Chemical Sodiation of V₂O₅ by Na₂S

Robert Haberkorn,*^[a] Jessica Bauer,^[a] and Guido Kickelbick^[a]

Keywords: X-ray diffraction; Rietveld analysis; Sodiation; Cathode material; Vanadium

Abstract. Chemical sodiation of V_2O_5 at low temperatures allows to synthesize $Na_xV_2O_5$ with $0 \le x \le 1$, while classic high temperature syntheses yield in either $x \le 0.02$ (α -phase) or $0.7 \le x$ (α' -phase), or other phases (β -phase, δ -phase) or mixtures thereof. A suspension of V_2O_5 in acetonitrile and Na_2S as sodiation agent were used. The maximum amount of sodiation was obtained by using an excess of Na_2S ,

Introduction

Sodium ion conductors are potential alternative materials to replace lithium ion conductors as cathode materials in batteries. In contrast to sodium compounds lithium compounds and their application as cathode materials are well established in literature. In commercially available batteries materials based on Li MO_2 (M = Co, Fe, Mn, Ni) and LiFe $PO_4^{[1]}$ are used. But also alternative compounds such as LiCo PO_4 ,^[2] Li_{1.2}V₃O₈,^[3] and LiVPO₄F^[4] have been investigated. Recently also corresponding Na containing compounds became of increasing interest, because sodium is less expensive and less toxic than lithium.^[5]

NaCoO₂^[5] also proved to be a suitable cathode material. Within the system Na₂O-V₂O₃-V₂O₅ the compounds Na_{0.02}V₂O₅ [space group *Pmmn*, α -Na_xV₂O₅, $0 \le x \le 0.02$), Na_{0.33}V₂O₅ (space group *C2/m*, β -Na_xV₂O₅, $0.25 \le x \le 0.45$), Na_{1.2}V₃O₈, NaVO₃, Na₄V₂O₇, and Na₃VO₄ may be synthesized in a high temperature process (HTP) in air. The compounds Na_{0.64}V₂O₅ (space group *C2/m*, τ -Na_xV₂O₅)^[6] and NaV₂O₅ (*Pmmn*, α' -Na_xV₂O₅, 0.7 < x < 1) ^[7] have been synthesized in high temperature processes, too, but using inert conditions.^[8] By an HTP no α/α' -Na_xV₂O₅ with $0.02 \le x \le$ 0.7 may be prepared.

Electrochemical sodiation or desodiation of α -Na_xV₂O₅, β -Na_xV₂O₅ and Na_xV₃O₈ is also reported.^[9] To the best of our knowledge chemical sodiation of these compounds is not described in literature yet.

refluxing the acetonitrile during the reaction, and precedent ball milling of the V₂O₅. If only low amounts of Na₂S were used as starting material, a mixture of fractions of Na_xV₂O₅ with different values of *x* was obtained. All these fractions belong to the α - or α' -phase, space group *Pmmn*.

Besides electrochemical lithiation and delithiation^[10–15] also chemical lithiation is reported. Most often this is done by butyl-Li,^[16] but also the use of LiI^[17] and Li₂S^[18] is mentioned. Since butyl-sodium is not commercially available NaI and Na₂S are promising candidates for chemical sodiation. Chemical lithiation is also reported for β -Na_xV₂O₅.^[19]

Results and Discussion

 NaV_2O_5 was prepared using a solid state reaction (ssr- NaV_2O_5). The Rietveld refinement provided lattice parameters and coordinates of sites, which showed good agreement with data from literature.^[20] Traces of $NaVO_3$ (<2 wt-%) could be found in the diffractogram. Some crystallographic data according to this refinement and of the refinement of the starting material V_2O_5 are given in Table 1. The corresponding diffractograms are given in Figure 1. The atomic positions are given in the Supporting Information together with a figure of the crystal structure of NaV_2O_5 .

Table 1. Lattice parameters and additional data for V_2O_5 and $ssrNaV_2O_5$ according to Rietveld refinements.

