compounds must have larger sites to accommodate Na<sup>+</sup> ions in the matrix. He found that MnO<sub>2</sub> can act as an intercalation compound and the constructed cell with NaOH electrolyte proved to have excellent electrochemical performance. Although sodium and sodium-ion batteries evolved in 2012, to the best of the candidate's knowledge, an aqueous cell has not been reported by then. Subsequently, he found that the aqueous rechargeable cell worked on the same principle as its non-aqueous counterpart, – i.e., reversible and rapid ion insertion and extraction (publication listed in #18 for comparison). During charge and discharge, Na<sup>+</sup> ions shuttle between the MnO<sub>2</sub> electrode and aqueous electrolyte hosts during the reduction and oxidation processes. Our results have renewed interest in sodium-ion battery development, particularly for stationary storage connected to renewable energy production where high power/weight becomes less critical. This intercalation chemistry should lead to considerably cheaper and longer-lasting (renewable) energy storage batteries. The discharge capacity of the pristine MnO<sub>2</sub> cathode for the NaOH cell was 225 mA h g<sup>-1</sup> (300 Wh Kg<sup>-1</sup>) compared to 142 mA h g<sup>-1</sup> (210 Wh Kg<sup>-1</sup>) for the LiOH cell using a 1 V cut-off voltage (publication listed in #57). The intercalation of sodium in an aqueous solution is confirmed through several physicochemical analyses of the discharged MnO<sub>2</sub> electrode. The different hydrated radii of the ions, their mobility, and ionic conductivity on LiOH, KOH, and NaOH electrolytes are shown to affect the performance of the battery (publication listed in #85). It has been explored in our work that large ionic size and strong interaction between cathodes and anions lead to diffusion-controlled slow kinetics and increased redox potential co-interaction of solvent molecules may result in electrolyte decomposition. Bismuth additives are added to the electrolyte to improve the microstructure of the electrodeposited cathode deposit while delaying cathode dissolution in the redox process. Alternatively, solid-state capacitors based on a conductive filler (SiO<sub>2</sub>) dispersed polymer electrolyte have also been demonstrated feasible for an energy storage system (publications listed in #44, and #48). The key article (#44) explains the synthesis of solid polymer electrolytes that received around 80 citations. This could be due to the novel approach to the conductivity of the polymer electrolyte having been shown to increase notably, which leads to the lower internal resistance of the electrochemical property. The adsorption-desorption of Ag ions in the polymer electrolyte seems reversible and stable for multiple cycles.

The outcome of the electrolyte materials, including liquid and solid-state polymer electrolytes, resulted in 9 peer-reviewed journal articles as a part of post-Ph.D. work, in which the candidate is the first author of 7 articles and the corresponding author for all the articles. This implies that the candidate has contributed (around 70%) significantly to conceptualization, investigation, methodology, data curation, and the original draft. The co-authors have contributed their areas of expertise. In the case of the other first author (M L Verma in publications #44, and #48), the candidate devised the research design with the experimental work carried out by their group in India. The candidate's contribution to these articles with MLV is 40%.

## **5. Hybrid Materials for Supercapacitors *comprising 17 publications.***

In this section, hybrid materials, which can deliver substantially high energy density (10 – 15 times that of lead-acid batteries) without the environmental challenges of the UltraBattery that couples

supercapacitor electrodes with a lead-acid battery system have been discussed. These sustainable materials exhibited a step-change in renewable energy storage technology.

### **5.1. Sustainable Electrodes for Supercapacitors**

***Comprising 4 peer-reviewed journal papers and one book chapter. Listed publications # I, #3, #16, #19, and #25; period 2019- 2022.***

Carbon-based electrode materials (publication listed in #I) such as activated carbon possess attractive features such as inexpensive, excellent chemical and thermal stability, high electrical conductivity, and large surface area, due to these merits they can be used in energy storage applications. The electrochemical properties of carbon electrodes depend strongly on the nature of the precursor that influences the distribution of pore size, surface functional groups presenting on the carbon surface, structure, and conductivity. During part of the candidate's post-Ph.D., he published a body of work in porous carbon derived from sustainable electrode materials derived from various sources, including discarded eggshells, mango seed husks, grape marc, and other biomass sources (publications listed in # I, #3, #16, #19, and #25). The simple scalable synthetic process, having rich heteroatom content (O, N, and S) with hierarchical porosity, allows the generating of additional reversible redox reactions suitable for both batteries and supercapacitors. Therefore, we developed high-performance electrodes by synthesizing low-cost materials that can be used for large-scale storage applications.

In Australia, the annual egg production averaged 6.2 billion eggs, which is about 16.9 million eggs every day for human consumption. On average, each Australian consumes 233 chicken eggs per year, consumed as both fresh eggs and egg products, which are generally found in ready-to-make foods. Due to the health benefits, positive attitudes, and perceptions of consumers of chicken eggs are reflected in massive global consumption. By 2030, as much as 89 million tonnes of eggs will be required to meet the global demand.

