

ROLE OF LI ON STRUCTURE STABILIZATION AND IONIC CONDUCTION OF CATION-DEFICIENT PEROVSKITE SOLID ELECTROLYTES

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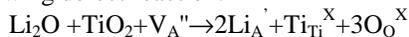
ABSTRACT

For the last two decades, lithium/lithium ion batteries have been one of the most important power sources for portable electronics due to their high energy density. In order to fulfill the compact requirement for portable electronics, the demand for lighter and thinner batteries is increasing. To reduce the battery size and weight, using inorganic solid electrolyte gives many advantages. In search for Li ion conducting solid electrolyte, cation-deficient perovskite with the addition of lithium ions has received considerable attention due to its high ionic conductivity. However, the stability, crystal structure and conductivity in Li-containing Perovskite systems have not been thoroughly studied. Thus, the objective of this work was to study the effect of lithium ion addition on the crystal structure and conductivity of cation-deficient perovskite.

In this work, two Li-containing perovskites $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ and $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ were prepared using La_2O_3 , Li_2CO_3 , TiO_2 and Ta_2O_5 as the starting materials. The concentration of lithium ions was varied from 0% to 50% of A-sites accordingly. The samples were sintered at 1300°C for 8h. Subsequently, the sintered samples were examined by XRD, SEM, and ICP.

The XRD results show that undoped mixture of La_2O_3 and TiO_2 cannot form an ABO_3 perovskite structure with La/Ti ions located at A/B sites. In this structure, La ion is trivalent and Ti ion is tetravalent. For lanthanum titanate to form a perovskite structure, the corresponding composition can be written as $\text{La}_{2/3}\text{TiO}_3$. There should be 33% of cation vacancies (in A sites) present in $\text{La}_{2/3}\text{TiO}_3$. Such a high concentration of defects makes this structure unstable. Therefore, $\text{La}_{2/3}\text{TiO}_3$ cannot form a perovskite when sintered in air as shown in Fig. #1. Similarly, for lanthanum tantalate to form a perovskite structure, the formula can be written as $\text{La}_{1/3}\text{TaO}_3$. There should be 66% of cation vacancies (in A sites) present in $\text{La}_{1/3}\text{TaO}_3$. Interestingly, La_2O_3 and Ta_2O_5 formed an ordered perovskite without Li dopant as shown in Fig. #2.

In $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$, the addition of Li ions into the A-site deficient perovskite can be rationalized using the following defect reaction:



In this equation, V_A'' represents the available A-site divalent cation vacancy. This reaction indicates that the addition of one Li_2O is able to eliminate one cation vacancy. Therefore, with the addition of lithium ions, the structure of perovskite is expected to be more stable. When 10% of Li was added, distorted perovskite structure was observed. As the concentration of Li increased to 0.5, the perovskite gradually shifted to cubic structure. Thus, the stability of $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ strongly depends upon the concentration of cation vacancy. Due to the presence of numerous cation vacancies in the lattice, local equilibrium in electroneutrality may not be satisfied. Thus, the repulsion force results from the absence of divalent cation

might be too strong to maintain the structural integrity when Li ions are not added. In $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$, A site should be occupied by monovalent cation since Ta ion is pentavalent. Compared with $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$, the repulsion force caused by the presence of A-site vacancy is expected to be less significant. Thus, $\text{La}_{1/3}\text{TaO}_3$ can crystallize in an ordered perovskite structure.

In this work, the lithium ion conductivity of perovskite should be proportional to the product of carrier concentration, i.e. $[\text{Li}]$ and the concentration of cation defects $[\text{V}_A'']$. Hypothetically, the maximum conductivity for $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ is expected when $[\text{Li}]=0.25$. In $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$, the maximum conductivity should occur at $[\text{Li}]=0.5$. In Figure #3, it was found that the maximum conductivity ($>10^{-5}$ S/cm) appeared at $[\text{Li}]=0.3$ in $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$. The maximum conductivity, however, was not observed in $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$. The reason is due to the reduced lattice parameter caused by the occupation of considerable amount of Li ions in the A-site cation sublattice.

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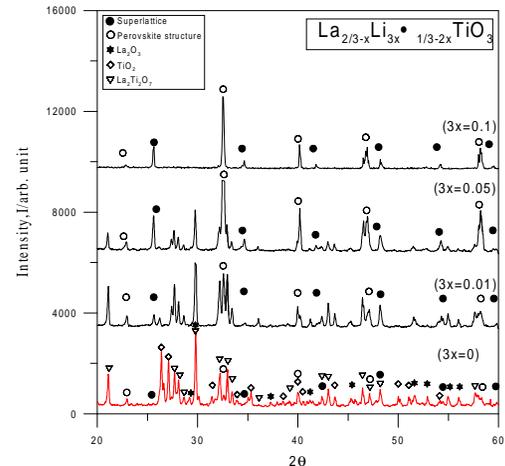


Figure #1. XRD traces of $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$, ($3x=0\sim 0.1$).

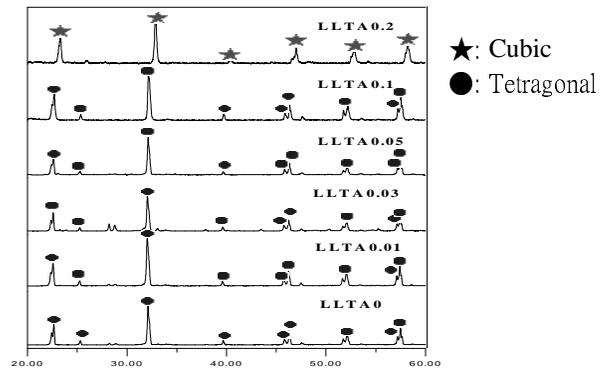


Figure #2. XRD traces of $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$, ($3x=0\sim 0.2$).

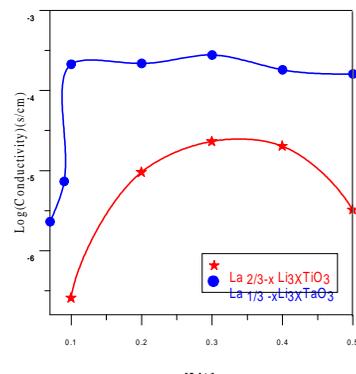


Figure #3. Conductivity of $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ and $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ plotted as function of Li concentration