

# CHAPTER 6

---

## Conclusion and future prospects

---

### 6.1 Conclusion

This chapter presents the key conclusions derived from the thesis. Electrochemical capacitors based on the Earth abundant elements have the potential to complement in the current range of energy storage technologies. In this regard, aluminum can play an important role in the energy conversion systems as it is the third most abundant element in the Earth's crust. It has also other advantages such as eco-friendly, ability to transfer three redox electrons per cation, higher volumetric capacity than Li, K, Na, Mg, Zn and Ca. Electrolytes can greatly influence the stability of the devices and storage performances. Aqueous and gel electrolytes are safer in environment compared to the other flammable non aqueous electrolytes. The significant results and focus points of the thesis are concisely summarized chapter wise as provided below.

#### **Chapter 2: Gel electrolyte assisted $\text{Al}^{3+}$ ion capacitor with electrospun $\text{MoO}_3$**

This study highlights the significant improvement in electrochemical performance achieved by integrating reduced graphene oxide (rGO) with electrospun  $\text{MoO}_3$  for  $\text{Al}^{3+}$  ion capacitors, particularly in gel electrolytes. When compared to earlier works that focused solely on  $\text{MoO}_3$  or similar materials in aqueous electrolytes [1-5], the results here demonstrate a marked enhancement in both energy density and power density. Specifically, while  $\text{MoO}_3$  alone delivered a modest energy density of 8 Wh  $\text{kg}^{-1}$  and power density of  $7.5 \times 10^3$  W  $\text{kg}^{-1}$  at a current density of 10 A  $\text{g}^{-1}$ , the incorporation of rGO into  $\text{MoO}_3$  boosted these values to 43 Wh  $\text{kg}^{-1}$  and 104 W  $\text{kg}^{-1}$ , respectively. Moreover, electrolyte type played a crucial role in improving the electrochemical performances, long-term cycling stability and self-discharge voltage. For example, in gel electrolytes, the rGO/ $\text{MoO}_3$  cell retained 38 % of its charge potential after 21 hours, which is a substantial improvement over the  $\text{MoO}_3$  only cell in aqueous electrolyte, which only retained 5 % after 12 hours. This demonstrates that gel electrolytes, combined with rGO enhanced  $\text{MoO}_3$  offer superior performance, addressing the common issue of low stability seen in aqueous electrolyte systems. Overall, this work underscores the importance of material design and electrolyte selection in enhancing the energy storage capabilities of  $\text{Al}^{3+}$  ion capacitors and positions rGO/ $\text{MoO}_3$  composites in gel electrolytes as a promising candidate for next-generation energy storage devices.

**Chapter 3: Al<sup>3+</sup> ion capacitor with vanadium oxy-acetylacetonate and polyaniline**

This study explores the electrochemical properties of Polyaniline (PANI) and Vanadium-oxy acetylacetonate (VOA) as electrode materials in Al<sup>3+</sup> ion capacitors. It was found that PANI can interact Al<sup>3+</sup> ion in the positive potential region where as VOA is in negative potential region. The measured specific capacitance values 182 Fg<sup>-1</sup> for VOA and 282 Fg<sup>-1</sup> for PANI at a current density of 1 Ag<sup>-1</sup>, highlights the favorable electrochemical behavior of both materials. Interestingly, VOA exhibited pseudocapacitance, while PANI provided surface charge storage, suggesting different mechanisms contributing to their overall performance. For the first time, PANI and VOA combined in an asymmetric cell configuration, which demonstrates an excellent electrochemical stability and significantly enhanced performance within the potential range of 0 to 2 V. The cell delivered an energy density of 15 Wh kg<sup>-1</sup> at a power density of 750 W kg<sup>-1</sup>, indicating its potential for high performance applications. Compared to other studies [6-9], the results suggest that combining materials with distinct charge storage mechanisms, like pseudocapacitance and surface charge storage, can lead to improved electrochemical performance. The cell's good stability and efficiency in a practical voltage range make it a promising candidate for advanced energy storage systems.