Chicken eggs and related products are used in large quantities in the food processing and manufacturing sectors, households, the nutrition industry, and even in the pharmaceutical industry, but their shells are typically sent as solid waste to landfills. However, eggshell and shell membranes are inedible with little nutrient value but contain a range of active chemical compounds. An eggshell comprises the outer hard shell, which is calcium carbonate ( $\text{CaCO}_3$ ), and the adjoined thin membrane called "eggshell membrane", which is composed of protein fibers that contain sulfur and carbon. Once the protein fibers from the inner membrane start to decompose, the foul smell of rotting egg occurs due to hydrosulphide gas release. Sending unprocessed eggshell waste to landfills is associated with a cost of more than \$40 a ton depending on the location of the landfill (published in #16, and #19). Most of the eggshell wastes are discarded in municipal dumps, except for a small portion being used as fertilizer and animal feed ingredients. Discarded chicken eggs increase toxicity, causing salmonella growth in landfills due to the protein membranes of the eggshell that remain. Chicken eggs are one of the primary sources of human salmonellosis, the most frequent cause of human nontyphoid infection. The odour from large quantities is also very unpleasant for workers and surrounding communities. To accelerate the transition from a linear economy to a circular economy, reducing, reusing, and recycling waste becomes a useful resource improving both sustainable development and addressing waste management.

Finding alternative solutions to this problem would reduce costs and could be financially rewarding to the egg industry as there is much research into the repurposing of this product. The

options for the valorization of this waste include the use of eggshells as an electrode and as a template for energy storage devices. Inspired by the high N-content and nanoporous structure of eggshells, we have converted eggshells into free-standing N-doped nanoporous carbon film through a carbonization and activation process (publication listed #3). The resulting electrodes show excellent performance as electrode materials for storing energy reversibly.

The candidate has carried out extensive research and found that biowaste eggshells could be used as a material for storing energy as a suitable waste management plan. Energy storage devices show great promise to meet the demands that the transition towards renewable energy sources and the electrification of the transport sector put forward. However, concerns regarding the current generation of batteries, including limited raw material resources and flammable electrolytes, necessitate research on alternative technologies. Biowaste electrodes derived from discarded chicken eggshells could be a suitable alternative. The inner eggshell membrane obtained from natural eggs with the main components of sulfur-containing amino acids was used as a template due to its high stability and high surface area with metal ion sorption capacity. Employing a biowaste template as a precursor for synthesizing nanoarchitecture metal oxide electrodes is a unique approach to producing porous material for energy storage applications and therefore the two articles (#16, and #19) received well attention through 50 and 35 citations, respectively. This piece of research "*biowaste eggshell to store energy*" has also attracted media coverage ([WA Today](#); and [Karlsruhe Institute of Technology](#), in Jan 2019) and a clip televised on Channel 7 in April 2019. One of the articles #19 has attracted a cover page of the journal, Dalton Trans. (2018).

The presence of functional groups and the fibrous nature of the eggshell membrane exhibited excellent electrochemical performance with high storage at an appropriate amount of eggshell membrane added. The porous nature of the eggshell membrane-derived metal oxide electrode enhances the penetration of NaOH ions to the bulk of the material during the redox process. The eggshell membrane is found to be stable, and insoluble in aqueous media, but it is completely burnt off during the heating process. Therefore, the final metal oxide electrode is unaffected and arranged in an open-weave structure that enhances the mesoporosity and conductance of the material (publication listed in #25). Secondly, the biowaste eggshell mainly  $\text{CaCO}_3$  has been crushed into a powder and for the first time used as an anode material suitable for energy storage. The electrochemical performance of eggshells showed that they are comparable with classical activated carbon electrodes involving adsorption/desorption of ions used widely for similar applications (publication listed in #19). Thirdly, when  $\text{CaCO}_3$  is heated to a higher temperature forming CaO shows typical redox-type behavior involving the transfer of electrons in the material illustrating battery-type behavior. The X-ray diffraction analysis of the eggshell calcined at 900 °C shows a thermal decomposition of calcite to form phase pure CaO material, indicating suitability for storing energy (publication listed in #16). The principle of storage operation in the eggshell is assumed to be based on the adsorption/desorption of  $\text{OH}^-$  ions (from/to salt-water electrolyte) on the surface area of the eggshell electrodes in the form of free ions. Changes in the morphology of the CaO with the influence of calcining temperature alter the particle size, surface area, and surface functional groups that determine the storage. The eggshell contributes to both faradaic and non-faradaic reactions. Overall, these outcomes explored the viability of biowaste eggshell-derived materials as a template and electrodes for energy storage use. In one of the candidate's other works, his Ph.D. student (Shaymaa Albohani) carried out work on an eggshell membrane, as a template to synthesize organic nickel molybdate ( $\text{NiMoO}_4$ ) cathode material. The rationale for using an eggshell membrane is due

to the presence of chelating functional groups that stabilize the formation of crystal structure in a particular orientation that not only acts as a structure-directing agent but also make the material porous. The porosity stems from the fibrous nature of the eggshell membrane. In the publication listed in #25, they reported the specific capacitance of the templated NiMoO<sub>4</sub> showed a significant increase over that of the pristine material, which is mainly attributed to fiber-like morphology arising from the eggshell membrane.

