**DETERMINATION OF SUPERIONIC CONDUCTIVITY IN LITHIUM SULPHATE/SILVER SULPHATE COMPOUNDS USING ELECTRICAL CONDUCTIVITY**

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**ABSTRACT**

Miniaturization of electronic devices in recent times has spun a lot of research into slid state energy sources that are compact and have high energy densities. At room temperature these materials are poor conductors, but at elevated temperatures their conductivity increases by several orders of magnitude, thus superionic conductivity sets in. in this work, pure samples of poly crystalline lithium and silver sulphate were subjected to varying temperatures up to 600OC from room temperature. The transition temperatures for observation of superionic conductivity were measured together with the character of the resistance and activation energies for the conduction. The silver sulphate sample was subjected to repeated thermal cycles and the same measurement was taken. Superionic conductivity was observed in the silver sulphate sample but not in lithium sulphate.

**1.0 INTRODUCTION**

Current trends in research have been geared towards the search for compact energy sources in the solid state, i.e. solid state electrolytes. There is a lot of advantages which solid state energy sources have over liquid electrolytes, the least of which are compactness, versatility and mobility, to name but a few. These materials can be used as anode/cathode materials for rechargeable batteries and also as electrolyte. These rechargeable batteries are found in devices like laptop computers, mobile phones, among others. The batteries are commonly based on lithium compounds (called lithium ion batteries). They derive their conductive properties from ions rather than electrons, mainly and it is normally achieved at higher temperature, during which superionic conductivity sets in.

However, the lithium compound-based batteries have a lot of problems (Weller, 2001; Vitioo, 1999) current research is therefore geared towards getting materials that will be cheaper for both electrodes and electrolytes; which are stable; environmentally friendly; have high charge capacity/density; longer cycling life and most importantly have higher conductivity at room or ambient temperatures (Hull et al, 2003; Vitioo, 1991, Weller, 1991). The most widely used materials are currently, LiCoO2 and have been associated with one or more of the above problems. There is the need to improve at the most fundamental level, the electrical/thermal properties of these compounds; hence the importance of the research in lithium/silver sulphate (which is a better conductor but expensive). Researchers have carried out different works on these compounds, for example, for application in gas sensors in environmental pollution (Teterycyz, et al, 1998, 2000). The Arrhenius plot (InσT Vs I/T) is used for the analyses of conductivity of ions. This has been adopted in this work. Conductivity is expressed as:

σ = /Texp(-Ea/T)

= preexponetial factor

= activation energy for the conduction and T is the absolute temperature.

Typical electrical conductivities are in the range 10-2-10-3Ω-1m-1 (Nalbadayan and Rao, 2003). In the present work report is presented on one sample of pure lithium and silver sulphates of differing masses (Ahmadu *et al*, 2004). Pelletized power samples have been used. The principal objective of the research is to observe superionic conductivity and the consequent transition temperatures fro both samples and the effect of thermal cycles on the transition temperatures for silver sulphate. In subsequent research it is intended to subject lithium sulphate to thermal cycles too. Explanations are based on literature findings.

**2.0 EXPERIMENTS**

The samples of lithium sulphate and silver sulphate chosen for the investigations were of high peruity of not less than 99% assay (analytical reagents) supplied by BDH. The samples were prepared at CERT (Centre for Energy Research and Training, Zaria). The powder samples were ground thoroughly in the appropriate proportion with binder of appropriate quantity added to enhance cohesion including adequate pressure during pelletization to ensure proper cohesion.

The thicknesses of the samples were between 1 – 3mm and their diameter 2.4 – 2.5cm, their masses were approximately 2.500 – 3.00g. Aquadaq (Achensen 331290) was painted on both sides of the surface to enhance electrical contact. Aluminum electrodes were used. Also a versatile heater (oven) was designed and a special ceramic core was constructed for the coil at IDC (Industrial Development Centre, Zaria). Asbestos rope was used for shielding of the nichrome tape which was used for the windings. The samples were held between two halves of aluminum holders constructed at IDC and physics Department A.B.U. Zaria. This was painted with Aquadaq at the point of contact with the sample. D.C. conductivity measurements were then carried out at different temperatures starting from room temperature. Preliminary results are for pure lithium and silver sulphates. Power supply unit with maximum voltage 60V at 3A (Marconi Instruments); a Variac (0.260V, 8A); temperature controller (supplied by APLAB, India, 12000C, max); Digital Multimeter (Gold Model, WG022) and Copper/Constantan thermocouple were used for the measurements. Acetone and deionized water were used for the measurements. Acetone and deionized water were used as cleaning agents.

