

Preface

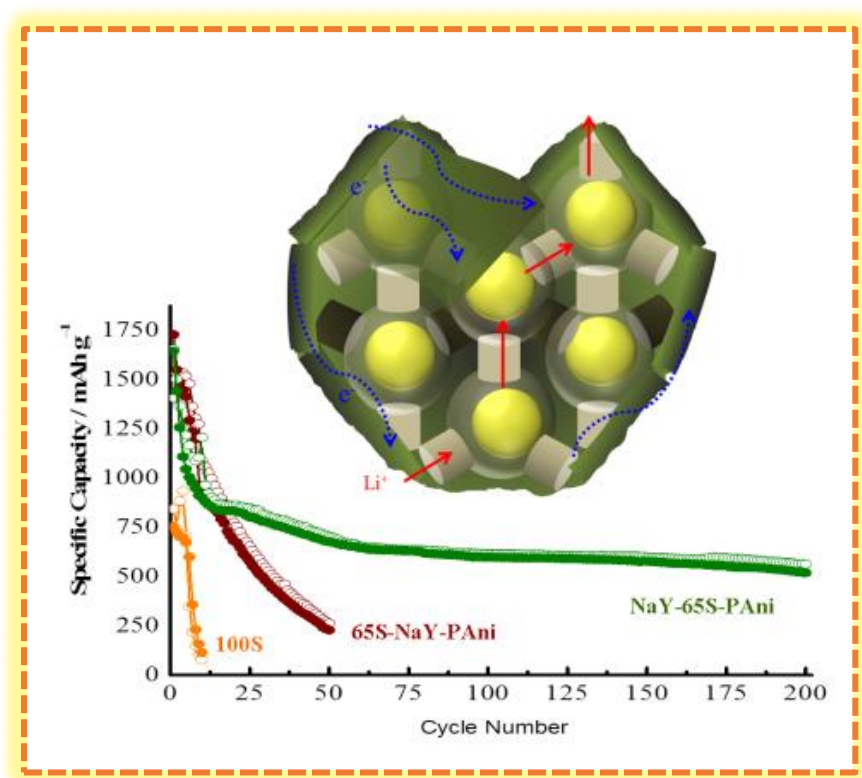
The present thesis discusses in detail various scaffolds for the precise encapsulation of chalcogens (e.g. sulfur-S and selenium-Se) and intermediate polychalcogenides (formed during the discharge/charge of the cell) for the use as high performance chalcogen-cathodes in alkali metal-chalcogen rechargeable batteries (metal: Li, Na). Apart from the chemical design aspects of the scaffolds, the thesis focusses in detail the state of the confined chalcogens (mainly sulfur) and it's critical influence on the energy storage mechanism of metal-chalcogen batteries. The various complex stages of the redox reactions occurring in the metal-chalcogen battery have been studied using various techniques including *in situ* monitoring of properties via a combined spectroscopic and electrochemical techniques. Bulk of the literature reports on the metal-chalcogen batteries focus only on the chemical design of chalcogen-cathode scaffolds. So, this thesis focusing on a combination of materials design and mechanism of energy storage is a paradigm shift from studies reported in the literature. Apart from metal-chalcogen batteries, which incidentally is the full cell configuration with chalcogen as the cathode and the alkali metal as the anode, the thesis also discusses a novel graphitic carbonitride as a possible alternative anode to conventional graphite in full Li-ion cells. The 2D graphitic carbonitride is interesting as it is a 2D-electron and a 3D-ion conductor. It's potential as an anode is demonstrated for the first time in a full cell Li-ion configuration with standard lithium transition metal oxides as cathodes. The thesis comprises of *six Chapters* and brief discussion of the contents and highlights of the individual chapters are described below:

Chapter 1 briefly reviews the element based full cell batteries specifically with respect to the chalcogen series elements of the periodic table. Recent trends in battery research emphasizes the utilization of elements in energy storage over the prevalent intercalation compounds

employed in the Li-ion batteries. Extensive research and development in Li-ion intercalation systems has shown that there is a limitation on the energy density associated with the intercalation compounds. One of the proposed strategies for the development of systems with higher energy densities is to replace high molecular weight compounds by low atomic weight elements. This straightaway increases the energy densities significantly compared to the intercalation chemistry. If the reversible redox chemistry involves a multielectron process, then the energy densities will be even higher reaching one order magnitude higher than the intercalation compounds. Apart from the chalcogen battery and chalcogen-electrodes, the chapter introduces the conventional Li-ion battery, drawbacks associated with the commercial graphite electrode and possible alternatives. The Chapter ends with discussions of the prime characterization techniques used for both *in situ* and *ex situ* studies.