Considering the economic and social aspects, we need to innovate waste valorization such as eggshells, eggshell membranes (food waste), biopolymer chitosan, (seafood waste), and wheat straw (agricultural waste) for repurposing waste into energy storage materials. These biomass/biowaste materials are reported for wastewater treatment, and adsorbent in the adsorption cooling system but they have not been widely reported for energy storage applications along with effective material designing to improve their performance. The candidate along with the Ph. D. student (K. Wickramaarachchi), repurposed the grape marc using different activating agents in the presence of dopants to accelerate the carbonization process. In continuation to this, they synthesized a series of KOH-activated carbon materials using mango seed husk as the biomass waste precursor. The activation temperature of the mango seed husk improved the morphological features, surface area, and pore-size distribution of the activated carbon which are determining factors for improved storage performance (listed in #3).

The ever-growing energy storage demand provides a massive market for biowaste eggshells that have been published recently and received wide attention. Since the eggshell-derived carbon material can be used to partially replace high-end carbon nanomaterials, such as the much more expensive graphene and carbon nanotubes, this high-end market possesses significant tolerance to the cost of discarded eggshells. Overall, our findings, as a value-added solution of eggshell waste, will make the egg industry more sustainable both economically and environmentally. This material acted as a pivotal point that could promote the growth of the egg industry and secure a leading position in green energy storage with a minimal ecological footprint. This is also evidenced by the number of citations for this article. The candidate's interest in sustainable materials for energy storage systems resulted in being a recipient of the [Winston Churchill Fellowship](#) (2019).

The outcome of the sustainable electrode materials resulted in 4 peer-reviewed journal papers and one book chapter as a part of post-Ph.D. work, in which he is the first author of three articles, and the corresponding author for all the articles. This implies that the candidate has contributed (around 70%) significantly to conceptualization, research design, investigation, methodology, data curation, and the original draft. However, the co-authors have contributed their areas of expertise. The candidate has attracted Winston Churchill Fellowship to continue this research and worked with Prof. Fichtner. The other first authors K. Wickramaarachchi (publication listed #3), and S. Albohani (#25) are his Ph.D. students at Murdoch University. As a Ph.D. supervisor, he mentored them and assisted in formulating the methodology and investigating the eggshell membrane and mango seed husk material with extensive analysis. His contribution to the student as the first-author article is 40% by validating the data and assisting in drafting a quality manuscript suitable for publication.

## 5.2. Electrochemical Hybrid (Asymmetric) Devices

*Comprising 11 peer-reviewed journal papers and one book chapter. Listed in #II, #6, #9, #10, #11, #14, #23, #29, #30, #36, #45, #50; period 2013 – 2022.*

**Batteries versus supercapacitors:** Among the other electrochemical energy storage devices (such as rechargeable batteries and fuel cells), electrochemical supercapacitors are known for their high-power densities. They can be regarded as a class of electrochemical energy storage devices that complement rechargeable batteries because the primary requirement for these devices is providing quick charge release when it is needed and the amount of charge they can accommodate is not as crucial as for batteries (discussed in Sections 3 - 4). Due to the nature of prospective applications (power back-ups, electric and hybrid vehicles, emergency doors, etc.), supercapacitors are also required to have a much longer cycle life than batteries. Conventional electrochemical double-layer capacitors (EDLC) utilize charge storage by adsorption of ions at the surface of electrodes composed of carbonaceous materials with huge surface areas. Rechargeable batteries store the most energy per unit volume but slowly deliver discharge because of sluggish kinetics. In contrast, EDLCs store charge electrostatically (~10 % of batteries) but will tolerate thousands of cycles because of fast kinetics. In the last two decades, a range of inorganic materials and conductive polymers have been proposed for the electrodes of hybrid supercapacitors. These materials possess the so-called pseudocapacitance, that is, most of the charge is stored not by the conventional EDL mechanism but is due to the presence of fast redox reactions on the surface of these materials (publications listed in #II, #14, #23, #30, and #50). The use of pseudocapacitive nanostructured transition metal oxides has been named one of the three greatest achievements in the field of supercapacitors in the last decade because these materials were able to deliver huge capacitances.

