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Short Communication

Intermediate Temperature Electrical Properties of a $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ Composite Electrolyte

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In this paper, a composite electrolyte of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ was synthesized using $Ti_{0.9}Mg_{0.1}P_2O_7$ and NaCl/KCl as raw materials. The composite electrolyte was characterized with XRD, SEM and EIS. The result of X–ray diffraction (XRD) indicated that an *in-situ* reaction fully occurred to Mg^{2+}-doped titanium pyrophosphate and inorganic molten salt to form the $Ti_{0.9}Mg_{0.1}P_2O_7$ and $(Na/K)Ti_2(PO_4)_3$ bimorph structure. It can be seen from scanning electron microscopy (SEM) images that $Ti_{0.9}Mg_{0.1}P_2O_7$ and $(Na/K)Ti_2(PO_4)_3$ are fused each other. The electrical conductivities results by electrochemical impedance spectroscopy (EIS) indicated that the $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ shows a greatly improvement of conductivities. Finally, an H_2/O_2 fuel cell employing $Ti_{0.9}Mg_{0.1}P_2O_7/(Na/K)Ti_2(PO_4)_3$ as electrolyte was fabricated.

Keywords: Fuel cells; *in-situ* reaction; Electrolyte; Conductivity

1. INTRODUCTION

Compared to fuel cells of low or high temperature, the fuel cells of intermediate temperature (300 °C ~ 800 °C) have many advantages. Exploring solid electrolyte materials which have high conductivity is key to the development of intermediate temperature fuel cells [1–7].

Over the past decade, TiP_2O_7-based electrolytes have been widely studied as intermediate temperature fuel cell electrolytes [8–12]. Lapina et al. researched the effect of sintering temperature and phosphorus content on the electrical conductivities of 10 mol % Y^{3+}-doped titanium pyrophosphate [10]. Norby et al. synthesized Al^{3+}-doped TiP_2O_7, and the isotope effect on conductivity showed that the sample had good protonic conduction [11]. More attractively, our previous work showed that $Ti_{0.95}Mg_{0.05}P_2O_7$ is an ionic conductor and has a high conductivity [12]. Unfortunately, the

single MP_2O_7 materials were impractical owing to their poor sintering abilities. The researchers have done a lot of research to overcome the shortcomings of MP_2O_7 single material [13–18]. For example, Hibino et al. prepared a dense H_3PO_4-doped polybenzimidazole / $Sn_{0.95}Al_{0.05}P_2O_7$ composite electrolyte by *in-situ* reaction [15].

Many studies have shown that titanium phosphate has good alkali metal salt ion conductivity and high long-term stability in alkali metal salt ion batteries [19–24]. Whitacre et al. studied the long-term stability of $NaTi_2(PO_4)_3$ which was used as an anode material [19]. Xu et al. synthesized $KTi_2(PO_4)_3$ by a hydrothermal method. Moreover, a carbon-coated $KTi_2(PO_4)_3$ was obtained and it had high electrochemical performances in a sodium-ion battery [20]. In our previous work, we explored a titanium pyrophosphate/corresponding phosphate composite electrolyte [25]. The above researches indicate that pyrophosphate/corresponding phosphate material could overcome the poor mechanical strength of MP_2O_7 single material.

In this study, a new composite electrolyte of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ was synthesized using $Ti_{0.9}Mg_{0.1}P_2O_7$ and NaCl/KCl as raw materials. The characterization properties of the sample were carried out by SEM and XRD. The electrical conductivities of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ were studied at 300–700 °C. An intermediate temperature H_2/O_2 fuel cell was also fabricated.

2. EXPERIMENTAL

A $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ was synthesized as follows. Reagent-grade MgO (0.24g), TiO_2 (4.32g) and 85 % H_3PO_4 (11.6mL) were used as raw materials to synthesize $Ti_{0.9}Mg_{0.1}P_2O_7$ [12]. Briefly, the raw materials were fully mixed and changed into a hard mud after heating at 350 °C for 1 h. $Ti_{0.9}Mg_{0.1}P_2O_7$ was obtained after the hard mud was grinded and calcined at 500 °C for 4 h. Then, NaCl/KCl (1:1 molar ratio) and $Ti_{0.9}Mg_{0.1}P_2O_7$ were mixed at a 1:4 weigh feed ratio and heated at 550 °C for 1.5 hours. After the complete reaction, the obtained powder was then heated at 600 °C for 1 h to get the $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$.

