Scandium-Substituted $Na_3Zr_2(SiO_4)_2(PO_4)$ as Superior Sodium-Ion Conductors

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Room-temperature Na-ion batteries (NIBs) show advantages of unlimited sources, low price of starting materials and easy recycling [1], which make them promising candidates for stationary energy storage applications. NIBs in all-solid-state design are regarded as the batteries of the next generation due to their non-leaking, non-volatile, non-flammable electrolyte and adaptability to temperature changes [2]. Trivalent cation-substituted $Na_3Zr_2(SiO_4)_2(PO_4)_3$ in NASICON structure are regarded as promising electrolyte materials for solid-state or high-temperature batteries because of their high Na^+ ion conductivity and reliable chemical and physical stability. In this study, scandium has been chosen as the substitution element in the solid solution $Na_{3+x+y}Sc_xZr_{2-x}(SiO_4)_y(PO_4)_{3-y}$ (NSZSP), because among all the trivalent cations, the ionic radius of Sc^{3+} (74.5 pm) is the closest to that of Zr^{4+} (72.0 pm), indicating that the substitution only generates a deficiency in positive charge, but does not cause distortions in the crystal structure. NSZSP has received hardly any attention so far and only few reports are available on this kind of materials [3, 4]. However, in the past the performance of NSZSP was compared at high temperatures (≈ 300 °C). Only a few conductivities at room temperature were mentioned, and they were rather moderate (maximum $5.0 \cdot 10^{-4}$ S $\cdot$ cm^{-1}). In this study, a solution-assisted solid-state reaction method was applied by which a series of NSZSP nano-powders with favorable microstructures were prepared. With increasing scandium substitution, the conductivity of sintered NSZSP samples also increases. $Na_{3.4}Sc_{0.4}Zr_{1.6}(SiO_4)_2(PO_4)$ shows the highest conductivity of the system. Higher amounts of scandium decrease the conductivity due to the decreasing number of available vacancies for Na^+ ion transport. The total ionic conductivity of $Na_{3.4}Sc_{0.4}Zr_{1.6}(SiO_4)_2(PO_4)$ reaches $4.0 \cdot 10^{-3}$ S $\cdot$ cm^{-1} at 25 °C [5]. To our knowledge, it is not only the best value for all materials with NASICON-type structure, but also the best reported value for all polycrystalline oxidic Na^+ ion conductors. It is even comparable with common liquid electrolytes of NIBs.

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