**Symmetric vs. Asymmetric:** The most traditional type of electrolytic capacitor is symmetric, consisting of two identical activated carbon electrodes relying on a double-layer charging mechanism, and the system is called an electrical double-layer capacitor (EDLC) that delivers poor energy density ~10 Wh Kg<sup>-1</sup>. The asymmetric Na-ion system is characterized by a combination of faradaic reactions (pseudo capacitance) and non-faradaic charge storage behavior (electrical double-layer capacitance), a new energy storage device. Asymmetric capacitors incorporate dissimilar (hybrid) electrodes, lithiated graphite *versus* activated carbon in the organic electrolyte which is expensive and has stringent safety issues and the best-reported value is ~25 Wh Kg<sup>-1</sup>. His proposed “*hybrid*” system comprises an activated carbon anode “capacitor type” electrode and a maricite cathode “battery type” electrode providing 35 Wh. Kg<sup>-1</sup>. The key to this finding is a novel hypothesis in “*hybrid sodium-ion capacitor*” that both an intercalation and double layer mechanism are involved in aqueous NaOH solutions containing redox additive and polymer electrolyte that improves the energy density and cycling stability (publication listed in #II, and #50). A redox additive (NaI as mediator) added into the polymer (polyvinyl alcohol) containing sodium electrolyte enhances the electrochemical performance. Extensive research has been done on metal oxides such as manganese dioxide (MnO<sub>2</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), tin oxide (SnO<sub>2</sub>), nickel molybdenum oxide (NiMoO<sub>4</sub>), and vanadium oxide (V<sub>2</sub>O<sub>5</sub>) as a positive electrode for capacitors but to the best of his knowledge no work has been reported until recently on asymmetric energy storage materials using sustainable electrodes such as eggshell anode combined with NiO/C<sub>3</sub>O<sub>4</sub> cathode in aqueous electrolytes (publication listed in #14). The synergy of two dissimilar electrodes in the hybrid device delivered a high energy density of 35 Wh. Kg<sup>-1</sup> and a power density of 420 W. Kg<sup>-1</sup> with long-term cyclability of 98% retention of initial capacitance after 1000 cycles. So, the choice of electrode materials is very crucial in developing

hybrid devices. We concluded that by mapping (a) suitable redox additives and polymer in the sodium electrolyte, (b) positive and negative porous electrodes innovatively, and optimizing the mass balance between the two electrodes, new possibilities arise that will provide synergistic benefits with an improved energy density of Li/Na-ion capacitor comprising of a battery type multi-component olivine cathode and a capacitive type of carbon negative electrode (reported in the list #45).

**Hybrid capacitors:** As a part of his post-Ph. D. work, he has focused on mapping a cheaper alternative to expensive ruthenium oxide. We have identified several binary transition metal oxides as potential candidates (publications listed in #6, #10, #11, #29, and #36) possessing high capacitance, exhibiting appropriately shaped (near-rectangular) charge and discharge curves, and being able to retain large capacitance when charged and discharged at high current rates. The binary transition metal oxides were relatively new in the field of hybrid capacitors and hence almost all our publications stated above received a good number of citations (> 70). We have synthesized a range of transition metal oxides and sustainable biomass-derived carbonaceous materials in the laboratory and extensively studied the promising nanostructures and their applications in hybrid supercapacitors (publications listed in #II, #14, #23, #30, and #50). The reported materials demonstrate capacitive and redox properties in aqueous electrolytes. Cyclic voltammetry (CV) is the most visual technique for assessing supercapacitor materials since the CV curves for suitable materials have an apparent “box-like” shape with the possible presence of some redox peaks for materials with pseudocapacitive behavior. The capacitance ( $F\ g^{-1}$ ) can be immediately estimated from readings (current) y-axis reflecting the area of the cyclic voltammogram, the total mass of the electrode, and its scan rate. However, galvanostatic charging/discharging will be performed to assess charging behavior and capacitance retention (rate capability) at various current rates to justify its practical purposes. Rate capability is a particularly crucial characteristic of an electrochemical supercapacitor because, by definition, such a device should be able to charge and discharge extremely quickly. The requirements for the cycle life of supercapacitors are stricter than those for batteries, and the stability of the electrochemical properties over 1,000 cycles will be assessed. In our experiments and the published work, we usually reported for around 2000 cycles. Part of the hybrid electrode (maricite) structural assessment was conducted at the Australian Synchrotron Far Infra-red beamline merit-based proposal (Sole CI Dr. Minakshi) with the beamline scientist Drs Appadoo and Martin.

