

Energy Storage

A P2-Type Layered Superionic Conductor Ga-Doped Na₂Zn₂TeO₆ for All-Solid-State Sodium-Ion Batteries

Yuyu Li,^[a] Zhi Deng,^[a] Jian Peng,^[a] Enyi Chen,^[a] Yao Yu,^[a] Xiang Li,^[a] Jiahuan Luo,^[a] Yangyang Huang,^[a] Jinlong Zhu,^[b] Chun Fang,^[a] Qing Li,^[a] Jiantao Han,^{*[a]} and Yunhui Huang^[a]



Abstract: Here, a P2-type layered Na₂Zn₂TeO₆ (NZTO) is reported with a high Na⁺ ion conductivity \approx 0.6 \times 10⁻³ S cm⁻¹ at room temperature (RT), which is comparable to the currently best $Na_{1+n}Zr_2Si_nP_{3-n}O_{12}$ NASICON structure. As small amounts of Ga³⁺ substitutes for Zn²⁺, more Na⁺ vacancies are introduced in the interlayer gaps, which greatly reduces strong Na⁺-Na⁺ coulomb interactions. Ga-substituted NZTO exhibits a superionic conductivity of $\approx 1.1 \times 10^{-3} \,\text{S}\,\text{cm}^{-1}$ at RT, and excellent phase and electrochemical stability. All solid-state batteries have been successfully assembled with a capacity of \approx 70 mAh g⁻¹ over 10 cycles with a rate of 0.2 C at 80 °C. ²³Na nuclear magnetic resonance (NMR) studies on powder samples show intra-grain (bulk) diffusion coefficients $D_{\rm NMR}$ on the order of $12.35 \times 10^{-12} \, {\rm m^2 \, s^{-1}}$ at $65 \, {}^\circ {\rm C}$ that corresponds to a conductivity $\sigma_{\rm NMR}$ of 8.16× 10⁻³ S cm⁻¹, assuming the Nernst–Einstein equation, which thus suggests a new perspective of fast Na⁺ ion conductor for advanced sodium ion batteries.

All solid-state sodium-ion batteries (SS-SIBs) are promising lowcost and high-safety alternatives to today's lithium-ion batteries (LIBs), especially for large-scale energy storage systems (ESSs).^[1] However, a critical challenge for developing safe SS-SIBs is the current lack of sodium solid-state electrolytes (SSEs) with high-ionic conductivity, comparable to organic liquid electrolytes (OLEs) ($\approx 1.0 \times 10^{-2}$ S cm⁻¹ at RT).^[2]

Sulfide glass and oxide ceramic sodium-ion conductors are two kinds of common inorganic crystalline SSEs.^[3] Usually, sulfide electrolytes have higher ionic conductivities than that of oxides at RT, but sulfide electrolytes create unfriendly environ-

[a]	Y. Li, Z. Deng, J. Peng, E. Chen, Dr. Y. Yu, X. Li, Dr. J. Luo, Y. Huang,
	Dr. C. Fang, Q. Li, Prof. J. Han, Prof. Y. Huang
	State Key Laboratory of Material Processing and Die & Mould Technology
	School of Materials Science and Engineering
	Huazhong University of Science and Technology
	Wuhan, Hubei 430074 (P. R. China)
	E-mail: jthan@hust.edu.cn
[b]	Prof. J. Zhu
	Center for High Pressure Science & Technology Advanced Research
	Beijing 100094 (P. R. China)
	Supporting information and the ORCID identification number for the

author of this article can be found under https://doi.org/10.1002/ chem.201705466. ments, easily releasing toxic H₂S gas.^[4] In 1976, Hong et al.^[5] discovered NASICON-type Na₃Zr₂Si₂PO₁₂, and at RT, its conductivity is $\approx 1.0 \times 10^{-3}$ S cm⁻¹. β/β'' -alumina superionic conductors are already commercialized, however, mainly in high-temperature Na-S batteries, due to poor conductivity at RT.^[6] None of these materials has acceptable stability in sodium-ion systems and poor electrolyte-electrode contact complicates large-scale application.^[7]

Remarkably, layered oxides have a degree of freedom to expand the interstitial space between strongly-bonded 2D layers.^[8] Thus, large Na⁺ ions gain a large migration space in layered compounds more easily than in close-packed oxide ceramic hosts that are bonded strongly in three dimensions.^[9] Larger migration paths induce longer Na-O bonds to decrease the attractive force between Na^+ and the O^{2-} , facilitating Na^+ ions' migration.^[10] Therefore, considerable attention has been given to exploring the intercalation and diffusion of Na in lamellar oxides.^[11] In 2011, a new family of layered sodium compounds, $Na_2M_2TeO_6$ (M = Ni, Co, Zn, Mg), was discovered.^[12] In this family, the zinc compound, NZTO, has the largest interlayer space (\approx 5 Å), which provides a large Na⁺ ion migration path. Furthermore, there are no variable valence elements in NZTO, which guarantees it as a potential Na⁺ ion conductor for SS-SIBs.