The major challenge of Li-S battery is to preserve the sulfur and also confine the intermediate polysulfides inside the non-electroactive host. **Chapter 2** discusses the efficient confinement of sulfur and polysulfides within a non-carbonaceous ion conducting zeolite (NaY) host wrapped inside electronically conducting polyaniline (PAni) sheaths as a low-cost, high performance cathode for rechargeable lithium-sulfur battery (Scheme 1). The sulfur is observed to be confined within the intra-crystallite and interstitial spaces of the NaY zeolite and the (PAni) sheaths and they prevent leakage of sulfur (and polysulfides). Additionally, this NaY-PAni assembly provides distinct pathways for electrons (through PAni) and ions (across PAni sheaths and through NaY channels) during battery operation. Raman spectroscopy (and EPR) confirms the presence of sulfur in diradical S_8^* chain forms in the cylindrical pores of NaY, which is probably the very first result demonstrating the stabilization of sulfur in its metastable state under confinement at ambient conditions. The NaY- x S-PAni is characterized by several methods:

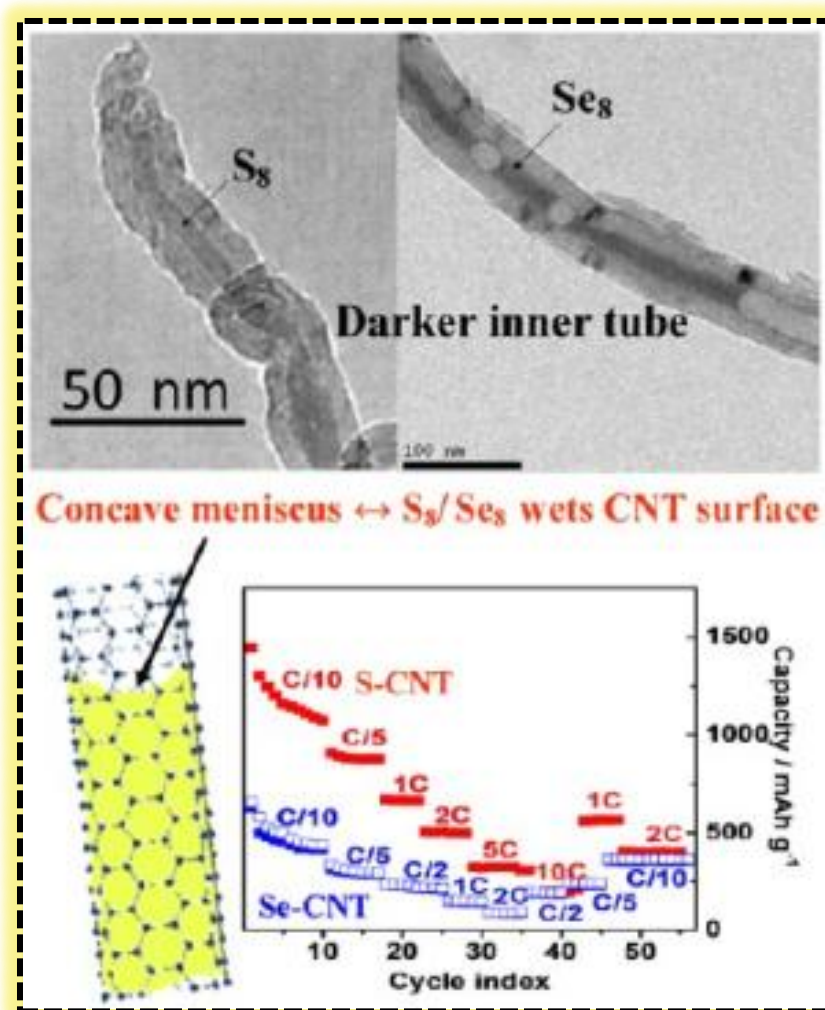
powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), ac-impedance spectroscopy and dc current-voltage measurements are performed to evaluate conductivity of NaY-*x*S-PAni cathode. A comparative electrochemical study, such as cyclic voltammetry, galvanostatic charge-discharge cycling, is undertaken to demonstrate most useful composition of NaY-*x*S-PAni in obtaining an optimized Li-S battery.