Among the several binary transition metal oxides examined by the candidate, the cobalt molybdate ( $CoMoO_4$ ) showed a specific capacitance of  $135\ F\ g^{-1}$  at a high current load of  $0.6\ A\ g^{-1}$  in galvanostatic charging / discharging experiments and an excellent energy density of  $31\ Wh\ Kg^{-1}$  at a high-power density of  $1000\ W\ Kg^{-1}$ . The available specific capacitance for this material ( $CoMoO_4$ ) increases until 300 cycles and then stabilizes over 2000 cycles at  $81\ F\ g^{-1}$ . The symmetric nature of the cyclic voltammetric curves (potentiostatic experiment) and the reversible current response on voltage sweep for the biopolymer-modified  $CoMoO_4$  electrode indicate nearly ideal pseudocapacitor behavior (publication listed in #36). The positive effect of the enhanced capacitance is due to the presence of amino groups ( $-NH_2$ ) in the biopolymer chitosan for the donation of electrons, which will eventually lead to a shifting of the Fermi level to the lowest unoccupied molecular orbital (LUMO). The high-rate properties (capacitance retention at high charging/discharging rates) of biopolymer and in-situ polymerization are attractive. Our findings showed that electrochemically engineered  $CoMoO_4$  nanoparticles to a polymer chitosan matrix can present superior characteristics and unique synergistic effects. This outcome provides academia and industry with superior materials for energy storage and so develops products that outperform alternatives. The number of citations (120 times) could measure

the impact of the work and the novelty. The influence of anions in the binary transition metal oxides (replacing molybdenum with tungsten) has also been studied (publication listed in #6), and the results showed that the formation of the  $\text{WO}_3$  layer on the surface of the electrode decreases the available specific capacitance. This is mainly due to the passivation layer on the electrode that inhibits the transportation of ions. We have also identified an efficient synthesis approach for carbonizing material with rich heteroatom content (O, N, and S) from various dopants. This approach will produce additional pseudocapacitance through redox reactions of carbon-based materials by enhancing the capacitance (publication listed in #3).

It remains a great challenge to achieve high storage capacity and fast kinetics of ion/electron storage existing in a single electrode. The hybrid capacitor studied in post-Ph. D. bridges the gap between batteries and capacitors and the features covering both specific energy and power can be achieved in this electrode. Our reported work on a hybrid (combination of energy from battery and power density from supercapacitor) Na-ion device has shown that intercalation of sodium and the formation of an electrochemical double layer (EDL) can reversibly occur over 2000 cycles that use a sodium electrolyte (listed in #50, cited 70 times). Part of this thesis develops a sodium-based hybrid cell made up of supercapacitor-type anode material and a battery-type cathode material with improved energy and power density as compared to lithium and another alkaline, organic counterpart. Specifically, identifying an efficient means of storage through mapping electrochemically engineered new materials for hybrid capacitor offers the utilization of renewable energies that is sustainable and green Australia. This will increase the economics of on-site power generation as well as help reduce carbon and other emissions and thus help Australia meet our net zero targets in 2025.

**Electrodes for hybrid devices:** To meet prerequisites for both high energy and high-power densities in a single application such as large-scale energy storage, devices must be developed with distinct charge storage mechanism for the positive and negative electrodes, one being capacitor-like and the other of the battery type. In contrast to the poor high-power performance of LIBs (as discussed in Section 3), hybrid capacitors are able to deliver high power density with pseudo-capacitive material/porous carbon combinations in an aqueous electrolyte. An ultra-battery system addressing this need has been developed earlier in the literature. However, the shortfall of the device performance with the marginal capacitance of this hybrid supercapacitor/lead-acid battery system is further offset by the significant negative environmental impacts of lead-acid batteries with minimal rechargeability. In contrast, a hybrid device ( $\text{NaNiPO}_4$ /carbon) reported by the candidate can deliver substantially high energy density (10 – 15 times that of lead-acid batteries) without the environmental problems of the lead-acid ultra-battery system. Although sodium and sodium-ion batteries had evolved by then in 2013, to the best of his knowledge, his contribution (publication listed #26) was the first to report phosphates and got wide attention through citations. There has been limited knowledge in the domain of understanding the mechanism involved in the hybrid capacitor using next-generation electrode materials. To examine the suitability of fabricated hybrid Na-ion capacitors consisting of maricite electrodes i.e. AC/ $\text{NaNiPO}_4$ , galvanostatic charge, and discharge were performed. The specific capacitance obtained for AC/ $\text{NaNiPO}_4$  is reported to be 71 and 59  $\text{F g}^{-1}$  at the current densities of 1.0 and 2.5  $\text{A g}^{-1}$ , respectively. Evidently, this excellent rate behavior is due to the in-situ carbon coating on the nickel phosphate that ensures a good cycle performance sustaining high rates to prevent the dissolution of Ni ions (as explained in one of the previous sections 4.2.2). Long-term charge/discharge cycling has been performed to verify the durability of the  $\text{NaNiPO}_4$  electrodes. Our works demonstrate excellent capacitance retention and coulombic efficiency of the cell measured at a current density of



2.5 A g<sup>-1</sup>. A total capacitance loss of only 18% is observed after the cell underwent 2,000 cycles, which indicates the excellent long-term stability of the hybrid cell over the performance of the sodium battery (publication listed #26). It was also found that 85 % of coulombic efficiency was retained at the end of 2,000 cycles with a power density of 1500 W/kg. To this end, we found biomass-derived carbon electrodes and binary transition metal oxides suitable for use in hybrid capacitors.