The crystallization of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ was tested by XRD. Surface and cross-sectional photos of the composite electrolyte were taken with SEM. To research the electrical conductivity of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$, 80%Ag-20%Pd paste and Ag wire were used as electrode and current collector, respectively. The conductivity was measured by an electrochemical analyzer (CHI660E) in the frequency range of $1\text{-}10^6$ Hz in a dry nitrogen atmosphere at 300–700 °C. The composite electrolyte (diameter 18 mm, thickness 1.0 mm) was sealed between two alumina tubes by low melting glass ointment at 600 °C for 1 h. To research the ionic conduction under different pO_2, oxygen concentration cell and $\log\sigma$ as a function of $\log(pO_2)$ plot were measured in the range of the test temperatures [26]. The oxygen concentration cell was constructed: air, Pd-Ag | $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ | Pd-Ag, O_2 at 400-700 °C. The H_2/O_2 fuel cell (H_2, Pd-Ag | $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ | Pd-Ag, O_2) of the composite electrolyte was also tested.

3. RESULTS AND DISCUSSION

Fig. 1 displays the crystal structure of the (Na/K)$Ti_2(PO_4)_3$/$Ti_{0.9}Mg_{0.1}P_2O_7$. The peaks at 22.60º, 25.31º, 27.79º and 37.88º agree well with the purity phase of TiP_2O_7 (JCPDS 38-1468) [10–12]. The strongest diffraction peaks at 24.19º and 24.25º are assigned to $KTi_2(PO_4)_3$ (JCPDS 79-1880) and $NaTi_2(PO_4)_3$ (JCPDS 84-2012), respectively [19–20]. This seems to indicate that a reaction fully occurred to Mg^{2+}-doped titanium pyrophosphate and inorganic molten salt to form the (Na/K)$Ti_2(PO_4)_3$/$Ti_{0.9}Mg_{0.1}P_2O_7$ [25].

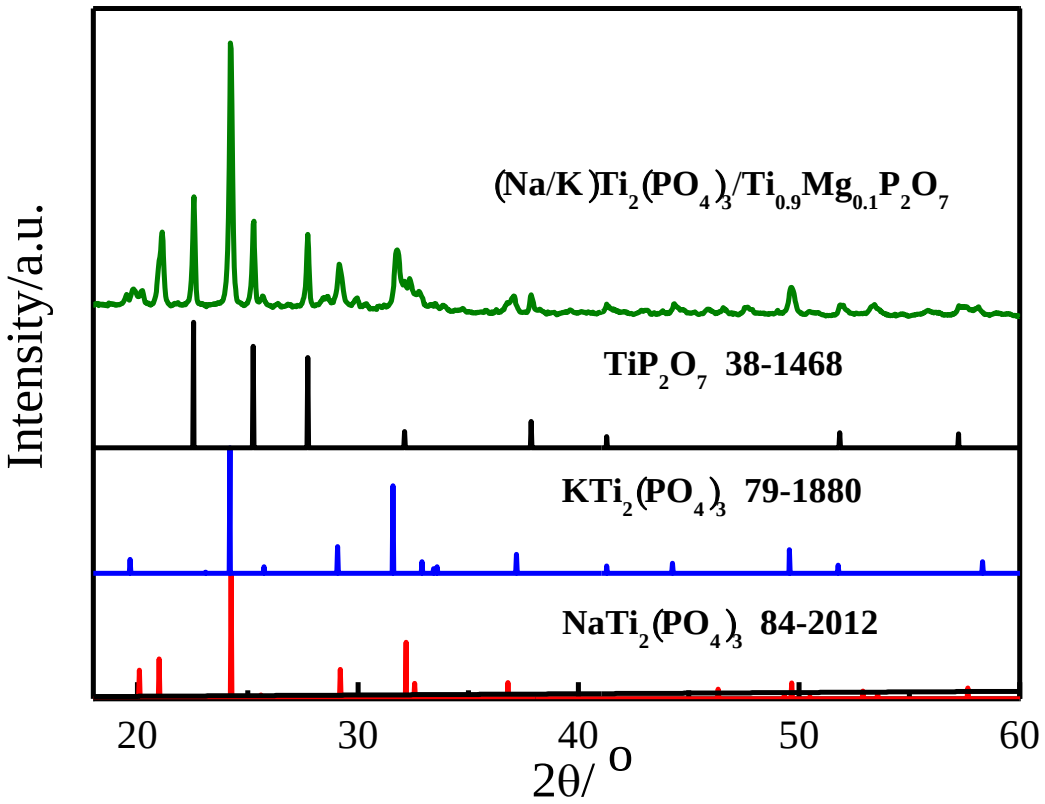

Figure 1. XRD pattern of (Na/K)$Ti_2(PO_4)_3$/$Ti_{0.9}Mg_{0.1}P_2O_7$.

