

P26. $\text{Li}_{0.3}\text{La}_{0.57}\text{Ti}_{1-x}\text{V}_x\text{O}_3$ vanadium doped to improve electrochemical performance as a solid electrolyte in lithium-ion batteries.

M.F. Mena¹, F.A. Vasquez¹, N.C. Rosero-Navarro², J. A. Calderon¹

¹Antioquia University, Avenue 53 #61-30, 050010, Medellin, Colombia.

²Instituto de Ceramica y Vidrio,

E-mail: maycolf.mena@udea.edu.co

All-solid-state Li-ion batteries (ASSB) are one of the future alternatives for electrochemical energy storage, because it improves energy density and safety. The solid electrolyte in the ASSB is a key element to improve the stability and reduce the flammability of lithium batteries [1-3]. Nevertheless, ASSBs industrial and commercial development have some challenges associated with the lower Li-ion conductivity of solid electrolytes $1.0 \times 10^{-4} \text{ S cm}^{-1}$ than liquid electrolytes $1.0 \times 10^{-2} \text{ S cm}^{-1}$, as well as high interfacial resistance due to the poor contact and interfacial reactions between the solid electrolyte and active materials. Although the $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_{2.94}$ perovskite (ABO_3) shows high chemical stability, high bulk ionic conductivity ($1.0 \times 10^{-3} \text{ S cm}^{-1}$), the total ionic conductivity is lower ($1.96 \times 10^{-3} \text{ S cm}^{-1}$) because of the grain boundary resistance, which reduces the Li^+ transport [4]. Doping the B site of the perovskite structure with cations of smaller ionic radius is an alternative to decrease the interatomic bonding forces and improve the lithium conductivity [5]. In this work, we present the synthesis of the material $\text{Li}_{0.3}\text{La}_{0.57}\text{Ti}_{1-x}\text{V}_x\text{O}_3$ ($x=0-0.05$) using the sol-gel method, thermal treated at 900°C for 12 hours and sintered at high temperature (1200°C) for 12 hours, for solid electrolyte of potential use in Li-ion batteries. The physicochemical characterization of the materials was performed by: TGA, DSC, Raman, XRD and SEM coupled to an EDS, while the electrochemical characterization was performed electrochemical impedance spectroscopy and chronoamperometry. The Raman spectra and XRD patterns indicate the perovskite structure formation in the orthorhombic crystal system of all compositions of materials $\text{Li}_{0.3}\text{La}_{0.57}\text{Ti}_{1-x}\text{V}_x\text{O}_3$ ($x=0-0.05$), showing lower lattice parameters with vanadium doping, which can be attributed to the V^{+5} substitution, which has an ionic radius (0.54 \AA), lower than Ti^{+5} (0.605 \AA) in B cation of perovskite structure. Vanadium-free $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$ solid electrolyte exhibits the highest total ionic conductivity $4.54 \times 10^{-3} \text{ S cm}^{-1}$, and $\text{Li}_{0.3}\text{La}_{0.57}\text{Ti}_{0.98}\text{V}_{0.02}\text{O}_3$ exhibits the high grain conductivity ($7.43 \times 10^{-4} \text{ S cm}^{-1}$). All solid electrolytes exhibit electron conductivities with magnitude $10^{-8} \text{ S cm}^{-1}$ required for the application of solid electrolytes in all-solid batteries.

References:

- [1] J. Lu, Y. Li, and Y. Ding, "Structure and Conductivity of $\text{Li}_3/8\text{Sr}_7/16-x\text{AxZr}_1/4\text{Nb}_3/403$ ($A = \text{Ca}, \text{Ba}$) Li-ion Solid Electrolytes," *JOM*, vol. 72, no. 9, pp. 3256-3261, 2020, doi: 10.1007/s11837-020-04239-9.
- [2] Z. Hu et al., "Enhanced Li ion conductivity in Ge-doped $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ perovskite solid electrolytes for all-solid-state Li-ion batteries," *New J Chem.*, vol. 42, no. 11, pp. 9074-9079, 2018, doi: 10.1039/C8NJ01113C.
- [3] R. Yao et al., "Effect of Sn or Ta doping on the microstructure and total conductivity of perovskite $\text{Li}_{0.24}\text{La}_{0.587}\text{TiO}_3$ solid electrolyte," *J. Alloys Compd.*, vol. 844, p. 156023, 2020, doi: <https://doi.org/10.1016/j.jallcom.2020.156023>.
- [4] "Yang, Y., Wei, P., Wei, D., et al. (2015). Day-Ahead Scheduling Optimization for Microgrid with Battery Life Model[J]. *Transactions of China Electrotechnical Society*, 30(22), 172-180."
- [5] H. T. Chung, J. G. Kim, and H. G. Kim, "Dependence of the lithium ionic conductivity on the B-site ion substitution in $(\text{Li}_{0.5}\text{La}_{0.5})\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Sn}, \text{Zr}, \text{Mn}, \text{Ge}$)," *Solid State Ionics*, vol. 107, no. 1-2, pp. 153-160, 1998, doi: 10.1016/S0167-2738(97)00525-0.