Chapter 1. Introduction and Literature Survey

1.1 Introduction

Alkali sulfate is a series of general molecular formula M_2SO_4 where M is a monovalent element or group ($M^+ = K^+$, Cs^+…and/or NH^+_4). These sulfate salts are a rather interesting series of compounds with unique properties arising from the ability to incorporate protons and some elements comparable to sulfur like phosphorus into a crystalline structure[1-7].

Ammonium sulfate is an interesting member in alkali sulfate series, which is commercially available, as a proton-conduction electrolyte for fuel cells systems where ammonium ions start free rotations at 440 K with activation energy E_a=0.35 eV[8-10]. Ammonium sulfate is known to undergo a first order ferroelectric phase transition at -50°C. The nature of this transition is rather unique and it has features, which are different from those of usual ferroelectrics. The peculiarity of this transition has been the subject of a large number of investigations, which include structural, mechanical, dielectric, magnetic resonance as well as infrared and Raman spectral studies [11-15].

Another interesting member in alkali sulfate series is cesium sulfate. The general feature of Cs_2SO_4 structure has been refined by three-dimensional X-ray diffraction. Accordingly, the crystals are orthorhombic, space group P_{nam} with a cell dimensions: a = 8.239, b = 10.944, c = 6.258 Å [16]. Structure analysis of molten Cs_2SO_4 showed that Cs atoms occupy the corner sharing sites with an average Cs-O distance of 3.07 Å and the others occupy the face sharing sites with an average Cs-O distance of 3.48 Å [17]. Matrix isolation infrared spectroscopic

studies of Cs_2SO_4 and their dimeration in nitrogen matrices indicated that the symmetry of these molecules is D_{2d} and the author assigns these bands to dimmers of D_{2h} symmetry [18].

The other member in alkali sulfate series is potassium sulfate. The crystal structure of the room-temperature phase is orthorhombic, space group P_{mcn} with lattice constants a = 5.76, b = 10.07 and c = 7.48 Å [19]. The high-temperature phase is hexagonal, space group P_{mmc}, with lattice constants a = 5.90 and c = 8.11 Å at 630°C [20]. This transition has been widely studied using differential thermal analysis (DTA), X-ray, electrical conductivity, dielectric constant, specific heat, IR and Raman scattering methods [21-25].

An incredible amount of research investigations have appeared the last 10 years in the field of hybrid materials indicating the growing interest of chemists, physicists and material researchers. They exploited this technical opportunity for creating materials and devices with the benefits of the better of the two worlds namely inorganic and organic [26-36]. Hybrid materials can be classified in many ways depending on the relative composition of the ingredient components, the nature of chemical interactions between them. The chemical composition is one of the most important parameter since its variation leads to hybrid materials with distinctive physico-chemical behaviors and profoundly different properties. Thus, there is a lot of interest in elucidating the fundamental principles governing the functionalization and dispersion of dielectric modifiers in organic polymer matrices and the properties of the resulting hybrid material. Two kinds of hybrids materials can be synthesized [37]:

Class I: Includes hybrids systems where one of the components (organic or inorganic) is entrapped within a network of the other component. In

that case there is a presence of weak-type interactions between the hosting network and the entrapped species. This class is essentially based on Van der Walls, Hydrogen bonding or electrostatic interactions.

Class II: Gathers the hybrids materials where the inorganic and organic parts are chemically bonded by a covalent or iono-covalent bonds. The frontier between both classes is not always simple and we can eventually have hybrids systems with class I and class II characteristics.

Nickel metal hydride batteries [38-51] (Ni/MH) are environment-friendly and have excellent performance such as high energy density, high power density, high rate capability, high safety, long cycle life and so on, which leads to various applications such as portable electric appliances, electric tools and pure and hybrid electric vehicles. However, since a conventional KOH aqueous electrolyte solution can freeze in cold climates and dry out on the way of charge-discharge cycles, it is significant to use a solid electrolyte instead of the liquid electrolyte.

Several groups investigated the Ni/MH batteries using solid electrolytes [51] although; inorganic solid electrolytes for Ni/MH battery have not been investigated in recent years because of their low proton conductivity. Thus, there is a lot of interest in recognizing the electrochemical behavior of Ni/MH battery using inorganic solid electrolytes show relatively high proton conductivity.

The aim of the present study:

When decreasing non – renewable energy supplies and increasing environmental concern about pollution are taken into consideration, there will be much from scientific community to offer by way of solutions. Indeed, viable, long term solutions to meet our energy needs while

maintaining the quality of our environment will increasingly depend on electrochemical processes within and at the surface of solids. Fuel cells and batteries are all devices in which energy storage or conversion relies on a coupling of chemical, thermal and/or electrical phenomena within the solid state. The direct coupling and elegant coupling of these phenomena is responsible for high efficiencies in fuel cells and batteries.

The unique properties of alkali sulfate arising from the ability to incorporate protons and some elements comparable to sulfur like phosphorus into it's crystalline structure can make them a promising solid electrolytes for fuel cells and nickel – metal hydride batteries. This paid to uncover the physical parameters of alkali sulfate under some modifications. Therefore, the present work aims to perturb the bonding scheme of alkali sulfates of M_2CO_3 : H_2SO_4 : H_3PO_4 system with mole ratio at 2:1:1 respectively, by introducing interstitial hydrogen into the structure and replace a significant number of sulfur atoms with the questionable phosphorus in order to improve the electrical properties. In addition, the study extends to synthesize hybrid materials poly methyl methacrylate / alkali sulfate electrolyte composites, with enhanced conducting properties. However, the broad objective is to develop a firm understanding of the correlation between the structure and the properties of alkali sulfate based solid electrolyte, so as to allow the engineering of these compounds with the desired properties for the application in the field of electronic elements.