**Chapter 4: Illustration of monovalent and polyvalent ion storage in vanadyl acetate**

This study investigates the ion storage capabilities of Vanadyl acetate (VA), in both aqueous and gel electrolytes. For the first time, electrochemical insertion of Na<sup>+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup> ions with VA was explored. It was found that VA demonstrated the best cycling stability for Na<sup>+</sup> ion storage in comparison to other ions. When employed in a symmetric supercapacitor configuration with gel electrolyte of composition 0.5 M Na<sub>2</sub>SO<sub>3</sub>/silica, it exhibited impressive electrochemical performance. The cell delivered a high energy density of 48 Wh kg<sup>-1</sup> and a power density of 1800 W kg<sup>-1</sup>, alongside excellent cycle stability, maintaining 60 Fg<sup>-1</sup> over 2000 cycles at a current density of 2 Ag<sup>-1</sup>. This performance, especially in gel electrolytes, underscores the potential of VA as an effective electrode material for energy storage devices. Compared to other electrode materials and electrolytes [10-14], VA's remarkable

performance with  $\text{Na}^+$  ions, particularly in gel electrolytes, positions it as a promising material for energy storage applications.

### **Chapter 5: A study on $\text{Al}^{3+}$ ion storage in hydrated vanadate and aluminium doped hydrated vanadate**

This study illustrates the  $\text{Al}^{3+}$  ion storage capabilities of hydrated vanadate (VOH) in both aqueous and gel electrolytes for the first time. The findings reveal that VOH exhibits impressive electrochemical performance for  $\text{Al}^{3+}$  ion storage. For example, in a 1 M  $\text{AlCl}_3$  aqueous electrolyte, VOH demonstrated a specific capacitance of  $434 \text{ Fg}^{-1}$  and maintained a stable capacitance of  $208 \text{ Fg}^{-1}$  over 100 cycles at a current density of  $1 \text{ Ag}^{-1}$ . When tested with gel electrolyte, VOH's performance was significantly improved, achieving a specific capacitance of  $772 \text{ Fg}^{-1}$  and a stable capacitance of  $236 \text{ Fg}^{-1}$  over the same 100 cycles at the same current density, highlighting the advantage of gel electrolytes in enhancing performance. Furthermore, the electrochemical study of aluminum-doped VOH did not result in any performance improvements compared to pure VOH, suggesting that aluminum doping does not enhance the capacitive behavior of VOH. In summary, compared with previous studies [15-16], VOH with gel electrolytes shows great potential as a high performance material for  $\text{Al}^{3+}$  ion storage, offering both high capacitance and excellent cycling stability.

### **6.2 Future Prospects**

This thesis focused on different electrode materials for the application of electrochemical capacitors. Some of the future outlooks of this thesis are as follows:

1. Different types of metal oxides, conducting polymers and vanadium based materials may be investigated for electrochemical capacitors using the Earth abundant metal ions.
2. Storage performances can be improved by making different composites materials.
3. Cycling stability can be enhanced using various gel electrolytes.

### **6.3 References**

- [1] Sangeetha, D.N., Bhat, D.K., and Selvakumar, M. h- $\text{MoO}_3$ /Activated carbon nanocomposites for electrochemical applications. *Ionics*, 25: 607-616, 2019.

