$Na_{1\pm y}Ti_{2-x}M_{x}(PO_{4})_{3}$ (M = Al(III), Hf(IV), Mg(II), Zr(IV)) Isovalent and Aliovalent Substitution Influence on Aqueous **Electrochemical Properties and Electrode Stability**



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Introduction

It is predicted that the electricity demand will increase from 30 to 50 percent by 2050, as a consequence of the ongoing transition from fossil fuels to renewable energy. Such a transition requires coordinated and comprehensive adaptations across a range of areas that affect society as a whole and should come together with state-of-the-art technologies. Efficient energy storage is considered to be the key for the successful and entire transition to renewable energy sources. Electrochemical energy storage technologies are and will be playing an important role for achieving this desirable goal - especially for mobile devices and the transportation sector, also stationary storage. In general, all applications require high energy and power density, low cost, safety, and preferably high sustainability. These characteristics vary significantly depending on the specific needs. Aqueous Na-ion based batteries are recognized as one of the promising candidates to replace Li-ion technologies, especially for stationary energy storage applications. NASICON-structured NaTi₂(PO₄)₃ (NTP) phosphate framework has already attracted a lot of attention and remains the most studied negative electrode material for aqueous Na-ion batteries. The major challenges to overcome are the NTP degradation in aqueous electrolytes during prolonged cycling and self-discharge. As it was presented in our previous research [Doi: 10.1149/1945-7111/ac0b5d], the electrochemical properties of carbonaceous NTP composite electrodes are strongly dependent on the synthesis route. However, elemental composition is prerequisite for material conductivity and electrochemical properties. Here, we present the results of electrochemical properties and cycling stability in aqueous electrolytes where Na_{1±v}Ti_{2-x}M_x(PO₄)₃ is substituted by M = Al(III), Hf(IV), Mg(II) and Zr(IV) in isovalent and aliovalent ratios.

Results

Empirical formula	NaTi ₂ (PO ₄) ₃	NaTiZr (PO ₄) ₃	NaTi _{1.5} Zr _{0.5} (PO ₄) ₃	NaTiHf(PO ₄) ₃	NaTi _{1.5} Hf _{0.5} (PO ₄) ₃	Na ₂ TiAI (PO ₄) ₃	Na ₃ Ti ₃ Al ₁ (PO ₄) ₃	Na ₃ TiMg(PO ₄) ₃	Na ₂ Ti _{1.5} Mg _{0.5} (PO ₄) ₃
Short name	NTP	NTZP_111	NTZP_11505	NTHP_111	NTHP_11505	NTAIP_211	NTAIP_331	NTMgP_311	NTMgP_21505
The ratio of substitution	-	Ti:Zr = 1:1	Ti:Zr = 1.5:0.5	Ti:Hf = 1:1	Ti:Hf = 1.5:0.5	Ti:AI = 1:1	Ti:Al = 1.5:0.5	Ti:Mg = 1:1	Ti:Mg = 1.5:0.5





- NTMgP_311 850 °C NTMgP_21505 800 °C

800

600

100

90

80

70 🛞

0 0 0 0 Coulombic efficiency (

55.9

28.8

25.8

180

20

10

200

Relative transmittance (arb. units)

Fig. 1. Powder XRD patterns from samples sintered at different temperatares. Red column bars represent a reference pattern of NTP crystalline phase $(NaTi_2(PO_4)_3 COD#1530649)$.

Fig. 4. Galvanostatic cycling performance of NTP, NTZP (Ti:Zr molar ratio 1.5:0.5) and NTAIP (Ti:AI molar ratio 1:1) electrodes in 1 M Na₂SO₄ (aq.) solution at 1C rate. Capacity retention values are 60.1 % of NTP, 38.9 % of NTZP and 53.1 % of NTAIP electrodes. Theoretical specific charge capacity values are 133 mAh g⁻¹ for NTP, 95 mAh g^{-1} for NTZP_11505 and 66 mAh g^{-1} for NTAIP_211 compounds.

The substitution of different elements strongly influences NTP phase formation temperature. In the synthesis where Ti⁴⁺ is substituted with Zr⁴⁺, Hf⁴⁺ and Al³⁺ cations, phase formation temperature increases up to 1050 °C (Zr and Hf) and 800 °C (Ti:Al molar ratio 1:1), when NTP phase forms at 750 °C temperature. However, the attempts to synthesize single phase NTP substituted with Mg²⁺ were unsuccessful, likewise with Al³⁺ in a Ti:Al molar ratio 1.5:0.5. The FT-IR (Fig. 2) support the results obtained by powder XRD analysis. The spectra from Zr and Hf substituted compound show NTP phase characteristic peaks. Nevertheless, low intensity band at around 744 cm⁻¹ is observed in the spectra of NTZP_11505 prepared at 950 °C. This band is known to be characteristic of the pyrophosphate (P_2O_7) groups and indicates a small amount of impurity. However, the 744 cm⁻¹ band disappears if sample is calcined at a

The very first electrochemical measurement results look promising; the obtained capacity retention values are falls from 60 % (NTP) to 39 % (NTZP) and 53 % (NTAIP). However, electrode active material synthesis conditions, material crystallinity, phase purity and substitution levels need to be optimized in order to increase electrode stability.



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