In addition to cyclability, and high discharge capacitance, an electrode material needs to possess high-rate capability for the purpose of fast charge or/and discharge. To meet this purpose, porous materials are expected to possess high-rate capability because the electrolyte can creep into active material and enhance the contact area of the electroactive surface with the aqueous electrolyte. As a result, the material can sustain high specific currents during multiple cycles. Porous materials can also sustain mechanical stress generated by volume expansion/contraction during electrochemical cycling. In our publications, we showed the active material (both oxide/phosphate) prepared by an inverse microemulsion route assisted by a soft polymer template, namely, Pluronic acid (P123) led to the porous nature of the electrode. By treating with dilute acid and heating, the compound may gain a large surface area and dual mesoporosity, as reported in our work resulting in enhanced electrochemical performance (publications listed in #29, and #30). The pseudocapacitive behavior is attributed to the presence of a mesoporous carbon network in the electrolytic production of Co-Ni binary oxides. This hybrid device with the interconnected porous network delivered 98% efficiency after 1000 cycles with 75% of the available capacitance retained even at a high current rate of 0.5 A g<sup>-1</sup>. We introduced conducting polymer composite on the electrolytic production of both Co-Ni binary oxides, and iron-based ternary metal oxide in combination with cobalt and nickel through a low cost (publications listed in #9, and #14) with a hierarchical nanoarchitecture. These materials shown to be with improved capacity retention and cyclability assert the next generation of low-cost, high-energy hybrid materials for electrochemical hybrid capacitors, however, the increasing Fe dopant in the Co-Ni binary oxides decreases the specific capacitance resulting in 14 Wh kg<sup>-1</sup> at a specific power of 500 W kg<sup>-1</sup>.

The outcome of the hybrid electrode materials resulted in 11 peer-reviewed journal papers and one book chapter as a part of his post-Ph.D. work, in which he is the first author for four outcomes (listed in #II, 14, #45, and #50), and the corresponding author for all the articles. This implies that the candidate has contributed (around 70%) significantly to conceptualization, research design, investigation, methodology, data curation, and the original draft. The first author (P. Sharma) in the publications listed in #6, #10, and #11 is his Ph.D. student who worked on the hybrid capacitor project and graduated recently. As a Ph.D. supervisor, he mentored her and assisted in formulating the methodology, and investigating the material with extensive analysis. His contribution to these articles is 40% by visualizing and validating the data and revising it critically for important intellectual content, suitable for publication. The Australia-Germany Joint Research Co-operation Project funded by Deutscher Akademischer Austauschdienst (DAAD CIs Minakshi and Garnweitner) for 2 years (in 2020) enabled the establishment of international networking between Murdoch University and the Institute for Particle Technology at Technische Universitat Braunschweig (TU-BS), Germany. This DAAD project delivered a supercapacitor electrode (listed in #6 co-authored with Prof. Garnweitner). The other first author named Drs. R. Ramkumar & M. Barni are his post-docs funded by Murdoch University and as a supervisor, he mentored their project and assisted in writing quality publications (listed in #29, #30, and #36) with a contribution of 40%. The first author in one of the other publications listed #23 (T. Watcharatharapong) was a Ph.D. student at Uppsala University. TW has

graduated in 2020. Uppsala University is a collaborative institution established through the candidate's visit to Uppsala in 2016 through the Endeavour Award to work with Professor Rajeev Ahuja's group. As a collaborator, he validated the energy storage material data and assisted in writing quality publications. His contribution to this article (#23) is 40%. The first author named (A. Biswal) in publication #9 is his post-doc funded by Murdoch University and as a supervisor, he mentored the project and assisted in writing quality publications. His contribution to this article (#9) is 40%.

## 6. Summary of the three themes

### Pre-PhD work of the candidate (2000 – 2003)

#### **6.1. Non-aqueous Energy Storage: rechargeable lithium batteries**

The lithium battery using non-aqueous electrolytes (organic solvents) is now the choice for portable electronic devices and is now challenging other battery technologies for hybrid vehicle applications. The most successful rechargeable lithium battery is the “rocking-chair battery” also called the “lithium-ion” battery. This battery uses an anode and a cathode, both of which can reversibly intercalate  $\text{Li}^+$  ions during charge/discharge cycles.

In the early 1990s, the well-established cathode materials for the Li-ion battery were limited to predominantly oxide-based materials such as lithium cobalt oxide ( $\text{LiCoO}_2$ ), lithium nickel oxide ( $\text{LiNiO}_2$ ), lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ), and lithium nickel-cobalt oxides ( $\text{Li}(\text{Ni}_x\text{Co}_{1-x})\text{O}_2$ ). Whereas lithium iron phosphate ( $\text{LiFePO}_4$ ) was introduced only around 1997 by Good Enough et al at U of Texas. The higher doctorate candidate explored alternative olivine-type phosphate cathodes with various cation substitutions in the early 2000s and brought insights into structural modifications by inserting lithium into NASICON frameworks and establishing its suitability for energy storage applications.

