Chapter 6

Summary and Future scope

6.1 Summary

The thesis aimed to develop novel structured metal-organic framework materials, especially the simple ones such as metal oxalates, phosphates to develop as pseudocapacitive electrodes to be applied as hybrid supercapacitor (HSC) mode where activated carbon can work as a negative electrode in bulk energy storage applications that can be utilized as uninterrupted power source in healthcare systems, households, etc. Materials such as RuO_2, MnO_2, and NiOOH become very important because they show Faradic pseudocapacitive storage in neutral or low pH aqueous electrolytes (KOH, KCl, and Na_2SO_4 media). Further intercalative pseudocapacitance is also evident in Nb_2O_5 and V_2O_5-based materials. In this thesis, we attempted to develop the high capacity pseudocapacitive electrode materials that can host guest ions through interactive diffusion inside the electrode material that enables high charge storage and fast power delivery to be applied for grid-scale electrochemical energy storage application. In **Chapter 1,** I presented the need for continuous power supply in healthcare systems and biomedical devices and materials developed especially for large-scale electrochemical energy storage devices and the need to develop strategic understanding and guidelines in terms of accessing redox properties with suitable crystal structure or lattice modification with novel doping or substitution to achieve the targeted electric and electronic properties and high surface active host lattice structure in the material for the desired application. I have also discussed the machine learning integration in data-driven novel electrode material screening for HSC and its performance prediction. **Chapter 2** deals with novel preparation methods for material synthesis and presents the know-how and detailed theoretical background of characterization techniques and electrochemical performance measuring techniques utilized in the dissertation. The chapter further explores the strategies utilized in machine learning research, including aspects such as data collection, feature engineering, model selection, and model evaluation.

We have shown in **Chapter 3** that the porous cerium oxalate decahydrate ($Ce_2(C_2O_4)_3.10H_2O$) is found to be a potential energy storage material partly because of the presence of planer oxalate anions ($C_2O4_2^{2-}$). In an aqueous 2 M KOH electrolyte, a superior specific capacitance of 78 mAh g^{-1}, equivalent to a capacitance of 401 F g^{-1} at a current density of 1 A g^{-1}, was observed within the potential window of -0.3 to 0.5 V. The dominant mechanism of pseudocapacitance found due to the extensive charge storage capacity of the electrode, which encompasses intercalative (diffusion-controlled) and surface-controlled charges. These charges are stored within the porous anhydrous $Ce_2(C_2O_4)_3.10H_2O$, with respective contributions of about 48% and 52% at a scan rate of 10 mV s^{-1}. In the full cell asymmetric supercapacitor (ASC) configuration, where porous Ce2(C2O4)3·10H2O serves as the positive electrode and activated carbon (AC) functions as the negative electrode, an operating potential window of 1.5 V yields a maximum specific energy of 96.5 W h kg^{-1}. This configuration also achieves a specific power of approximately 750 W kg^{-1} at a current rate of 1 A g^{-1}, alongside a high-power density of 1453 W kg^{-1}. Notably, the hybrid supercapacitor maintains an energy density of 10.58 W h kg^{-1} even at a current rate of 10 A g^{-1}, demonstrating impressive cyclic stability.

Highly porous, flake-type $KNiPO_4$ showed robust electrochemical performances in **Chapter 4** as a result of its open framework structure and active participation of the $Ni^{2+/3+}$ redox couple that results in superior pseudocapacitive intercalating charge storage in the aqueous KOH electrolyte. The $KNiPO_4$ electrode demonstrates a specific charge storage capacity of 168.5 mAh/g, corresponding to a capacitance of 935 F/g, when subjected to a current rate of 1 A/g within a potential window of 0.65V in a 2M KOH aqueous electrolyte. These electrodes exhibit remarkable long-term cycle stability, maintaining 87% of their initial capacity after 5000 cycles at a current rate of 10 A/g, alongside a coulombic efficiency of 95.1% following the same number of cycles. Additionally, in a full cell hybrid supercapacitor (HSC) configuration, where porous KNiPO4 serves as the positive electrode and activated carbon (AC) as the negative electrode, the highest energy density achieved is 200 Wh/kg, with a power density of approximately 819 W/kg at a current rate of 1 A/g. At an increased current rate of 10 A/g, the hybrid supercapacitor reaches an impressive power density of 7981 W/kg while retaining an energy density close to 75 Wh/kg, demonstrating excellent cyclic stability. The coulombic efficiency in full cell mode experiences only a 3.4% decline, with a capacity retention of 92.3% after 2200 cycles. The robust performance and extended cycle life of the electrode in full cells affirm the material's suitability for powering implantable biomedical devices.

In **Chapter 5** the Machine learning methodologies were employed to predict the capacitance of cerium-based supercapacitors. A thorough compilation of experimental datasets sourced from various publications was gathered to train the machine learning models, facilitating the evaluation of the importance of different electrode features. The findings reveal considerable variability in the performance of the algorithms assessed. Notably, the Voting classifier emerged as the most proficient model in this investigation, achieving a Precision of 85.80, Recall of 85.70, F1-score of 85.70, and an Accuracy of 85.744. Ensemble techniques, including Bagging and AdaBoost, enhance the performance of models by capitalizing on the advantages of multiple classifiers. Bagging (Bootstrap Aggregating) enhances stability and accuracy by generating multiple iterations of a training dataset through resampling and averaging the predictions from distinct models, which is especially advantageous for decision trees that are susceptible to overfitting. The ensemble methods, particularly the Voting classifier, exhibited superior performance, underscoring their efficacy in accurately categorizing materials into different. The experimental outcomes (~401 F g^{-1}, Grade B) significantly corroborate the predictive methodology presented in this chapter.

Chapter 6 summarises the entire study and concludes that the high-power density coupled with superior electrochemical energy storage capability and ample cyclic stability of developed framework-based electrode materials could be applied as the hybrid supercapacitor (HSC) electrode for energy storage applications and catering the power need of different healthcare systems. The machine learning-based study reflects its applicability in screening and predicting the performance of novel electrode materials.

6.2 Future Scope

Metal-organic frameworks (MOFs) exhibit a fascinating open framework architecture, wherein materials are formed by the combination of metal-containing components and organic linkers, utilizing robust bonds that ensure permanent porosity. In this project, the focus will be on the exploration of oxalates and phosphate-based framework electrodes that can have superior performances in aqueous electrolytes. On the other hand, Machine learning techniques have shown significant promise in enhancing both fundamental and applied research by extracting patterns from datasets and creating predictive models. Development of novel electrode materials for reversible anion intercalation battery type supercapacitors will enhance and strengthen the domestic battery industry and will certainly contribute to the "make in India drive" and will help to build indigenous (swadeshi) energy storage and delivery technology to fulfill our domestic energy needs and overcome the global imbalance in Energy demand vs. supply.

Further studies can be carried out are…

1. Performance study and operating voltage window optimization of the electrode in a different type of electrolytes.

2. Optimization of electrode-based hybrid supercapacitor assembly at the device level according to the energy requirements of different biomedical devices ranging from small-scale pacemakers to high energy-consuming ultrasound, MRI machines, etc.
3. Real life testing of full fabricated cell on biomedical devices
4. Further Nanoengineering of electrode materials to improve its surface and electronic properties
5. Comparison of the performance of the cell with other competitive technologies Search of alternate framework structured materials
6. Implementing feature engineering strategies in machine learning-based study to enhance model performance for performance prediction and novel material screening.