Scheme 1: Schematic depiction of the efficient confinement of sulfur and polysulfides within a non-carbonaceous ion conducting zeolite (NaY) host wrapped inside electronically conducting polyaniline (PAni) sheaths as a low-cost, high performance cathode for rechargeable lithium-sulfur battery. The performance of the Li-S battery depends on the extent of sulfur loading inside the zeolite-host and is superior to the unconfined sulfur nanoparticulate S-cathode.

In the previous chapter the encapsulation of sulfur in commonly occurring zeolite viz. NaY using a novel pressure induced encapsulation technique was discussed. In *Chapter 3*, the

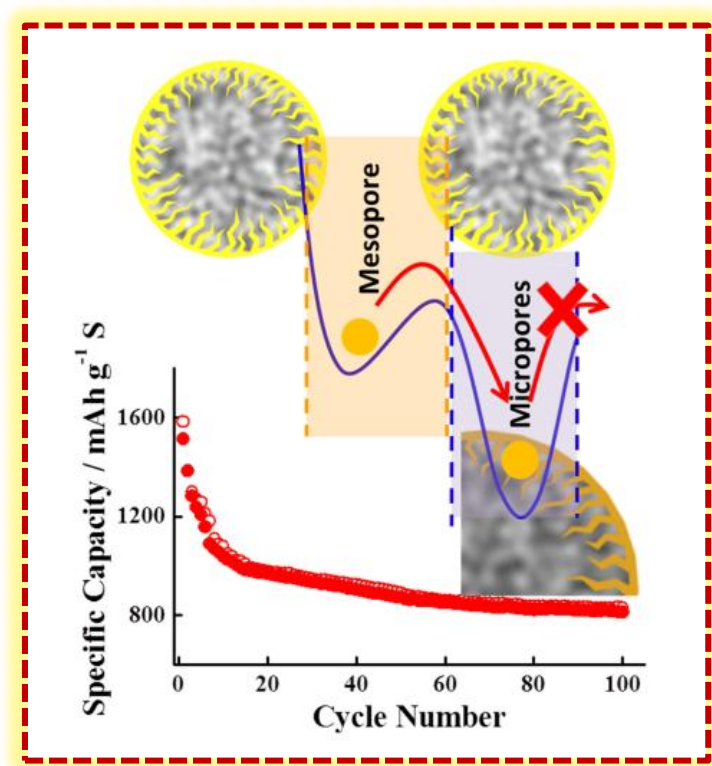
confinement of the chalcogens viz. sulfur and selenium inside multiwalled carbon nanotubes (MWCNTs) using the same procedure employed in chapter 2. The main motivation here has been to quantify exactly and precisely the location of the chalcogens with respect to the MWCNT. This is a long-standing problem which incidentally is also co-related to the Li-S battery performance. Confinement lead to lowering of the surface tension of molten S/Se resulting in superior wetting and ultra-high loading of the CNTs. Higher than 95% of the CNTs are loaded and very high loading, nearly 85% of S/Se inside the CNTs is achieved. The chalcogens loaded CNTs are systematically characterized using XRD, FTIR and Raman spectroscopy, HRTEM and EFTEM microscopy. When assembled at a very high areal loading ($\sim 10 \text{ mg cm}^{-2}$) in the Li-S/Se battery, the S/Se-CNT cathodes exhibited very stable cyclability and high values of specific capacity at widely varying operating current densities (0.1-10 C-rates).



Scheme 2: Illustration of the precise confinement of the chalcogens viz. sulfur (S) and selenium (Se) inside multiwalled carbon nanotubes (MWCNTs, cut-open on both ends) using a pressure induced capillary filling method for operation in Li-S and Li-Se rechargeable batteries. The S/Se entrapped inside MWCNTs show excellent rate capability at widely varying current densities. The chalcogen cathodes also show good recovery of specific capacities following the transition from high low current densities.

