

**STRATEGIES TO DEVELOP MATERIALS FOR
LITHIUM STORAGE IN HIGH-PERFORMANCE
LITHIUM-SULFUR BATTERIES AND
PSEUDOCAPACITORS**

*A thesis submitted
in partial fulfillment for the degree of*

Doctor of Philosophy

by

HARITHA H.



**Department of Chemistry
Indian Institute of Space Science and Technology
Thiruvananthapuram-695547**

July 2020

ABSTRACT

With the rising demand for the hybrid electric vehicles and portable electronic devices, clean and sustainable alternative energy solutions have become indispensable to avoid environment pollution and to mitigate the energy crisis. State-of-the-art electrochemical energy storage systems, such as batteries and supercapacitors, are receiving more attention since they can efficiently store energy and synchronously work as power sources. Lithium-sulfur batteries (LSBs) and lithium-ion capacitors (LICs) are considered as the most viable options due to their high energy and power densities compared to conventional energy storage devices such as lithium-ion batteries and capacitors. This thesis work aims to address the challenges in the LSBs and LICs by the rational selection and development of materials, followed by their electrochemical evaluation. The detailed investigation on the developed materials for LSB and LIC were carried out and the description of the obtained results were presented in six chapters (chapter 2-7).

First chapter provides a general introduction on LSBs and LICs including its principle, limitations and state-of-the-art literature survey. More emphasis is given to aspects which are currently focused on the thesis.

In the second chapter, a highly permselective lithiated poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (LPAMPS) modified Celgard (CG) separator has been developed to improve capacity and cycling stability of LSB. The negatively charged $-\text{SO}_3^-$ groups present on the LPAMPS impart selective diffusion of lithium ions, at the same time repelling polysulfide anions via coulombic interactions. Besides, the LPAMPS@CG separator possesses excellent electrolyte wettability, interfacial contact and ionic conductivity. The Li-S cell (areal sulfur loading 0.9 mg cm^{-2}) containing LPAMPS@CG separator exhibited significant improvement in the electrochemical performance, with a high initial capacity of 1486 mAh g^{-1} and coulombic efficiency of $\sim 99\%$. It is noted that the LPAMPS@CG separator impedes shuttle effect by inhibiting PS crossover towards lithium anode, resulting a stable discharge capacity of 1060 mAh g^{-1} even after 200 cycles. Further, galvanostatic charge-discharge studies were carried out for Li-S cells with higher sulfur loadings of 2.5 and 4.2 mg cm^{-2} (This work was published in *Electrochimica Acta*, 2019).

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is one of the most investigated and extensively used conducting polymer with wide applications. In the third chapter, we propose a novel approach of decorating commercial separator by bifunctional lithiated PEDOT:PSS (Li^+ -PEDOT:PSS@CG). Owing to strong chemical interactions of PEDOT with insoluble polysulfides and the electrostatic repulsion between the negatively charged $-\text{SO}_3^-$ groups present in PSS and polysulfide anions, the Li-S cell (areal sulfur loading 3.9 mg cm^{-2}) with Li^+ -PEDOT:PSS@CG separator demonstrated a high initial discharge capacity of 1360 mAh g^{-1} and coulombic efficiency of $\sim 99\%$. It is notable that the Li^+ -PEDOT:PSS@CG

separator possesses excellent electrolyte wettability, interfacial properties and ionic conductivity, resulting in a stable discharge capacity of 1047 mAh g⁻¹ even after 300 cycles at 0.1 C with 77% capacity retention.

In the fourth chapter, we propose a carboxyl functional lithiated polymer, lithiated poly(acrylic acid-co-maleic acid) (LPAM) coated onto Celgard separator (LPAM@CG) for LSBs. The LPAM@CG separator effectively inhibits the shuttle effect of polysulfides, also promotes the diffusion of lithium ions. Particularly, the -COO⁻ groups present in the LPAM allow the rapid transfer of positively charged lithium ions while preventing the diffusion of negatively charged PS anions through coulombic interactions. Besides, the LPAM@CG membrane possesses good interfacial properties, ionic conductivity, excellent electrolyte wettability and remarkable electrolyte uptake. The Li-S cell (areal sulfur loading 4.1 mg cm⁻²) with LPAM@CG separator exhibits significant improvement in the electrochemical performances, with a high initial discharge capacity of 1213 mAh g⁻¹, an excellent rate capability of 637 mAh g⁻¹ at 3 C, and a good capacity retention of 957 mAh g⁻¹ (~79% over 300 cycles).

Micro and nanocrystalline LiCoVO₄ were synthesized via conventional solid-state reaction and hydrothermal reaction followed by calcination, respectively. In particular, nanocrystalline LiCoVO₄ demonstrated better lithium-ion intercalation properties benefited from its small crystallite size with highly exposed lithium-ion selective crystallographic pathways towards electrolyte. The nanocrystalline LiCoVO₄ electrode demonstrated high specific capacitance (929.58 F g⁻¹ at 1 A g⁻¹) and excellent cycling stability in aqueous electrolyte. On the grounds, we fabricated an asymmetric LIC (nanocrystalline LiCoVO₄//MWCNT) using aqueous and non-aqueous electrolyte. The LIC cell in non-aqueous electrolyte displays a specific capacitance of 67 F g⁻¹ at a current density of 1 A g⁻¹, and good reversibility with a capacitance retention of ~93% after 10000 cycles. The energy performance of the hybrid LIC cell reported here reaches 315.7 Wh kg⁻¹ (at a power density of 399.6 W kg⁻¹) (A part of this work was published in *ACS Applied Energy Materials*, 2018).

The nanocrystalline LiNiVO₄ was prepared via a hydrothermal route followed by calcination and used as a high-performance pseudocapacitive material for lithium storage in aqueous electrolyte. The electrochemical evaluation of LiNiVO₄ electrode in aqueous electrolyte demonstrated good capacitive performance with a specific capacitance of 406 F g⁻¹ at 1 A g⁻¹. The cycle stability test reveals exceptional capacitance retention of ~99% even after 1000 cycles owing to the unique structural feature which permits intercalation mechanism. Further, asymmetric LIC cell has been assembled with LiNiVO₄ as negative electrode and MWCNT as positive electrode in non-aqueous electrolyte. The assembled hybrid cells exhibited a high energy density of 255 Wh kg⁻¹ with maximum power density of 22325 W kg⁻¹ and excellent capacitance retention of ~92% after 10000 cycles at 5 A g⁻¹ (A part of this work was published in *Journal of Solid State Electrochemistry*, 2018).

In the seventh chapter, nanoscale LiMnVO_4 was synthesized by a facile hydrothermal approach and subsequent calcination. The intercalation pseudocapacitive lithium storage behaviour of the LiMnVO_4 electrode material was investigated in aqueous electrolyte, which demonstrated a high specific capacitance of 961 F g^{-1} at a current density of 1 A g^{-1} with a capacitance retention of $\sim 99\%$ after 1000 cycles. Further, an asymmetric LIC device has been fabricated with LiMnVO_4 as negative electrode and MWCNT as positive electrode in non-aqueous electrolyte. The device delivers a specific capacitance of 81 F g^{-1} (with a wide voltage window of 3 V), and good rate performance of 47 F g^{-1} at 30 A g^{-1} . Further, they show an energy density of 368 Wh kg^{-1} and a maximum power density of 24781 W kg^{-1} in association with superior cycling stability ($\sim 97\%$ capacitance retention after 10000 cycles at 5 A g^{-1}).

Finally, the conclusion part of this thesis presents an understanding of, how the logical selection of materials can meet the present energy and power demands and conquer the technical challenges associated with the LSBs and LICs.