Parameter	V ₂ O ₅	NaV ₂ O ₅	
Name of phase	α -Na _x V ₂ O ₅	α' -Na _x V ₂ O ₅	
Sample	JBB000	JBB061	
Na contents as x	0.00	1.00	
Space group	Pmmn	Pmmn	
2θ range /°	7-120	7-120	
a /Å	11.5131(1)	11.3195(1)	
b /Å	3.5644(1)	3.6131(1)	
c /Å	4.3736(1)	4.8055(1)	
$V/Å^3$	179.49(1)	196.54(1)	
Ζ	4	4	
$d_{\rm X-ray}$ /g·cm ⁻³	3.365	3.462	
R _{wp}	0.110	0.146	
R _{Bragg}	0.072	0.103	
wt%	100	98.6(1)	
No. of refined parameters	36	44	

^{Dr. R. Haberkorn} Fax: +49-681-302-70652 E-Mail: haberkorn@mx.uni-saarland.de
[a] Anorganische Festkörperchemie Universität des Saarlandes Box 151150 66041 Saarbrücken, Germany

Supporting information for this article is available on the WWW

under http://dx.doi.org/10.1002/zaac.201400381 or from the author.



Figure 1. Main part of the XRD patterns of V2O5 and ssr-NaV2O5.

The samples obtained by tribochemical reactions (tcr- $Na_xV_2O_5$) were measured on a low background sample holder (lbsh) with 20 min scan time immediately after opening the beaker. A second measurement of the dried material was carried out later in a standard sample holder (stsh) with 2 h scan time. Some crystallographic information and additional parameters of these samples are given in Table 2. The corresponding diffractograms of the measurements with stsh are shown in Figure 2.



Figure 2. Main part of the XRD patterns of tcr-Na_xV₂O₅.

After evaporation of acetonitrile the sample JBB104 showed small bright yellow needles, which could be identified as sulfur (space group $P2_1/c$). After homogenization of the material no sulfur could be found in the diffractogram anymore, but traces of an additional unknown phase. The amount of this phase increased with increasing amount of Na₂S as starting material. Probably the reaction may be written as

$$V_2O_5 + \frac{x}{2}Na_2S \rightarrow Na_xV_2O_5 + \frac{x}{2}S$$
⁽¹⁾

The sulfur was at least partly dissolved in the acetonitrile and crystallized, while acetonitrile evaporated. Perhaps, by homogenization of the mixture, the sulfur reacted with an additional byproduct to an unknown compound.

The diffractograms of the tcr-Na_xV₂O₅ samples show a rather sharp peak close to 20.3 °C, the peak position of the (001)-peak of V₂O₅. In the 2 θ range from 19° to 20° is a broad (001)-peak of sodiated V₂O₅. The extreme broadening is caused by a distribution of *x* in Na_xV₂O₅. For Rietveld analysis a model of 34 fractions of Na_xV₂O₅ with different values of *x* (see Experimental Section) enabled a rather proper fit of the complete diffractogram including the (001) peak. From the weight fractions of the Na_xV₂O₅ "phases" relative mol fractions n could be calculated yielding a distribution function n(*x*) and their average value $\langle x \rangle$ is a measure of the amount of sodiation.

According to Equation (1) and taking the weight fraction of the starting materials into account a maximum value x_{max} of xis defined. This value is only a nominal value and should not be confused with the maximum value of x found in any of the fractions of Na_xV₂O₅. For low weight fractions of Na₂S within the starting materials (JBB101, JBB102) the amount of sodiation increases about linearly with $\langle x \rangle = x_{max}/2$. For a higher weight fraction of Na₂S (JBB104) only a minor increase of sodiation was observed.

The distribution functions n(x) of the tcr-Na_xV₂O₅ samples are shown in Figure 3.



Figure 3. Distribution functions of n(x) of tcr-Na_xV₂O₅.

Table 2. Sodium contents and additional data for tcr-Na_x V_2O_5 according to Rietveld refinements.