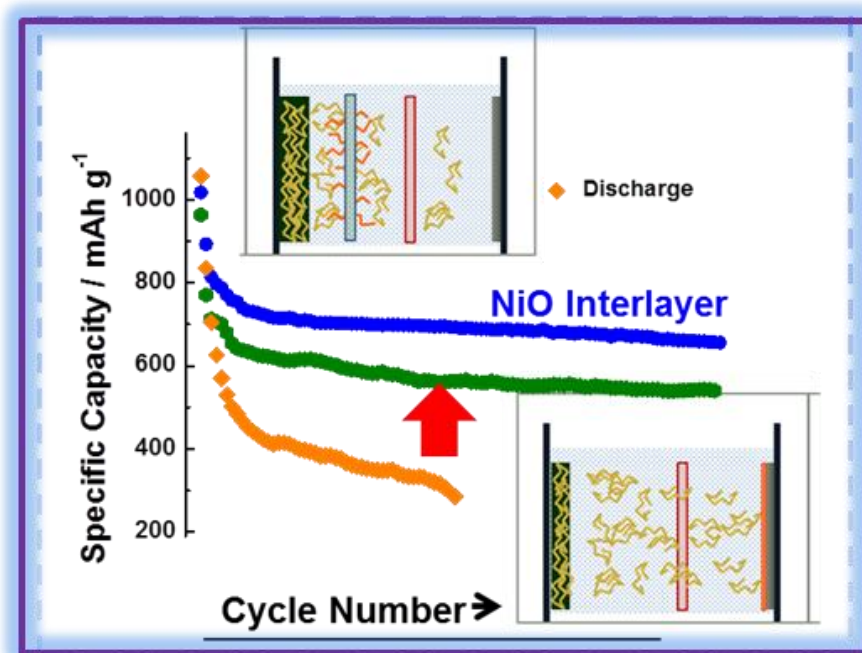
In *Chapter 4*, a high surface area porous carbon synthesized using a sacrificial-template assisted synthesis protocol, is demonstrated as a host for the confinement of sulfur for use in Li-S and intermediate temperature (25-70 °C) Na-S rechargeable batteries. Unlike the MWCNTs discussed in the previous chapter 3, which possess a fairly trivial configuration of nearly uniformly sized pores, the hierarchical porous pillared carbon host comprises of an intricate

network of mesopores and micropores. These provide a landscape of sites with varying strength of interaction with sulfur which is expected to be beneficial for stronger confinement of polysulfides. The amount of sulfur (and associated polysulfides) inside this carbon host is predetermined by the host structural characteristics rather than by the loading protocol. The mesoporous-microporous carbon led to sulfur content in excess of 70%. While the bulk of S (and polysulfides) are stored inside the mesopores of the carbon host, the micropore apart from sulfur storage strongly contributes towards the modulation of sulfur flux during charge-discharge cycling. The S-C cathode exhibited remarkable cycling and rate capability with Li and also against Na at intermediate temperature (25-70 °C). This result is a paradigm shift from the conventional Na-S electrochemistry which is known to efficiently work only at elevated temperatures, in the temperature range starting from excess of 100 °C to 300 °C.



Scheme 3: A high surface area porous carbon synthesized using a sacrificial-template assisted synthesis protocol as a host for the confinement of sulfur for use in Li-S and intermediate temperature (25-70 °C) Na-S rechargeable batteries.

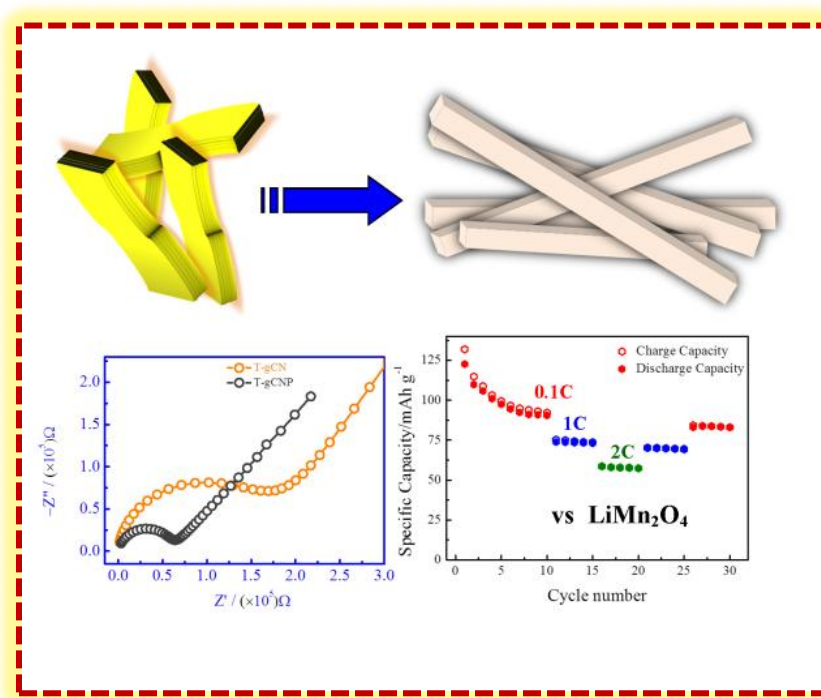
Majority of the work related to Li-S batteries focuses on design of suitable hosts for complete retention of sulfur and various polysulfides such that their presence in the electrolyte is negligible. Chapters 2-4 have dealt with this very important point in great detail. In *Chapter 5*, a pseudocapacitive metal oxide as interlayer for efficient anchoring of polysulfide was employed. This work demonstrating the use of Ni(OH)₂ and NiO as an interlayer is rare. The strategy employed here is targeted towards maximum usage of the host geometrical dimensions leading to drastic enhancement in the sulfur loading. Oxide based compounds exhibit superior ability to hold the lower order polysulfides at the cathode by bonding interactions thereby providing additional encapsulation measures at the cathode as well as efficient protection of the anode. In this chapter, it was shown that the use of Ni(OH)₂/NiO interlayer introduces an alternative pathway for sulfur reduction and oxidation. This simultaneously caused a phenomenal reduction in the shuttle effect especially at extremely high loadings of sulfur ($\approx 15 \text{ mg cm}^{-2}$). With the incorporation of the NiO/Ni(OH)₂ interlayer a massive improvement in the cyclability and rate capability performance for the conventional S/C composite cathode is observed vis a vis the battery with no interlayer.



Scheme 4: Improved Li-S battery configuration with a pseudocapacitive metal oxide near the S-cathode as the interlayer for efficient anchoring of polysulfide. The Li-S battery with NiO as the interlayer is observed to exhibit the best performance to the battery with Ni(OH)₂ as the interlayer and with no interlayer.

There is still a sustained effort to explore and develop new electrode materials for Li-ion rechargeable batteries. Presently, materials exploration not only focuses on the enhancement of Li-ion battery performance, but also targets to make them cheaper and safer. This expectedly will make them market competitive against established battery chemistries. Graphitic carbon nitride (abbreviated gCN), which has emerged as an important photon harvesting material, is demonstrated in *Chapter 6* as a potential efficient and cost effective alternative anode for Li-ion cells. The gCN, synthesized here from pyrolysis of thiourea, possess a unique intrinsic crystal structure (T-gCN). The layers in T-gCN, which comprise of an interconnected network of melem units, contain triangular shaped holes. The intercalation of Li⁺ ions in the densely packed layered structure of T-gCN (lithiated T-gCN) results in a 4-fold increase of ionic conductivity compared to the non-lithiated T-gCN. The remarkable enhancement in the ionic conductivity has been

attributed to the unique 3-D ion transport, i.e. ion transport in the interlayer region (*a-b*) and through the triangular holes in the layers (*c*-direction). The T-gCN when treated with an acidified dichromate solution disintegrates in to filaments, which on prolonged stirring self-assemble in to pillar-like gCN structures (T-gCNP). The T-gCNP exhibited an even higher ionic conductivity, being one order higher compared to the T-gCN. The T-gCN and T-gCNP deliver modest specific capacities however, when coupled with cathodes such as LiFePO_4 and LiMn_2O_4 in a full Li-ion cell delivers stable cyclability and good current rate capability over widely varying current values. This is remarkable as the total carbon percentage in T-gCN /T-gCNP is low, average being only 31%. The superior performance of the full cell is attributed to the unique structure which provides fast electron (in 2-D) and ion transport pathways (in 3-D) necessary for operation at high currents.



Scheme 5: 3-D Li-ion conducting pillar-like graphitic carbonitride (gCN), synthesized from pyrolysis of thiourea, as a novel alternative hetero-doped carbon anode for practical Li-ion batteries. The gCN showed good performance in Li-ion cells with lithium manganese oxides (LiMn_2O_4) and lithium iron phosphate (LiFePO_4) cathodes.