Protective layers of B containing glass ceramic and LiPON for lithium electrode in rechargeable Li-O_2 batteries

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Rechargeable Li-air battery based on the protected lithium electrode is still in development stage, but is expected to achieve much higher energy density than commercial Li-ion battery. In particular, the use of a solid electrolyte membrane in advanced Li-air technology eliminates self-discharge and hydrogen evolution, leading to exceptionally good shelf life and safety. Furthermore, the inorganic solid electrolyte layer may effectively supress the dendritic growth of lithium toward the cathode. The LAGP glass ceramic is a good candidate for solid electrolyte in lithium battery. However, the LAGP is not stable when in contact with lithium. Therefore, the employment of interlayer between lithium and LAGP is needed. In addition, further improvement in the conductivity of LAGP is required to enhance the reaction kinetics of the battery. The objective of this study is to increase the ionic conductivity of LAGP glass ceramic (GC) by adding B_2O_3 to LAGP and to stabilize the protected lithium electrode by using the LiPON interlayer between the LAGP and lithium metal.

The B_2O_3 added LAGP glass ceramic was prepared using melt-quenching method. The crystallization temperature of LAGP decreased with increasing B content in the LAGP. XRD analysis confirmed the crystal structure of LAGP and B_2O_3 added LAGP glass ceramics composed of the $LiGe_2(PO_4)_3$ as a major crystalline phase and the Li_2O and $AlPO_4$ secondary phases. With the increase in B_2O_3 content, the distinction between grain and grain boundaries in LAGP became clearer. The ionic conductivity of LAGP increased with small addition of B_2O_3, but decreased with further addition of B_2O_3. The highest ionic conductivity measured at 25 ^oC was obtained for LAGP glass ceramics containing 0.05% B_2O_3. Fig. 1 shows the Arrhenius plots for the total ionic conductivity of LAGP glass ceramic with different B_2O_3 content measured in the temperature range of -20 ^oC to 80 ^oC.

Furthermore, the protective layer of LiPON film was deposited on the glass ceramic by RF sputtering technique using sintered Li_3PO_4 target under nitrogen atmosphere. The RF power was adjusted to obtain films thicker than 1 μm with optimized ionic conductivity. The SEM micrographs showed that the film deposition rate was proportional to the substrate temperature. The ionic conductivity of LiPON thin film increased with increase in N/P ratio. The double and triple co-ordination of nitrogen with phosphorous in LiPON film was confirmed by XPS. Linear sweep voltammetry (LSV) study revealed that the LiPON/GC protective layer was stable in the operating potential window of Li-O_2 cell. Li-O_2 cell employing LiPON/GC as protective layers for lithium exhibited the capacity of 1000 mAh/g.

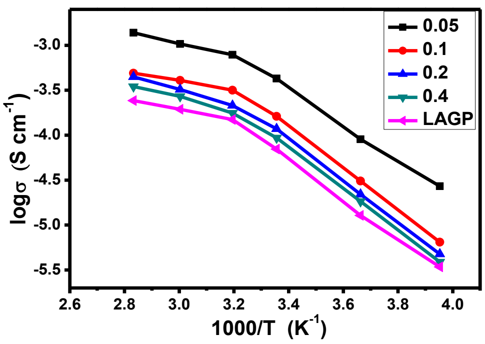

Fig. 1 The Arrhenius plot of total conductivity (σ_t) of LAGP glass ceramic specimens with different B_2O_3 content, crystallized at 825 ^0C for 5 h.