Alteration on the olivine-type phosphate cathode materials has been performed through synthetic strategies and metal ion doping. This resulted in reduced particle size with carbon (conductive) coating on the surface that improved the conductivity and specific capacity of the energy storage device reported in publications. The amount of defect has been reduced by a low concentration of dopants, choosing suitable synthesis methods, and optimized reaction conditions. The lattice defects owing to metal ion doping and its influence in improving the cathode performance of the olivine phosphates and lithium-free oxide materials have been established during this pre-PhD period. Even during the post-Ph. D., the candidate continued working on non-aqueous batteries and published around 7 articles that have been included in this thesis but the major focus after his Ph.D. studies was on aqueous solutions.

### Post-PhD work of the candidate (2007 – 2022)

#### **6.2. Aqueous Energy Storage: rechargeable lithium/sodium batteries**

The safety of lithium-ion (Li-ion) batteries using non-aqueous electrolytes is an important factor in their utility. This factor, along with a battery’s storage and multiple charge-discharge cycling capacities, exerts a profound influence on the acceptance of an energy storage device in the marketplace. The organic electrolytes currently in use have several safety issues including flammability and electrochemical instability. Present rechargeable Li-ion batteries fail rapidly at temperatures more than  $60^\circ\text{C}$  and may explode at  $80^\circ\text{C}$ .

For safety concerns, aqueous electrolytes are the natural choice in this field. Water is much cheaper than organic solvents, is easier to purify, and has fewer disposal and safety issues. The ionic conductivity of aqueous electrolytes is two orders of magnitude greater than that of some organic electrolytes, allowing higher discharge rates and lower voltage drops due to electrolyte impedance. Batteries with aqueous electrolytes do not need to be sealed tight against the entry of water vapor.

During overcharge, the decomposition products (oxygen and hydrogen) diffuse through the separators and are converted back to water at the electrodes. The main disadvantage of using an aqueous electrolyte is that the battery voltage is limited to  $\sim 2$  V. To offset the effects of this voltage limit, the storage capacity and the charge-discharge characteristics of the aqueous system must be significantly superior to those of the non-aqueous system. The candidate's post-PhD work has been focused on aqueous-based storage devices. The candidate has investigated a range of additives (biodegradable redox polymers, transition metals, and rare earth elements) in this thesis suitable for cathode materials to improve the cycle life of a battery device and its voltage profile against structural changes during cycling.

The cell  $\text{MnO}_2|\text{NaOH}|\text{Zn}$  showed an important new family of energy storage devices based on an affordable, globally available element, sodium. The innovative science in this part of the higher doctorate thesis involves reversible aqueous sodium electrochemistry at room temperature (against the available relatively high temperature, at which Na is molten). The electrochemical behavior of the Zn-MnO<sub>2</sub> alkaline cell showed that the NaOH electrolyte functions quite differently from our conventional cell, which uses a LiOH electrolyte. The absence of non-rechargeable products formed in NaOH cells leads to higher storage. When a cell containing NaOH is discharged, sodium is intercalated into the host MnO<sub>2</sub> structure and the mechanism appears to be quite identical to that of LiOH cell but the larger size of Na<sup>+</sup> ion limits the cyclability. Intercalation of sodium in an aqueous solution is confirmed through structural analyses of the discharged MnO<sub>2</sub> electrode. The aqueous sodium battery has potential interest for large-scale energy storage systems such as smart grid applications.

### **6.3. Electrochemical asymmetric supercapacitors (2014- 2022): Beyond Lithium**

Electrochemical capacitors are energy-storing devices capable of delivering high power with a long cycle life and excellent reversibility. In asymmetric supercapacitors, the charge is stored by both faradic and non-faradic mechanisms. Alternative energy storage mechanisms using abundant and environmentally friendly materials are critical for the development of renewable energy technology. In contrast to lithium resources, sodium sources are plentiful and cheap. Next to lithium, the electrochemical properties of sodium are the most attractive for battery and supercapacitor applications.

Research into sodium-ion (Na-ion) storage devices has been limited (in 2010) and the number of published reports on sodium batteries is small relative to those reporting Li-ion battery chemistry and associated successes. The reported sodium batteries are limited to non-aqueous solvents. Building on his previous successes in introducing and developing novel electrolyte systems in aqueous-based lithium technology, the candidate has developed an ambient-temperature aqueous sodium hybrid energy storage device that is capable to store the renewable energy supply. The novel asymmetric capacitor having olivine-type phosphate polymorphs (such as triphylite and maricite) as a cathode coupled with activated carbon (AC) as an anode has been discussed. This hybrid capacitor has shown potential for renewable energy storage applications using aqueous NaOH electrolytes owing to excellent structural and electrochemical perspectives. Most of the asymmetric devices existing in the literature used lithium metal phosphates and activated carbon as electrode materials. However, apart from the candidate, there is no work on the hybrid device made on sodium transition metal phosphates

(publications listed in #23, #26, and #50) in which maricite structured material was used as a material for electrodes.