**3.0 RESULTS AND DISCUSSIONS**

The material investigated revealed high electrical conductivity at elevated temperatures, particularly Ag2SO4. It was difficult to obtain a stable lithium sulphate (Li2SO4) sample due to cracking/shorting of sample at moderate temperatures (e.g. 200 – 4000C) long before superionic conductivity sets in. sample preparation plays an important role in ionic transport (Sunandana and Kumar, 2004). Lithium sulphate also showed high degree of polarization due to its hygroscopic nature. This affects the onset of superionic conductivity which has been observed at ~ 6960C (Teteracyz *et al*., 1998) due to its extremely high resistance at low temperatures. Polarization has been observed in d.c conductivity measurements (Blakely, 2003; Corish *et al*., 1977). The Arrhrenius plot for pure lithium sulphate is shown in fig. 1. The activation energy calculated at the lower temperature region was ~ 0.35eV; much lower than the work of Teteracyz *et al*. (1998, 2000) who got ~ 1.2eV. The low activation energy could be due to grain boundary effect which could increase or decrease activation energy observed in polycrystalline materials (Garg. 2003). Crystallographic direction has been shown to affect conductivity which in turn affects activation energy (Lockwood and Choi, 1989). The resistance at room temperature ~ 348KΩ reduced to 4.3KΩ at 2900C, the maximum temperature reached, showing that conductivity increased with temperature even though superionic transition was not observed, owing to sample instability.

The high temperature activation energy could not be computed due to the shorting of sample at the maximum temperature. However, at the maximum temperature region, activation energy roughly computed was 0.34eV. Further research is required on this material.

However, the Arrhrenius plot of silver sulphate (Ag2SO4 temperature region from room temperature – 5100C) showed superionic conductivity with activation energy of 0.32eV at the higher temperature region, compared to that of literature (Tetercyz *et al*., 1998, 2000) 0.83eV and 0.57eV (at the lower temperature) which compares well. Room temperature resistance fell from 1.71KΩ to 13.4Ω at maximum temperature reached. However, superionic conductivity was observed at a much lower temperature, 2600C compared to Tetercyz *et al*. (1998, 2000) who observed it at 4200C. fig. 2 shows the plot. This shows that the temperatuee of superuinic transition is not well defined. Variables such as preparative and thermal history, composition and crystallinity may affect the result (Sunandana and Kumar, 2004). The low activation energy observed could be attributed to structural transformations that occur at phase transition kand mobility of silver ions. Fig 3(a-c) depicts the characteristics of the sample through three (3) thermal cycles (rom temperature to superionic transition).

The activation energy decreased appreciably to 0.04eV by the first cycle (~50-3900C) at the lower temperature region and was 0.26eV at the superionic region. Ambient temperature resistance was measured as ~23Ω and superionic transition was observed at ~2700C, almost unchanged “the second cycle (~80-5800C) had average resistance at lower temperature of ~33Ω and at superionic transition ~2.4Ω; whereas the respective activation energies were 0.21eV and 0.38eV in their regions. The third cycle (~27-4900C) average resistances at lower superionic region were 56Ω and ~0.003Ω with the respective activation energies as 0.07eV and 1.32eV. These values are in good agreement with literature, including the character of the plot. Conductivity has increased by many orders of magnitude going through the thermal cycles. The superionic transition in the second thermal cycle was sharp at ~3480C whereas in the third cycle, it showed exponential increase in conductivity at higher temperature.

 **CONCLUSION**

Pure lithium sulphate sample exhibited thermoactivation of conductivity, however due to the instability of the sample higher temperature could not be reached to observe superionic conduction due to shorting or cracking of sample. However a drastic reduction in resistance of sample was observed for the highest temperature reached.

Further research is been carried out to characterize the behaviour of the sample in this temperature region. However, silver sulphate exhibited superionic conductivity at a temperature of 2600C with consequent several orders of magnitude reduction in resistance through the superionic transition temperature. In general, successive reduction was observed through the three (3) thermal cycles in resistance compared to the pure sample. Research results on other samples of the material are at the analyses stage to ascertain the consistency of this behaviour and also mixed compositions of lithium and silver sulphate in different mole proportions. The research is relevant to the development of our electronic industry, particularly, with the present information and communickation technology and could serve as a foundation research in Raw Materials Research Development Council of Nigeria (RMRDC).

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