In the present work, we report Na-ion SSEs of Na_{2-x}Zn_{2-x}Ga_xTeO₆ (NZTO-Gx, x = 0, 0.05, 0.1, 0.15, respectively, that is, NZTO, NZTO-G0.05, NZTO-G0.1, NZTO-G0.15). The highest Na⁺ ion conductivity of 1.1×10^{-3} S cm⁻¹ at RT is achieved in NZTO-G0.1 with respect to the endmember compounds NZTO and NZTO-G0.15, which is most likely related to the reduced amount of Na⁺ ions between the layers, and agrees with a recent report of NaFeO₂-related structure Na_{3-x}Sn_{2-x}Sb_xNaO₆ (x=0.8 with a maximum conductivity of 1.43×10^{-3} S cm⁻¹ at 500 °C).^[13] ²³Na-NMR studies reveal that the conductivity improvement stems from an interlayer cation deficiency, which is also a simple way to create phases with deficient Na layers.

Figure 1 a shows the crystal structure of NZTO with a $P6_{3}22$ space group. The layers are comprised of two ZnO₆ octahedra and one TeO₆ octahedron ordered in the plane with a shared edge, and each TeO₆ octahedron is surrounded by six ZnO₆, forming a honeycomb structure, whereas Na⁺ ions are ordered in the plane between two honeycomb layers. NZTO has two different Zn sites at Wyckoff positions 2*b* (Zn1) and 2*d* (Zn2), while both of their polyhedra are formed by six regular bonds

Wiley Online Library



Figure 1. Upper: Transformation of partial crystal structure before and after Ga substitution in NZTO. Lower: The XRD pattern of NZTO and results of Rietveld refinement.

with different lengths, 2.013 and 2.011 Å, respectively. Meanwhile, NZTO has three different Na sites at 6g (Na1), 2a (Na2), and 4f (Na3). Na1 is located midway between two tetrahedral holes, formed by two ZnO₆ and one TeO₆ octahedra and a large vacancy is introduced in the Na1-site by Ga³⁺ ion substitution on the Zn-site of NZTO. Na2 is sandwiched between the triangular faces of the ZnO₆ octahedra, and Na3 is between the ZnO₆ octahedra and TeO₆ octahedra. Based on a molecular dynamics (MD) simulation of Na⁺ ion transport in Na₂Ni₂TeO₆ (NNTO), Na⁺ ions migrate from Na1 to Na2, but with less contribution from Na3 because the potential energy of Na1 and Na2 (-2.45 and -2.65 eV, respectively) is much lower than that of Na3 (-2.32 eV).^[14] However, our bond valence sum (BVS) studies show that Na3 has nearly equal potential energy to Na1 and Na2 in Na₂Zn₂TeO₆ (NZTO) (see Figure S1, Supporting Information) because the repulsion of Na⁺ with Zn²⁺ of NZTO is much less than that of Na^+ with Te^{6+} of NNTO.

Figure 1 b shows the XRD pattern and Rietveld refinement of NZTO. The crystal parameters of NZTO are a=b=5.2874(1) Å and c=11.2781(4) Å, and most reflections can be indexed in the $P6_322$ space group. Obviously, the superlattice reflections are observed at *l*-odd-index peaks (101 and 103), as well as with two weak *l*-even-index peaks (100 and 102). This means that solely Zn atoms occupy the columns, which agrees with Evstigneeva's results.^[12]