Fig. 2 displays the SEM photos which showed the external and cross-sectional surfaces of the (Na/K)$Ti_2(PO_4)_3$/$Ti_{0.9}Mg_{0.1}P_2O_7$. In Fig. 2(a), the external surface of the (Na/K)$Ti_2(PO_4)_3$/$Ti_{0.9}Mg_{0.1}P_2O_7$ exhibits an approximate cubic shape, and the solid surface is adequately covered by a fused layer. In Fig. 2(b), the cross-sectional surface has a small number of holes, however, the experimental test proved that they are closed holes [25].

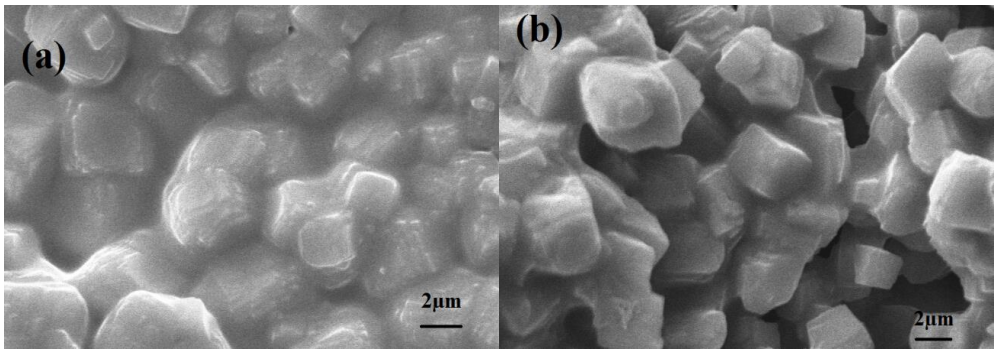

Figure 2. The SEM photos of the $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ (a, b).

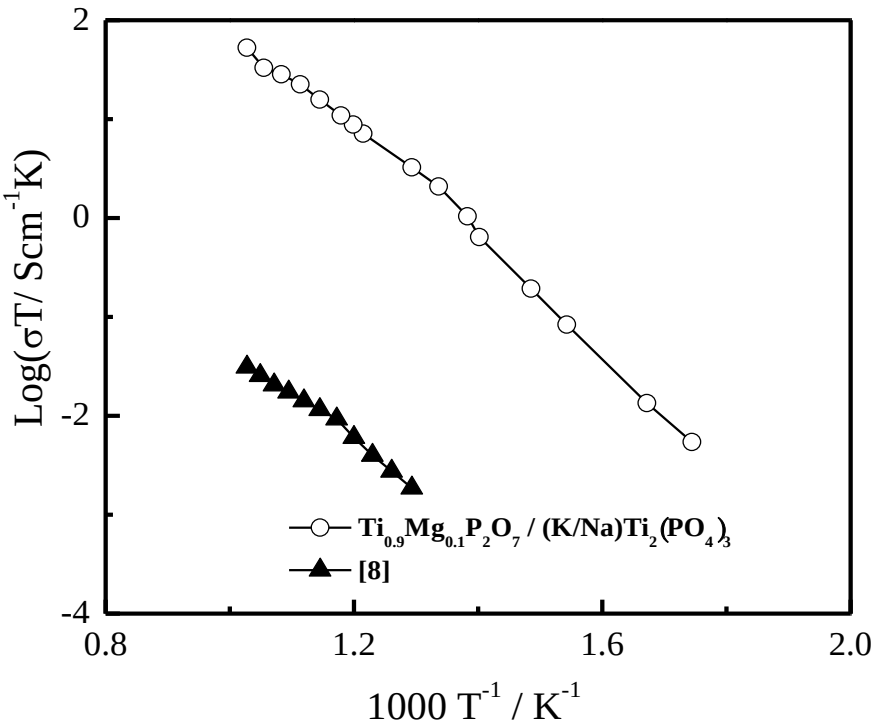

Figure 3. The plot of $\log(\sigma T) \sim 1000\ T^{-1}$ of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ at 300–700 °C in dry nitrogen atmosphere.