- [2] Zhao, N., Fan, H., Zhang, M., Ma, J., Du, Z., Yan, B., Li, H., and Jiang, X. Simple electrodeposition of MoO<sub>3</sub> film on carbon cloth for high-performance aqueous symmetric supercapacitors. *Chemical Engineering Journal*, 390: 124477, 2020.
- [3] Cao, X., Zheng, B., Shi, W., Yang, J., Fan, Z., Luo, Z., Rui, X., Chen, B., Yan, Q., and Zhang, H. Reduced graphene oxide wrapped MoO<sub>3</sub> composites prepared by using metal organic frameworks as precursor for all solid state flexible supercapacitors. *Adv. Mater.*, 27: 4695-4701, 2015.
- [4] Elkholy, A.E., Duignan, T.T., Sun, X., and Zhao, X.S. Stable  $\alpha$ -MoO<sub>3</sub> electrode with a widened electrochemical potential window for aqueous electrochemical capacitors. *ACS Appl. Energy Matter.*, 4: 3210-3220, 2021.
- [5] Wang, F., Liu, Z., Wang, X., Yuan, X., Wu, X., Zhu, Y., Fu, L., and Wu, Y. A conductive polymer coated MoO<sub>3</sub> anode enables an Al-ion capacitor with high performance. *J. Mater. Chem. A*, 4: 5115-5123, 2016.
- [6] Wang, H., Lin, J., and Shen, Z. X. Polyaniline (PANi) based electrode materials for energy storage and conversion. *J. Science: Adv. Mater. and Devices*, 1: 225-255, 2016.
- [7] Eftekhari, A., Li, L., and Yang, Y. Polyaniline supercapacitors. *J. Power Sources*, 347: 86-107, 2017.
- [8] Ryu, K. S., Kim, K. M., Park, N. G., Park, Y. J., and Chang, S. H. Symmetric redox supercapacitor with conducting polyaniline electrodes. *J. Power Sources*, 103: 305-309, 2002.
- [9] Wang, X., Wang, S., Zhang, Y., and Du, H. Organic vanadium oxy-acetylacetonate as electroactive anode material with high capacity and rate performance for lithium-ion batteries. *Energy Mater.*, 53: 9701-9709, 2018.
- [10] West, K., Christiansen, B. Z., Jacobsen, T., and Skaarup, S. Vanadium oxide xerogels as electrodes for lithium batteries. *Electrochem. Acta*, 38, 1215-1220, 1993.
- [11] Khan, Z., Singh, P., Ansari, S. A., Manippady, S. R., Jaiswal, A., and Saxena, M. VO<sub>2</sub> nanostructures for batteries and supercapacitors: A review. *Small*, 17: 2006651, 2020.
- [12] Feng, J., Sun, X., Wu, C., Peng, L., Lin, C., Hu, S., Yang, J., and Xie, Y. Metallic few-layered VS<sub>2</sub> ultrathin nanosheets: high two-dimensional

- conductivity for in-plane supercapacitors. *J. Am. Chem. Soc.*, 133: 17832-17838, 2011.
- [13] Wen, N., Chen, S., Li, X., Zhang, K., Feng, J., Zhou, Z., Fan, Q., Kuang, Q., Dong Y., and Zhao, Y. Facile synthesis of one-dimensional vanadyl acetate nanobelts toward a novel anode for lithium storage. *Dalton Trans.*, 50: 11568-11578, 2021.
- [14] Li, Y., Zhao, Y., Wen, N., Zhou, H., Kuang, Q., Fan, Q., and Dong, Y. Solvothermal synthesis of organic-inorganic cathode vanadyl acetate nanobelts for aqueous zinc-ion batteries. *ACS Sustainable Chem. Eng.*, 11: 5105-5114, 2023.
- [15] Zheng, J., Liu, C., Tian, M., Jia, X., Jahrman, E. P., Seidler, G. T., Zhang, S., Liu, Y., Zhang, Y., Meng, C., and Cao, G. Fast and reversible zinc ion intercalation in Al-ion modified hydrated vanadate. *Nano Energy*, 70: 104519, 2020.
- [16] Liu, C., Neale, Z., Zheng, J., Jia, X., Huang, J., Yan, M., Tian, M., Wang, M., Yang, J., and Cao, G. Expanded hydrated vanadate for high performance aqueous zinc-ion batteries. *Energy Environ. Sci.*, 12: 2273-2285, 2019