The refinement parameters and crystallographic data of NZTO-Gx are shown in Table S1, Figure S2 and S3 (Supporting Information), respectively, and graphed in Figure S4. As Ga content x increases, the a lattice parameter decreases, confirming the introduction of Ga into the compound given the smaller radius of Ga^{3+} (0.69 pm) than that of Zn^{2+} (0.74 pm). As shown in Figure 1a, Ga enters into the Zn2 site selectively and preferably. Meanwhile, Na1-site vacancies are generated in the NZTO-Gx system, which is consistent with the lattice parameter trend that exhibits shrinking of the honeycomb layer. The mor-

phologies of cross sectional of NZTO-Gx samples are investigated by scanning electron microscopy (SEM, see Figure S5), demonstrating that the particle size of all NZTO-Gx samples are $\approx 2 \,\mu$ m. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves displayed in Figure S6a and S6b show a less than 1% weight loss and a small endothermic peak observed at 100°C, which are mostly related to the water absorbed on particle surfaces and a little hygroscopy. Furthermore, compared to fresh as-prepared samples, the lattice parameters of a one-month-stored sample have no significant change (see Figure S7), which reveals another key factor for SSE consideration.

Figure 2a shows the electrochemical impedance spectra (EIS) of NZTO and NZTO-G0.1 at RT, with a calculated conductivity of 0.63×10^{-3} and 1.1×10^{-3} S cm⁻¹, respectively. The details of total conductivity are shown in Table 1and Figure S8d

Table 1. Total resistance and conductivity, electron resistance and conductivity at room temperature and activation energy data for NZTO-Gx (x =0-0.15).							
Sample	$R_{ ext{total}}$ [Ω]	$\sigma_{ m total}$ [S cm ⁻¹]	$R_{\rm e} \left[\Omega \right]$	$\sigma_{ m e}$ [S cm ⁻¹]	Ratio [%]	E _a [eV]	
NZTO NZTO-G0.05 NZTO-G0.1 NZTO-G0.15	158.39 156.96 96.162 147.56	6.29×10^{-4} 7.43×10^{-4} 1.09×10^{-3} 7.34×10^{-4}	4.4×10^{5} 2.4 × 10 ⁶ 2.6 × 10 ⁵ 1.7 × 10 ⁵	$2.3 \times 10^{-7} 4.8 \times 10^{-8} 4.1 \times 10^{-8} 6.4 \times 10^{-8}$	0.036 0.007 0.004 0.008	0.327 0.298 0.271 0.281	

(Supporting Information). Figure S8c shows DC-polarization properties of NZTO-Gx. The stabilized currents of NZTO-Gx are much smaller than the initial current. This illustrates that the resistance of electronic conductivity is much lower than the ionic one in NZTO-Gx. The electronic conductivities of NZTO-Gx are shown in Table 1. The ratios of electron conductivity in total conductivity are less than 0.1%, which proves that NZTO-Gx are real Na⁺ ion conductors.

Figure 2 b shows the temperature dependence of conductivities in NZTO and NZTO-G0.1. The activation energy (E_a) of the ionic conductor is calculated using the equation: $\sigma_T = Aexp(-E_a/k_bT)$, where σ_T is the total conductivity, A is the preexponential parameter, T is absolute temperature, and k_b is the Boltzmann constant. As a result, E_a of NZTO and NZTO-G0.1 are 0.327 and 0.271 eV, respectively (see Figure 2b and Table 1). Figure 2c shows representative Nyquist plots of NZTO-G0.1 in a temperature range of 50 °C to 120 °C. As shown in Nyquist plots at 120 °C, the high-frequency semicircle vanished. This phenomenon is attributed to the increasing relaxation frequency of the bulk NZTO-G0.1, caused by temperature-dependent resistance.^[15]

Figure 2d displays the Arrhenius curves of NZTO, NZTO-G0.1, and typical sodium oxide SSEs. At about 100 °C, NZTO-G0.1 gives a higher ionic conductivity than single crystal β/β'' -alumina,^[6] Na₃Zr₂Si₂PO₁₂ (NASICON),^[16] and Ti-doped NASI-CON,^[17] but lower than Y-doped NASICON.^[18] Table 2shows the E_a of each oxide SSE displayed in Figure 2d. NZTO-G0.1 gives a lower E_a than NASICON, and its ionic conductivity is higher than other sodium oxide solid electrolytes, except for Y-doped

www.chemeurj.org





Figure 2. a) EIS measurements of NZTO and NZTO-G0.1 at RT from 1 Hz–1 MHz. b) Arrhenius conductivity plots of NZTO and NZTO-G0.1 from 50 to 120 °C. c) Nyquist impedance plot of NZTO-G0.1 from 50 to 120 °C. d) Arrhenius conductivity plots of NZTO, NZTO-G0.1, and other oxide sodium ion conductors prepared by conventional solid-state reactions.