According to the electrical conductivities of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ shown in Fig.3, as expected, the ionic conductivity of the sample increases with increasing test temperature and reaches the maximum ionic conductivity is 5.4×10^{-2} $S\cdot cm^{-1}$ at 700 °C. Compare with the literature, the $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ is about four orders of magnitude higher than low valence metal ion doped TiP_2O_7 [8]. It can be attributed to the phase structure (Fig. 1) and additional transport pathways for protons (Fig. 2) formed by titanium phosphate with NASICON structure [25].

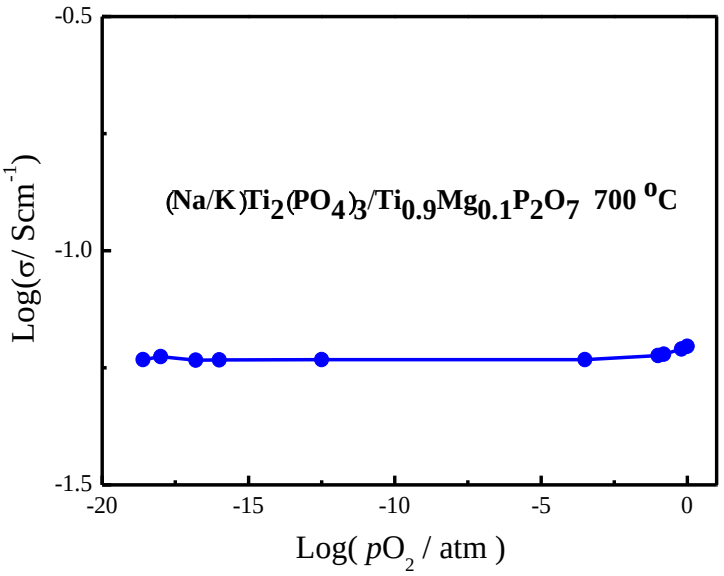

Figure 4. The logσ versus log(pO$_2$) plot of (Na/K)Ti$_2$(PO$_4$)$_3$/Ti$_{0.9}$Mg$_{0.1}$P$_2$O$_7$ at 700 °C.

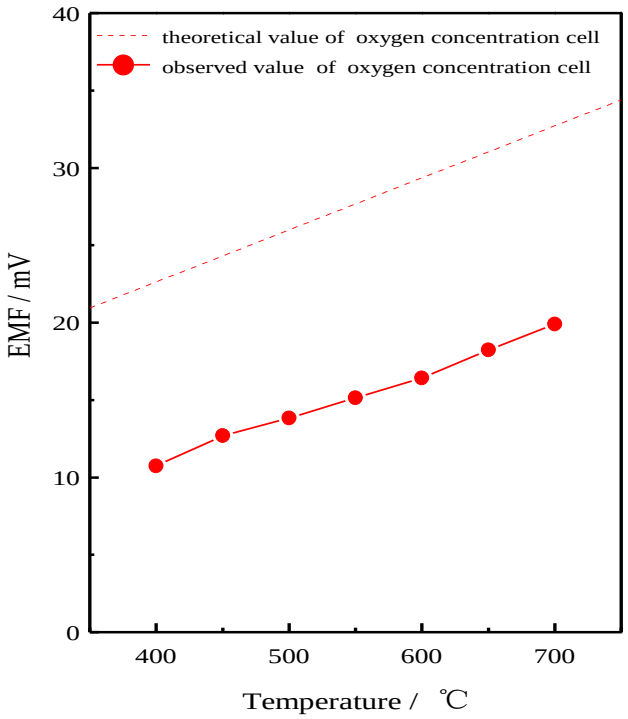

Figure 5. The relation between EMF and temperature of oxygen concentration cell: air, Pd-Ag| (Na/K)Ti$_2$(PO$_4$)$_3$/Ti$_{0.9}$Mg$_{0.1}$P$_2$O$_7$| Pd-Ag, O$_2$.

