The mixed ionic and electronic conductor LLZO solid electrolytes for lithium-ion battery cathodes

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Ni-rich layered oxide cathode materials for Li-ion batteries decompose by reacting with the liquid electrolyte species, and their capacity is reduced during cyclic charge and discharge. Therefore, the cathode surface is coated to prevent reactions between the liquid electrolyte and the cathode material. $Li_7La_3Zr_2O_{12}$ (LLZO) is a potential candidate as a coating material due to its high ionic conductivity and chemical stability [1]. When the cathode surface is coated with LLZO, a protective interface is formed between the cathode material and the liquid electrolyte. Therefore, the cathode active material surface is protected from unwanted side reactions without compromising the Li-ion transport. Thus, the surface of the active cathode material becomes more stable, its cyclic stability is improved, and the battery life is extended [2]. On the other hand, solid electrolyte materials with good Li ion conductivity are poor in electronic conductivity. The slowdown in electron transport between the cathode and the current collector adversely affects the rate performance of the battery. Therefore, the electronic conductivity of LLZO solid electrolyte coatings for cathode surface modification must be improved. Substitution of elements such as Fe, Ni, and Co into the LLZO is known to improve electron transport as well as Li-ion transport. Cheng et al. synthesized the garnet-type LLZO by introducing Fe, Co, and Ni, improving its electronic conductivity around 2.75×10^{-6} S cm^{-1} by Co doping [3]. Samson et al. reported the effect of Mn, Fe and Co doping on the cubic structure of garnet-type cubic $Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ structure. Among these elements, 0.1 Co doping provided a good combination of ionic conductivity (2.5×10^{-4} S cm^{-1}) and electronic conductivity (10^{-8} S cm^{-1}) [4].

In this study, garnet-type cubic LLZO was synthesized by doping Ni, Co, and Urea to improve its electronic conductivity. Composite electrodes were prepared by homogeneously mixing the synthesized LLZO and the active particles of the commercial NMC622 cathode. The crystal structure of the NMC622/LLZO compounds is shown in Figure 1. It can be seen that the cubic-LLZO is formed, and the layered structure of NMC622 is maintained. Galvanostatic charge/discharge tests were carried out to see the effect of the LLZO dopant on the battery performance. Li-ion cells having NMC622/LLZO composite cathode using Ni, Co and Urea as a dopant have improved discharge capacity at 1C rate than the undoped sample (Figure 2). All in all, the enhanced rate performance of the composite cathodes having doped LLZO solid electrolytes is attributed to the enhanced electronic conductivity.

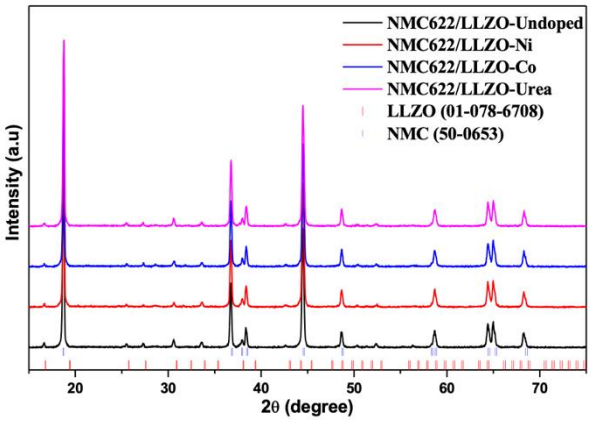

Figure 1: XRD analysis of the NMC622/LLZO-X doped (X=Ni,Co and Urea) composite electrodes

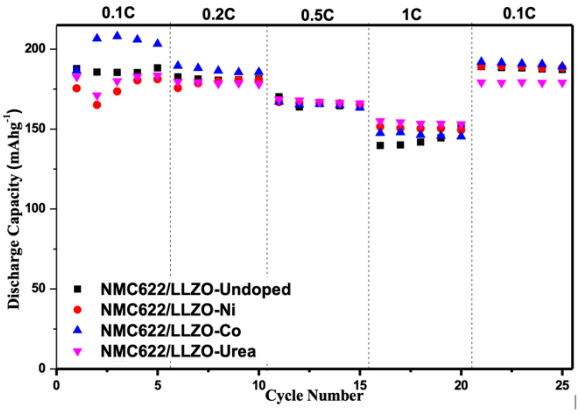

Figure 2: Rate performance of the NMC622/LLZO-X doped (X=Ni,Co and Urea) composite electrodes between 2.75V and 4.6 V versus Li^+/Li.

Acknowledgements
Authors acknowledge that this study was supported by the TÜBİTAK 2209-A Research Project Support Programme for Undergraduate Students, No. 1919B012113633.

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