Table 2. Activation energy for NZTO, NZTO-G0.1, and other oxide Na con- ductors prepared by conventional solid-state reaction.							
Composition	Activation energy [eV]	Ref.					
$\begin{array}{l} Na_{1,9}Zn_{1,9}Ga_{0,1}TeO_{6}\\ Na_{2}Zn_{2}TeO_{6}\\ Na_{3}Zr_{2}Si_{2}PO_{12}\\ Na_{3}Zr_{1,7}Ti_{0,3}Si_{2}PO_{12}\\ Na_{3,1}Zr_{1,9}Y_{0,1}Si_{2}PO_{12}\\ Na-\beta''-Al_{2}O_{3} \end{array}$	0.271 0.329 0.385 0.259 0.210 0.205	this work this work [15] [16] [17] [6]					

NASICON. The main reasons could be: 1) large ionic migration interlayers in NZTO-G0.1, because Ga³⁺ substitution does not change the crystal structure of NZTO and the size of the Na⁺ migration pathway in NZTO-G0.1 is 5.58 Å, larger than that of NASICON and β/β'' -alumina, inducing longer Na–O bonds and decreasing attractive force between Na⁺ and O²⁻. 2) Enough

Na-site vacancies in NZTO-G0.1 as these vacancies not only increase the concentration of current carriers, but decrease the migration energy (E_m) of sodium ions^[19] because of a similar ionic radius of Ga³⁺ with Zn²⁺, and no distortion is generated in the crystal structure.

Figure 3 a shows ²³Na NMR spin-lattice relaxation rates T_1^{-1} versus inverse temperature of NZTO and NZTO-G0.1, respectively. For these two samples, T_1^{-1} increases linearly to a maximum and then drops off with increasing temperature. At the maximum, the motional correlation time (i.e., the Na⁺ hopping time τ) is optimal for the frequency distribution to be effective for relaxation, and condition $\omega_0 \tau \approx 1$ is fulfilled. In Figure 3 a, as $\omega_0/2\pi = 105.8$ MHz, the Na⁺ hopping rate $\tau_0^{-1} \approx 6.6 \times 10^8 \text{ s}^{-1}$ of the two samples can be reached at the different temperatures. ²³Na NMR results show that the two sample diffusion coefficients are 5.46×10^{-12} and $12.35 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at 65 °C, respectively. Figure 3 b shows that the comparison of two samples, E_a





Figure 3. a) ²³Na NMR spin-lattice relaxation rates T_1^{-1} versus inverse temperature for NZTO and NZTO-G0.1. b) E_a calculated by EIS from bulk Na-ion conductivity of NZTO and NZTO-G0.1 compared with E_m calculated by ²³Na NMR T_1^{-1} measurements.

and E_m from EIS and NMR, respectively, shows these two kinds of results are significantly close, 0.136 and 0.12 eV for NZTO, and 0.07 and 0.05 eV for NZTO-G0.1, and they both confirm each other.

Figure 4a shows the electrochemical stability of NZTO-Gx with metallic Na investigated by cyclic voltammetry (CV) measurements in Na/NZTO-Gx/Steel cells. Obvious anodic peaks appear at close to 4.5 V, which shows that NZTO-Gx are electrochemically stable in conjunction with metallic Na with similar electrochemical windows of \approx 4.0 V and no adverse side reactions. Figure 4b displays galvanostatic cycling of a symmetric Na/NZTO-Gx/Na cell with a current density of 0.1 mA cm⁻² at 45 °C. The results demonstrate that sodium is plated and stripped fully reversibly with a low overpotential, reaching a maximum of \approx 50 mV for 50 cycles; the resistance of Na and NZTO-G0.1 is \approx 225 Ω calculated by Galvanostatic cycling, smaller



Figure 4. a) Cyclic voltammogram in a Na/NZTO-Gx/Steel cell (x = 0, 0.1) between -0.5 and 4.5 V at scanning rate of 5 mV s⁻¹. b) Cyclability of NZTO and NZTO-G0.1 in a symmetric Na/NZTO-Gx/Na (x = 0, 0.1) cell with current density of 0.1 mA cm⁻² at 45 °C. c) Charge/discharge curves of NVP/NZTO-Gx/Na (x = 0, 0.1) with 0.2 C at 80 °C. The insert displays the polarization of the two cells and d) cycle performance of NVP/NZTO-Gx/Na (x = 0, 0.1) with 0.2 C at 80 °C.