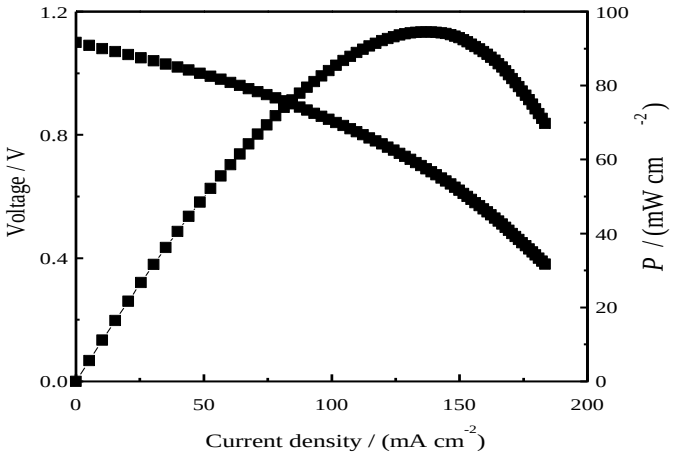

Figure 6. The H_2/O_2 fuel cell *I-V-P* curve of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ at 700 °C.

The $\log\sigma \sim \log(pO_2)$ plot of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ represented in Fig. 4, was used to study the ionic conduction at 700 °C. The left half of Fig. 4 is horizontal in a reductive atmosphere ($10^{-20} \sim 10^{-10}$ atm), which confirms that $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ is a good ionic conductor [26]. Meanwhile, the right half of Fig. 4 is upwards as the pO_2 increases, which means $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ is a mixed conductor of electron hole and oxide ion in a oxidizing atmosphere ($10^{-10} \sim 10^{0}$ atm) [27-28].

To study the oxide ionic conduction of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ in a oxidizing atmosphere, an oxygen concentration cell was devised and the results are displayed in Fig.5. The oxide ionic transport numbers (t_O) could be calculated on the basis of $t_O = EMF_{obs} / EMF_{cal} = 0.47\text{-}0.61$. The EMF_{cal} and EMF_{obs} are the theoretical and observed electromotive forces of the oxygen concentration cell, respectively. The EMF_{cal} is calculated as: $EMF_{cal} = \frac{RT}{4F} t_O \ln[p_{O_2\,(A)} / p_{O_2\,(B)}]$ when $t_O = 1$. The results are agreed with the right half of Fig. 4($10^{-10} \sim 10^{0}$ atm) and prove that electron hole conduction exists besides the oxide ionic conduction.

Fig. 6 shows the *I-V-P* characteristics of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$. Fig. 6 shows that the voltage is about 1.1 V which indicates there is no crossover of H_2 or O_2. The peak power output density of the $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ (thickness = 1.0 mm) is 94.5 $mW \cdot cm^{-2}$ at 700 °C. Chen et al. got a peak power density of 17.3 $mW \cdot cm^{-2}$ at 700 °C using $Sn_{0.9}In_{0.1}P_2O_7$ as electrolyte (thickness = 0.78 mm) [29]. Compared with the MP_2O_7-based single electrolytes, the $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ not only improves fuel cell performance, but also increases the application temperature range.

4. CONCLUSIONS

In this paper, a novel composite electrolyte of $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ was successfully synthesized by a one-step approach using Mg^{2+}-doped titanium pyrophosphate and inorganic molten salt as precursors. The SEM results demonstrated that two phases of $Ti_{0.9}Mg_{0.1}P_2O_7$ and corresponding phosphate, $(Na/K)Ti_2(PO_4)_3$, are interconnected a dense electrolyte. The highest conductivity of the

composite electrolyte was 5.4×10^{-2} $S\cdot cm^{-1}$ in dry N_2 at 700 °C. The results of electrical conductivity measurement and $\log\sigma \sim \log(pO_2)$ plot show that $(Na/K)Ti_2(PO_4)_3/Ti_{0.9}Mg_{0.1}P_2O_7$ is a mixed conductor of oxide ions and electron holes in a oxidizing atmosphere and an ionic conductor in a reductive atmosphere. The peak power output density of the composite electrolyte reached 94.5 $mW\cdot cm^{-2}$ at 700 °C.

