Ain Shams University
Faculty of Education
Department of Physics

Enhancing the efficiency of Li-ion Batteries by modifying the Solid Garnet Electrolytes

Thesis

Submitted in partial fulfilment of the requirements for the Degree of Doctor of Teacher's Preparation in Science (Physics)

By
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Abstract

Lithium garnet oxides are highly considered as very promising solid electrolyte candidates for all-solid-state lithium ion batteries (SSLiBs). My thesis's goal is to explore new garnet electrolyte materials by tuning the substitution in the frame structure. A systematic study on lithium-stuffed garnet-type $Li_{5+2x}La_3Ta_{2-x}M_xO_{12}$ (M= Sm, Gd; $0 \leq x \leq 0.55$) has been carried out to understand the effect of both Gd, Sm - and Li- content on the structural, electrical, physical, chemical and electrochemical properties. The results from Powder X-ray diffraction (PXRD) and Scanning Electron Microscopy (SEM) suggested structural and morphological transformation as a function of dopant concentration. PXRD studies have revealed the cubic garnet-type structure of the materials with space group *Ia-3d*, and also have proved that the lattice parameter increases with an increase in Sm, Gd, and Li-content. The AC electrochemical impedance spectroscopy (EIS) has shown that the sample with 0.35 doping percent is the best Li+ ion conductor, with a conductivity of 2.25×10^{-5} and 8.18×10^{-5} Scm^{-1} at room temperature for Sm and Gd-doped samples, respectively.

Evaluation of dielectric properties of $Li_{5+2x}La_3Ta_{2-x}M_xO_{12}$ (M= Sm, Gd; $0 \leq x \leq 0.55$) has been carried out by employing AC EIS method. In addition, the dielectric properties were also investigated in the light of electron energy loss functions, which showed some surface energy loss function (SELF) and negligible volume energy loss function (VELF) for the studied garnets. Surface and volume energy loss of a mixed conducting $LiCoO_2$ was also studied for comparison.

Furthermore, the long-term stability of the garnet samples was performed on aged samples using PXRD, SEM, Raman spectroscopy, Thermogravimetric analysis (TGA) and AC impedance spectroscopy. The influence of the conventional solid state synthesis method that has been used to prepare Li stuffed garnets on the microstructure and porosity of $Li_{6.1}La_3Ta_{1.45}M_{0.55}O_{12}$ (M = Y, Zr, Sm, Gd) has also been studied. Moreover, electrochemical stability of $Li_{5.65}La_3Ta_{1.675}Gd_{0.325}O_{12}$ electrolyte (as a representative example) with Li anode was studied. Total conductivity of 4.86 $x10^{-5}$ $S.cm^{-1}$ and 1.6 $x10^{-5}$ $S.cm^{-1}$ were calculated for $Au/Li_{5.65}La_3Ta_{1.675}Gd_{0.325}O_{12}/Au$ and $Li/Li_{5.65}La_3Ta_{1.675}Gd_{0.325}O_{12}/Li$ symmetrical cells at 25^{o}C, respectively. Cyclic Voltammetry of $Li_{5.65}La_3Ta_{1.675}Gd_{0.325}O_{12}$ electrolyte showed that it is electrochemically stable up to 5.3 V.

To sum up, the most interesting findings raised in my thesis can be summarized in the following points. Firstly, we successfully prepared two novel garnets like structure families with using two different doping (Sm and Gd). The obtained results assured the possibility of using them as promising electrolytes in commercial Li-ion batteries. Secondly, the optimum composition with highest conductivity in both families is 0.35 doping percent. Thirdly, 0.55 doping composition in both families revealed naturally high porosity level which suggests the possibility of using them as new separators in Li ion batteries. Finally, the studied samples showed good electrochemical stability, air and CO_2 stability as comparing with literature.

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