Chem. Eur. J. 2018, 24, 1057 - 1061

www.chemeurj.org

© 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



than that of Na and NZTO at \approx 360 Ω . Importantly, the stability between NZTO-Gx SSEs and the metallic Na anode has been significantly improved by Ga substitution.

Figure 4c shows the charge and discharge curves of NVP/ NZTO-Gx/Na (x = 0, 0.1) cells with a current rate of 0.2 C at 80 °C. These solid-state batteries with NZTO-G0.1 electrolyte illustrate a smaller polarization and a higher reversible capacity of \approx 70 mAh g⁻¹ over 10 cycles at 80 °C. The EIS of the solidstate batteries with NZTO and NZTO-G0.1 are shown in Figure S10; the total resistance of solid-state batteries with NZTO-G0.1 is much smaller than with NZTO, illustrated that Ga doping can reduce the resistance of SS-SIBs. Figure 4d shows that the two kinds of SS-SIBs exhibit excellent cycle performances at 80°C. Though the performance of SS-SIBs is inferior to conventional batteries with liquid electrolyte (see Figure S10), and the Coulombic efficiencies of SS-SIBs with NZTO-0.1G is only \approx 70% (see Figure S11), the performance of the two kinds of SS-SIBs demonstrate that NZTO-Gx compounds are applicable as electrolytes for fabricating advanced SS-SIBs.

In summary, we report a novel NZTO-G0.1 superionic conductor as a solid electrolyte for SS-SIBs. This solid electrolyte requires a simple solid-state synthetic route and shows excellent chemical stability under ambient conditions. Moreover, remarkable electrochemical stability with a metallic Na is also demonstrated. Importantly, it also gives an amazing ionic conductivity of 1.1×10^{-3} S cm⁻¹ at RT as a result of a large 2D-reticulate Na-ion migration pathway provided by its layered structure, which benefits fast Na^+ ion transport. Combining ²³Na-NMR, EIS, and BVS analyses with electrochemical results, the extraordinary conductivity in NZTO-Gx is mainly attributed to Na-site vacancies slightly decreasing the number of mobile Na^+ ions. Meanwhile, it facilitates Na^+ ion motion by increasing the mobility of the Na^+ ions. The discovery of these layered sodium-ion SSEs will lead to a progressive development of SS-SIBs.

Acknowledgements

This work was supported by the National Key R&D Program of China (Grant Nos. 2016YFB010030X and 2016YFB0700600), National Natural Science Foundation of China (Grant Nos. 51772117 and 51732005). The authors also thank the Analytical and Testing Centre of HUST and the State Key Laboratory of Materials Processing and Die & Mould Technology of HUST for XRD, SEM, TEM, Raman, TGA, and other measurements.

Conflict of interest

The authors declare no conflict of interest.

Keywords: all-solid-state batteries • P2-type • sodium-ion batteries • superionic conductor