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References

1. J. Luo, A.H. Jensen, N.R. Brooks, J. Sniekers, M. Knipper, D. Aili, Q. Li, B. Vanroy, M. Wübbenhorst, F. Yan, L.V. Meervelt, Z. Shao, J. Fang, Z.-H. Luo, D.E.D. Vos, K. Binnemans and J. Fransaer, *Energy Environ. Sci.*, 8(2015) 1276.
2. X. Gao, J. Ma, Y. Li and H. Wei, *Int. J. Electrochem. Sci.*, 12 (2017) 11287.
3. T. Hibino, K. Kobayashi, P. Lv, M. Nagao, S. Teranishi and T. Mori, *J. Electrochem. Soc.*, 164 (2017) F557.
4. K. K. Hansen, *Int. J. Electrochem. Sci.*, 12 (2017) 11540.
5. T. Hibino, K. Kobayashi, M. Nagao and S. Teranishi, *ChemElectroChem*, 4 (2017) 3032.
6. O. K. Alekseeva, E. K. Lutikova, V. V. Markelov, V. I. Porembsky and V. N. Fateev, *Int. J. Electrochem. Sci.*, 13 (2018) 797.
7. X. Zhang, J. Luo, P. Tang, J. R. Morante, J. Arbiol, C. Xu, Q. Li and J. Fransaer, *Sens. Actuators B Chem.*, 254 (2018) 272.
8. V. Nalini, M. H. Sorby, K. Amezawa, R. Haugsrud, H. Fjellvag and T. Norby, *J. Am. Ceram. Soc.*, 94 (2011) 1514.
9. B. Singh, H. N. Im, J. Y. Park and S. J. Song, *J. Phys. Chem. C*, 117 (2013) 2653.
10. A. Lapina, C. Chatzichristodoulou, J. Hallinder, P. Holtappels and M. Mogensen, *J. Solid State Electrochem.*, 18 (2014) 39.
11. V. Nalini, R. Haugsrud and T. Norby, *Solid State Ionics*, 181 (2010) 510.
12. H. Wang, L. Sun, C. Luo, R. Yin and Y. Cui, *Ceram. Int.*, 41 (2015) 2124.
13. Y. Sato, Y.B. Shen, M. Nishida, W. Kanematsu and T. Hibino, *J. Meter. Chem.*, 22 (2012) 3973.
14. B. Singh, J. H. Kim, O. Parkash and S. J. Song, *Ceram. Int.*, 42 (2016) 2983.
15. Y.C. Jin, M. Nishida, W. Kanematsu and T. Hibino, *J. Power Sources*, 196 (2011) 6042.
16. P. Heo, Y. Shen, K. Kojima, C. Pak, K. H. Choi and T. Hibino, *Electrochim. Acta*, 128 (2014) 287.
17. Q. Li, H. A. Hjuler and N. J. Bjerrum, *J. Appl. Electrochem.*, 31 (2001) 773.
18. J. Liao, J. Yang, Q. Li, L. N. Cleemann, J. O. Jensen, N. J. Bjerrum, R. He and W. Xing, *J. Power Sources*, 238 (2013) 516.
19. A. I. Mohamed and J. F. Whitacre, *Electrochim. Acta*, 235 (2017) 730.
20. J. Han, M. Xu, Y. Niu, M. Jia, T. Liu and C. M. Li, *Journal of Colloid and Interface Science*, 483 (2016) 67.
21. N. Li, Y. Wang, R. Rao, X. Dong, X. Zhang and S. Zhu, *Applied Surface Science*, 399 (2017) 624.
22. M. Bian and L. Tian, *Ceram. Int.*, 43 (2017) 9543.
23. H.J. Zhang, *Acta Cryst.*, E67 (2011) i51.

24. P. Hu, J. Ma and T. Wang, *Chem. Mater.*, 27 (2015) 6668.
25. R. Shi, R. Du, J. Liu and Hongtao Wang, *Ceram. Int.*, 44 (2018) 11878.
26. J. Guan, S.E. Dorris, U. Balachardran and M. Liu, *Solid State Ion.*, 100 (1997) 45.
27. G. Ma, T. Shimura and H. Iwahara, *Solid State Ion.*, 120 (1999) 51.
28. N. Sammes, R. Phillips and A. Smirnova, *J. Power Sources*, 134 (2004) 153.
29. X. Chen, C. Wang, E. A. Payzant, C. Xia and D. Chu, *J. Electrochem. Soc.*, 155 (2008) B1264.