

Electrochemical Magnesium Insertion to $A_{0.5}Ti_2(PO_4)_3$ (A=Mg, Ca, Sr, Ba)

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INTRODUCTION

Magnesium cells may be expected to be low costs and safety compared to lithium cells, because magnesium as an anode material is more abundant in nature and less dangerous than lithium. However, Mg^{2+} insertion into ion-transfer host proceeds slowly owing to the strong solvation of small and divalent Mg^{2+} compared to Li^+ . Consequently, magnesium cells have lower capacity than lithium cells at usual current density [1]. In this study, a series of titanium phosphates having the same lattice as the well-known fast ionic conductor of NASICON [2], $A_{0.5}Ti_2(PO_4)_3$ (ATP, A=Mg, Ca, Sr, Ba), are investigated as magnesium hosts and it may be clarified for relationship between extents of Mg insertion and unit cell volume.

EXPERIMENTAL

$A_{0.5}Ti_2(PO_4)_3$ samples were prepared as follows; 0.1 mol dm^{-3} $A(CH_3COO)_2 \cdot nH_2O$ (A=Mg, Ca, Sr or Ba) and 0.1 mol dm^{-3} $NH_4H_2PO_4$ aqueous solutions were prepared separately, in addition to 0.1 mol dm^{-3} $C_4H_9O[Ti(OC_4H_9)_2O]_4C_4H_9$ ethanol solution. These solutions were mixed at the calculated ratio to give the stoichiometric composition. The obtained sol solution was further stirred at 70 °C for 6 h to form a gel, which was dried at 90 °C for 12 h to give a powder. It was heated at 300 and then 500 °C to remove ammonium and acetate groups, followed by final firing at 700 or 900 °C for 24 h.

Electrochemical magnesium insertion from 1 mol dm^{-3} $Mg(ClO_4)_2 / PC$ solution was performed in a cylindrical glass cell. Sample electrode was prepared from the mixture of $A_{0.5}Ti_2(PO_4)_3$, acetylene black and PTFE (mass ratio; 70:25:5). Magnesium ribbon was used as a counter electrode. Reference electrode consisted of silver wire immersed in 0.1 mol dm^{-3} $AgClO_4 / PC$, which was separated from the cell electrolyte by a glass filter.

RESULTS AND DISCUSSION

BaTP having the same lattice as MgTP are hexagonal, and belong to the space group $R\bar{3}c$. On the other hand, CaTP and SrTP having the same lattice as MgTP are hexagonal but belong to the space group $R\bar{3}$ [4]. The effects of ionic radius of A^{2+} on unit cell volume are shown in Fig. 1, where the expansion in unit cell volume occurs when ionic radius becomes larger.

Discharge curves at various current densities of ATP are compared in Fig. 2. The potential plateau at about -1.6 V (vs. Ag^+ / Ag) appears and continues until the limit of one-electron accommodation by Ti^{4+} / Ti^{3+} (reduction of Ti^{4+} to Ti^{3+}) defined as $x = 1.0$ at low current density in common with all samples, where x denotes the calculated amount of inserted Mg^{2+} per formulae. At the discharge potential below -2.4 V, an unexpected reaction such as solvent decomposition might occur. However, it is found that the extent of Mg insertion is different at the relatively high current density. When ionic radius becomes larger (i.e. SrTP and BaTP), the extents of Mg insertion are scarcely dependent on current density. These results may

suggest that Mg^{2+} diffusion in host lattice becomes faster when unit cell volume becomes larger. From these results, it may be suspected that unit cell volume is an important factor which affects the extents of Mg insertion. Consequently, Mg insertion hosts require the design of materials to reduce the time constant of Mg^{2+} diffusion.

REFERENCES

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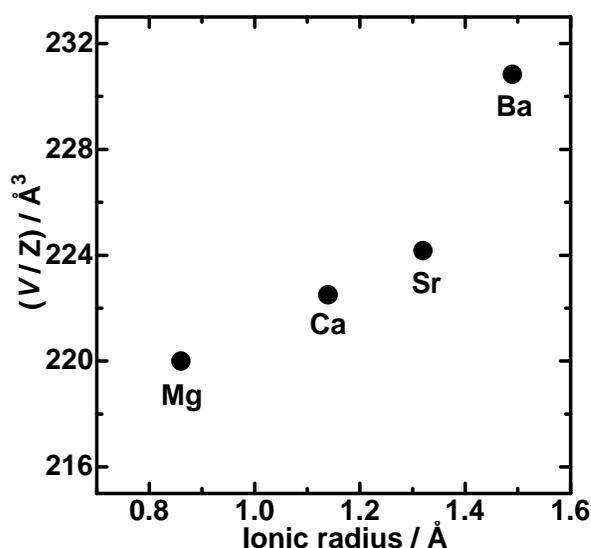


Fig.1 Relationship between unit cell volume of $A_{0.5}Ti_2(PO_4)_3$ and ionic radius.

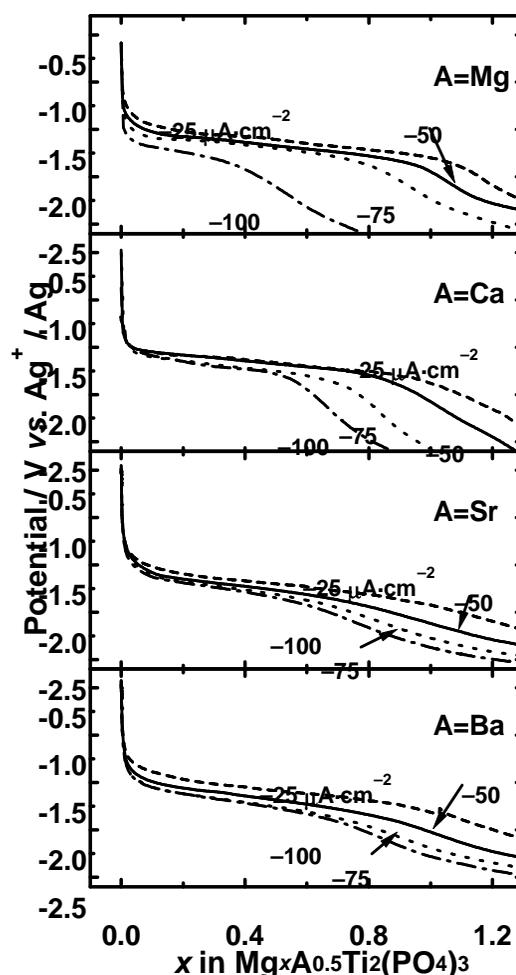


Fig.2 Discharge curves of $A_{0.5}Ti_2(PO_4)_3$ at various current densities.