- a) M. Armand, J. M. Tarascon, *Nature* 2008, 451, 652–657; b) X. Li, Y. Huang, Y. Li, S. Sun, Y. Liu, J. Luo, J. Han, Y. Huang, *RSC Adv.* 2017, 7, 4791–4797; c) Y. Huang, X. Li, J. Luo, K. Wang, Q. Zhang, Y. Qiu, S. Sun, S. Liu, J. Han, Y. Huang, *ACS Appl. Mater. Interfaces* 2017, 9, 8696–8703; d) J. Luo, S. Sun, J. Peng, B. Liu, Y. Huang, K. Wang, Q. Zhang, Y. Li, Y. Jin, Y. Liu, Y. Qiu, Q. Li, J. Han, Y. Huang, *ACS Appl. Mater. Interfaces* 2017, 9, 25317–25322.
- [2] a) C. Sun, J. Liu, Y. Gong, D. P. Wilkinson, J. Zhang, *Nano Energy* 2017, 33, 363–386; b) N. J. D. J. B. Bates, B. Neudecker, A. Ueda, C. D. Evans, *Solid State Ionics* 2000, 135, 33; c) J. C. Bachman, S. Muy, A. Grimaud, H.-H. Chang, N. Pour, S. F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano, Y. Shao-Horn, *Chem. Rev.* 2016, 116, 140–162; d) Z. Yu, S. L. Shang, J. H. Seo, D. Wang, X. Luo, Q. Huang, S. Chen, J. Lu, X. Li, Z. K. Liu, D. Wang, *Adv. Mater.* 2017, 29, 1605561; e) Y. Li, W. Zhou, X. Chen, X. Lu, Z. Cui, S. Xin, L. Xue, Q. Jia, J. B. Goodenough, *Proc. Natl. Acad. Sci. USA* 2016, 113, 13313–13317.
- [3] a) J. F. Wu, W. K. Pang, V. K. Peterson, L. Wei, X. Guo, ACS Appl. Mater. Interfaces 2017, 9, 12461–12468; b) Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, R. Kanno, Nat. Energy 2016, 1, 16030; c) W. Luo, Y. Gong, Y. Zhu, K. K. Fu, J. Dai, S. D. Lacey, C. Wang, B. Liu, X. Han, Y. Mo, E. D. Wachsman, L. Hu, J. Am. Chem. Soc. 2016, 138, 12258–12262.
- [4] a) C. Yu, S. Ganapathy, N. J. de Klerk, I. Roslon, E. R. van Eck, A. P. Kentgens, M. Wagemaker, J. Am. Chem. Soc. 2016, 138, 11192–11201; b) H. Wang, Y. Chen, Z. D. Hood, G. Sahu, A. S. Pandian, J. K. Keum, K. An, C. Liang, Angew. Chem. Int. Ed. 2016, 55, 8551–8555; Angew. Chem. 2016, 128, 8693–8697.
- [5] H. Y. P. Hong, Mater. Res. Bull. 1976, 11, 173-182.
- [6] J. W. Fergus, Solid State Ionics 2012, 227, 102-112.
- [7] a) Z. Zhang, Q. Zhang, J. Shi, Y. S. Chu, X. Yu, K. Xu, M. Ge, H. Yan, W. Li, L. Gu, Y.-S. Hu, H. Li, X.-Q. Yang, L. Chen, X. Huang, *Adv. Energy Mater.* **2017**, *7*, 1601196; b) W. Zhou, Y. Li, S. Xin, J. B. Goodenough, *ACS Cent. Sci.* **2017**, *3*, 52–57.
- [8] a) V. B. Nalbandyan, A. A. Petrenko, M. A. Evstigneeva, Solid State lonics 2013, 233, 7–11; b) A. Gupta, C. B. Mullins, J. B. Goodenough, J. Power Sources 2013, 243, 817–821.
- [9] K. M. Bui, V. A. Dinh, S. Okada, T. Ohno, Phys. Chem. Chem. Phys. 2016, 18, 27226 – 27231.
- [10] H. Park, K. Jung, M. Nezafati, C. S. Kim, B. Kang, ACS Appl. Mater. Interfaces 2016, 8, 27814–27824.
- [11] M. Catti, M. Montero-Campillo, Phys. Chem. Chem. Phys. 2011, 13, 11156-11164.
- [12] M. A. Evstigneeva, V. B. Nalbandyan, A. A. Petrenko, B. S. Medvedev, A. A. Kataev, Chem. Mater. 2011, 23, 1174-1181.
- [13] R. W. Smaha, J. H. Roudebush, J. T. Herb, E. M. Seibel, J. W. Krizan, G. M. Fox, Q. Huang, C. B. Arnold, R. J. Cava, *Inorg. Chem.* **2015**, *54*, 7985– 7991.
- [14] K. Sau, P. P. Kumar, J. Phys. Chem. C 2015, 119, 1651-1658.
- [15] R. Wagner, G. J. Redhammer, D. Rettenwander, G. Tippelt, A. Welzl, S. Taibl, J. Fleig, A. Franz, W. Lottermoser, G. Amthauer, *Chem. Mater.* 2016, 28, 5943-5951.
- [16] M. Samiee, B. Radhakrishnan, Z. Rice, Z. Deng, Y. S. Meng, S. P. Ong, J. Luo, J. Power Sources 2017, 347, 229–237.
- [17] T. Takahashi, K. Kuwabara, M. Shibata, Solid State Ionics 1980, 1, 163– 175.
- [18] A. G. Jolley, G. Cohn, G. T. Hitz, E. D. Wachsman, *Ionics* **2015**, *21*, 3031–3038.
- [19] C. Bernuy-Lopez, W. Manalastas, J. M. Lopez del Amo, A. Aguadero, F. Aguesse, J. A. Kilner, *Chem. Mater.* 2014, *26*, 3610–3617.

Manuscript received: November 17, 2017 Accepted manuscript online: December 10, 2017 Version of record online: January 4, 2018

Chem. Eur. J. 2018, 24, 1057 – 1061

www.chemeurj.org

1061

© 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim