

## ABSTRACT

A great deal of research work is being focused on the rational design and development of solid state proton-conducting materials due to their applications in various fields such as membranes in fuel cells, electrochromic devices, humidity sensors, storage and separation of gases and in other related functional areas. Generally these materials are permeable to protons that are generated in the anodic compartment of the electrochemical device and allow them to migrate towards cathodic side, besides physically separating the electrodes. Traditionally, Nafion based materials are used as solid electrolyte membranes for conventional polymer electrolyte membrane fuel cells. The main drawbacks of these membranes are their high cost, lower working temperatures, loss of conductivity at low humidity condition, high fuel cross over etc. Such difficulties have lead to the development of alternate proton conducting materials.

Nowadays, a lot of modified materials are being developed for proton conducting applications. Recently, Coordination Polymers (CPs) and Metal Organic Frameworks (MOFs) are also identified as alternate proton conducting materials and are extensively researched for their solid state proton transporting characteristics. The advantageous aspects of CPs and MOFs such as possibilities of exploring the solid state structures, well defined pores, relevant hydrogen bonded pathways for efficient proton conduction, wide scope for design have thus fuelled the activities in this domain. Present thesis investigates facile crystallization and characterization of environmentally benign CPs and MOFs involving bio-relevant ligands and examining their proton conducting applications.

The thesis consists of five chapters; First chapter begins with the precise introduction about fuel cells, chemistry of coordination polymers, types and its familiar application in various fields. In addition, this chapter describes the basic theories of involving electrochemical impedance spectroscopy, a tool that is being used to characterize the ionic electrolyte performances of materials. This chapter also provides various experimental methods of crystallization of CPs and MOFs with special emphasis on reactive crystallization. Particularly, a brief review on the recent developments involving the CPs and MOFs as solid proton electrolytes is discussed at the end of this chapter.

Chapter two presents the objectives of the work. A part of the objective is to screen and identify the previously reported CPs and MOFs involving bio relevant ligands that are structurally characterized, but unnoticed for proton conducting applications. Hence exploring environmentally benign routes, for crystallization is also a primary concern. Similarly, designing of newer metal carboxylates and imidazole based bio-CPs and bio- MOFs and examining their proton transporting capabilities is also an another aspect of the chosen work.

Chapter three projects the solid state proton transport characteristics of  $[\text{Cu}(\text{tart})(\text{H}_2\text{O})].2\text{H}_2\text{O}(1)$  &  $[\text{Ca}(\text{tart})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}(2)$ . They are known to exhibit relevant structural features and other physical characteristics. However, the proton electrolyte performances of these complexes have not been explored previously and thus the present work highlight the usefulness of these simple and environmentally non-hazardous frameworks for proton conduction applications. A simple and scalable reactive crystallization method has been identified for complexes 1 & 2. Structural authenticity and reproducibility of the complexes have been confirmed using cell parameter analysis from the single crystal X-ray

diffraction analysis. Bulk purity of the materials, prepared according to the new route, is ascertained by elemental analysis & PXRD analysis. As anticipated, both 1 & 2 show the characteristic Nyquist plots in the AC impedance studies, exhibiting significant proton conductivities in the order of  $10^{-5} \text{ S cm}^{-1}$  under 100% RH condition at 25°C. The magnitudes of conductivity are quite comparable to those of the other proton conducting electrolytes reported in the literature. The  $E_a$  value determined, suggests that the Grotthuss mechanism of proton conduction is obeyed during the process.

Chapter four describes the synthesis, X-ray structural characterization and the proton conduction evaluations of two new supramolecular zinc frameworks,  $[\text{Zn}(2\text{-MeBIM})_2(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$ (3) and  $[\text{Zn}(2\text{-MeBIM})(\text{Pht})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (4) (where, 2-MeBIM = 2-methyl benzimidazole, OAc = acetate anion and Pht = dianion of phthalate). From the structural analysis, it has been observed that the complex 3 is a discrete molecule, composed of OAc and 2-MeBIM ligands, besides with lattice water molecules. Whereas, the complex 4 has been identified as a 1D coordination polymer, due to the  $\mu_2$ -1-6 bridging action of phthalate ligand. In complex 4, each Zn (II) on the chain, further possesses one coordinated water, and one 2-MeBIM. The water molecules of the complexes 3 & 4 are extensively engaged in the construction of hydrogen-bonded networks with the coordinated moieties of the ligands, thus providing 3D status to the solid state structure of the complexes 3 & 4. Thermal analysis also has been performed to distinguish the behaviour of lattice and coordinated water molecules of complexes 3 and 4. It is to be noticed that the complex 4, exhibits the carboxylate–imidazole–zinc triads as well, like found in many zinc enzymes. Supramolecular features of both the 3 & 4 resemble those of the carbonic anhydrase, involved in proton transport based mechanistic

events in nature. Hence both the complexes 3 & 4 are regarded as bio-inspired models for proton conducting applications.

Moreover, chapter four also describes an one step room temperature crystallization of another zinc based supramolecular complex  $[\text{Zn}_3(\text{btc})_2(\text{H}_2\text{O})_{12}](5)$  (where, btc = 1,3,5 benzenetricarboxylic acid) by reactive crystallization method. As the ligand is highly bio compatible, the complex is environmentally less hazardous. This complex also, like those of complex 1 & 2, is known to possess very relevant structural features for proton conduction, but remained unexplored in this line, and thus included in the present work. Reactive crystallization route has been successfully employed for the preparation of complex 5. The structural integrity and authenticity of complex 5, which is prepared according to the new method, has been confirmed using cell parameters analysis by single crystal X-ray method. The bulk purity of complex 5, has been confirmed using PXRD and elemental analysis.

AC impedance studies on 3, 4 & 5, carried out under humid conditions reveal that the complexes 3, 4 and 5, are efficient solid state proton electrolytes, exhibiting the magnitude of conductivity in the order of  $10^{-5} \text{ S cm}^{-1}$  under ~100% RH condition at 25°C, which is comparable to the level of other classical proton electrolytes. Temperature dependent proton conduction studies have been performed in order to identify the activation energy and mechanisms of the process, based on which Grotthuss conduction mechanism has been identified. The results highlight that the complexes 1–5 are efficient proton electrolytes in the solid state under fully humidified conditions. Hence, the work strongly suggests that the bio- CPs and MOFs, or other bio-mimicking models, which are routinely studied for various other functional characteristics, could very well explored for their proton transporting applications as well.