Various transition metal oxides such as cobalt, nickel, and manganese have been extensively researched. Manganese dioxide ( $\text{MnO}_2$ ) is one of the most promising electrode materials with high specific capacitance. However, the candidate has shown that poor electrical conductivity and cycling stability limited its application. Phosphate-based electrode materials, especially the phospho-olivine owing  $\text{LiMPO}_4$  framework (where  $M = \text{Fe, Mn, Co, and Ni}$ ) are being recognized as attractive alternatives to oxide materials. The presence of  $(\text{PO}_4)^{3-}$  polyanions with a strong P-O covalent bond in the olivine-type structure provides a stable system when the electrode is fully charged. Hence, it seems attractive to use phospho-olivine of  $\text{LiMPO}_4$  as a cathode material. On the other hand, molybdate materials such as cobalt molybdate ( $\text{CoMoO}_4$ ;  $\text{NiMoO}_4$ ) are well known for excellent catalytic activity and good electrochemical properties and they are also environmentally friendly.

This thesis has also included research on the molybdate structural framework of the various metal cations and has shown their potential in energy storage materials. Among the metal cations studied in the molybdate framework, nickel molybdate exhibited great interest due to their high redox potential, low cost, low toxicity, and environmentally friendly. Cobalt oxides are another favorable candidate for supercapacitors as they possess a fast reversible redox reaction but are less electrochemically active. The phosphates provide a fundamental understanding of the electron transport of  $\text{Na}^+$  from aqueous solutions in new cathode materials while molybdate compounds ( $\text{CoMoO}_4$ ) that are seldom reported in the literature appear to have a better interest in the field of aqueous rechargeable batteries, in terms of safety, reliability, and potential for commercialization

In conclusion, the collection of research publications submitted for the D. Sc. Thesis represents a significant contribution to understanding the electrochemical activity of the different transition metal cations in different structures with different polyanions, in-situ polymer templated materials enhanced the storage capability. The synthesis route and the obtained nanostructure showed to influence the storage characteristics by as much as 30% resulting in a specific capacitance of  $135 \text{ F g}^{-1}$  at  $0.6 \text{ A g}^{-1}$  and an excellent energy density of  $31 \text{ Wh Kg}^{-1}$ . However, the non-templated synthesis route and the choice of ex-situ additives in the conventional solid-state reaction resulted in meager performance.

The key findings of this thesis are (i) the use of highly conductive aqueous lithium and sodium electrolytes and the conversion of an existing “Duracell” primary battery technology into a viable secondary (rechargeable) one. Please make a note that “Duracell” uses potassium hydroxide as an electrolyte and it remained primary, the differences are due to the size effect of potassium ion. (ii) the nature of additives in the electrode material increases the usable time of the battery in any appliance (iii) the choice of electrode materials (such as oxides, phosphates, and molybdates) dictates the storage performance and durability.

## 7. Outcomes

**The outcomes of this higher doctorate thesis could lead to new research directions, as stated below:**

(1) The production of a new olivine-type compound cathode material that is suitable for aqueous batteries, which have high energy capacity, long cycle life, and low cost.

(2) Identification of the mechanism of lithium intercalation into the host oxide materials demonstrated how fundamental science has immediate industrial applications. The fundamental understanding of the hypothesis involved in solid-state electrochemistry and repurposing the materials will reduce the carbon footprint of the battery manufacturer.

(3) Extensive studies on additives to the cathode material led to the development of low-cost, low-toxicity battery materials for potential application in storing renewable energy.

(4) A comprehensive understanding of the redox potential and electrochemical phenomena involved in non-aqueous and aqueous electrolyte batteries exhibited the basic scientific understanding of solid-state phenomena.

(5) A study on intercalation chemistry of a  $\text{Zn-MO}_2/\text{LiMPO}_4$  (where  $\text{M} = \text{Mn, Ni, or Co}$ ) system containing  $\text{LiOH}$  and  $\text{KOH}$  electrolytes paves the way for an aqueous rechargeable battery.

(6) Additives, including polymers with both a conducting polymer backbone and redox-active group, exhibit properties of both faradaic and non-faradic processes, which could be highly beneficial in electrical energy storage applications.

(7) The natural biodegradable polymers functionalized with molybdate nanoparticles having a uniform structure for aqueous rechargeable energy storage applications will enhance the electrochemical properties.

(8) The stated hybrid cell (battery cathode coupled with capacitor anode) will bring the increased high-rate capability to store energy generated from non-conventional energy sources and, with it, reduce dependence on natural gas and coal power plants.

(9) Novel sustainable materials play a key role in making further progress in the field of energy storage.