Sample Method Sample holder $x_{max} < x >$ Additional phases	
JBB101 tcr lbsh 0.20 0.09 none	
stsh 0.20 0.07 traces of unknown ph	ase
JBB102 tcr lbsh 0.50 0.26 traces of unknown ph	ase
stsh 0.50 0.28 traces of unknown ph	ases
JBB104 tcr lbsh 1.00 0.25 traces of unknown ph	ase
stsh 1.00 0.29 unknown minor phase	es



Table 3. Sodium contents and additional data for strt1- and strt7- $Na_xV_2O_5$ according to Rietveld refinements.

Sample	Method	Sample holder	x _{max}	<_x>	Additional phases
JBB069	strt1	dome	0.50	0.32	none
JBB066	strt1	dome	1.00	0.48	2 wt% Na ₂ S, 2 wt% α -Na ₂ S ₂ , traces of unknown phase
JBB072	strt1	dome	2.00	0.48	9 wt% Na ₂ S, 5 wt% α -Na ₂ S ₂ , 7 wt% β -Na ₂ S ₂ , traces of unknown phase
JBB070	strt7	dome	1.00	0.55	none

Table 4. Sodium contents and additional data for strf1-, strf7-, bmrf1-, and bmrf7-Na_xV₂O₅ according to Rietveld refinements.

Sample	Method	Sample holder	x _{max}	<x></x>	Additional phases
JBB073	strf1	dome	2.00	0.63	4 wt% Na ₂ S, 7 wt% α -Na ₂ S ₂ , 10 wt% β -Na ₂ S ₂ , traces of unknown phase
JBB085	strf1	dome	4.00	0.71	24 wt% Na ₂ S, 10 wt% Na ₂ S ₂ , 7 wt% α-Na ₂ S ₂ , 10 wt% β-Na ₂ S ₂ , traces of unknown phase
JBB074	strf7	dome	2.00	0.80	3 wt% α -Na ₂ S ₂ , 12 wt% β -Na ₂ S ₂ , traces of unknown phase
JBB084	bmrf1	dome	2.00	0.80	1 wt% α-Na ₂ S ₂ , 12 wt% β-Na ₂ S ₂ , unknown minor product
JBB088	bmrf1	dome	4.00	0.97	8 wt% Na ₂ S, 3 wt% α-Na ₂ S ₂ , 17 wt% β-Na ₂ S ₂ , un- known minor product
JBB098	bmrf7	dome	4.00	0.98	17 wt% β -Na ₂ S ₂ , unknown minor product

If a mixture of Na_2S , V_2O_5 , and acetonitrile was stirred under inert atmosphere for 1 d (strt1-method) a similar behavior could be found. The results are given in Table 3.

A low amount of the starting material Na₂S showed a rather high yield, but even with $x_{max} = 2$ only $\langle x \rangle = 0.48$ was achieved, the same value as for $x_{max} = 1$. If the suspension was stirred for 7 d a slight increase of the sodiation could be observed ($\langle x \rangle = 0.55$ for JBB070).

Some samples were prepared by heating the suspension to reflux for 1 d (strf1-method) or 7 d (strf7-method). Also V_2O_5 , which had been ball milled for 2 h, was used as starting material and the suspension stirred for 1 d (bmrf1-method) or 7 d (bmrf7-method). The results are given in Table 4.

For most of the sodiated samples $\langle x \rangle \leq x_{max}/2$ is valid. Samples, especially with excess of Na₂S synthesized, often show Na₂S₂ as a byproduct. Therefore,

$$V_2O_5 + xNa_2S \rightarrow Na_xV_2O_5 + \frac{x}{2}Na_2S_2$$
⁽²⁾

might be the dominant reaction instead of the redox process according to Equation (1).

In order to obtain a better overview of these results the values of $\langle x \rangle$ of all sodiated samples mentioned above in dependence on the x_{max} are graphically represented in Figure 4.

Each preparation method tends to converge with increasing amount of Na₂S to an individual maximum of sodiation $\langle x \rangle_{max}$. Ball milling for 2 h (tcr-method) had the lowest $\langle x \rangle_{max}$ of about 0.3. Stirring for 1 d enabled a higher sodiation and $\langle x \rangle_{max} \approx 0.5$. If the suspension was stirred for 7 d, the sodium content only increased slightly and $\langle x \rangle_{max} \leq 0.6$ may be estimated.

While refluxing the suspension at 81 °C the sodiation significantly improved. Stirring for 1 d (strf1) suggests $\langle x \rangle_{max} \approx 0.7$ and stirring for 7 d (strf7) enables at least $\langle x \rangle_{max} \approx 0.8$. Although the V₂O₅ was a fine powder the influence of ball



Figure 4. Amount of sodiation $\langle x \rangle$ dependent on x_{max} for different preparation methods.

milling the starting material only prior to weighing was tested. If refluxing the suspension for 1 d (bmrf1) a sodiation of $\langle x \rangle_{max} \approx 1.0$ was obtained. No significant increase was found for a prolonged reaction time of 7 d (bmrf7). This is equivalent to a compound NaV₂O₅, where one half of vanadium atoms have the oxidation state +4, the other half the oxidation state +5.

For selected measurements Figure 5 shows a 2θ range within which the (001)- and (101)-peak of Na_xV₂O₅ appear. The shift of the peak positions to lower 2θ values with increasing $\langle x \rangle$ may be clearly seen. The sample JBB088 shows (in the displayed 2θ range) nearly the same peak positions as ssrNaV₂O₅. The peaks are significantly, but not drastically broadened.

The measurements with a smaller amount of sodiation show more severely broadened peaks. Figure 6 shows the distribu-

ARTICLE



Figure 5. XRD patterns of selected $Na_xV_2O_5$ samples.



Figure 6. Distribution functions of n(x) of selected samples $Na_xV_2O_5$.

tion functions n(x) calculated from the same measurements as displayed in Figure 4.

The top and bottom curves in Figure 5 represent the reference materials V_2O_5 and NaV_2O_5 . Minor sodiated samples (JBB102, JBB069) still show a significant mol fraction with $x \approx 0$. For $x \approx 0.3$ and $x \approx 0.6$ a fraction peak may be found, which is broader than for the reference materials with x = 0and x = 1, but rather small in comparison with distributions n(x) with maxima at other values of x. This behavior was also found for samples not displayed in Figure 6. This might be correlated with ordering of sodium as it is described for lithiation of $Li_{1.2}V_3O_8$ ^[21]. However the quality of the measurements with severely broadened Bragg peaks did not allow determination of such an effect.

The complex model of the Rietveld analysis of the XRD measurements enables a rather proper fit even of the Na_xV₂O₅ phase. In Figure 7 the Rietveld-Plot of observed, calculated, and difference intensities is given. But the markers of the 34 fractions of Na_xV₂O₅, the three reference phases, and Na₂S₂ have not been implemented. The fraction distribution n(x) calculated from this fit is shown as an inlet. Again maxima in the fraction distribution at $x \approx 0.3$ and $x \approx 0.6$ may be seen.



Figure 7. Rietveld plot of XRD pattern for JBB066 and (small picture) fraction distribution n(x).

For many systems a linear relation between lattice parameters and composition may be found. Assuming such linear correlation in the case of the fractions of the phase Na_xV₂O₅ caused a significant misfit by Rietveld analysis. Therefore as simple extension a combination of two linear ranges for n(*x*) were assumed instead of one: linear correlation for the *a*, *b* and *c* axes for the range $-0.12 \le x \le 0.5$ and $0.5 < x \le$ 1.2. The dependence of the lattice parameters *a*, *b*, and *c*, as determined by the Rietveld analysis of the XRD pattern of the sample JBB066 is given in Figure 8 for the range $0 \le x \le 1$. Especially the *b* axis shows these two different ranges of linear correlation. The lattice parameters of "Na_{0.5}V₂O₅" are given in the Supporting Information (Table S3).



Figure 8. Lattice parameters of the fractions of the phase $Na_xV_2O_5$ vs. amount of sodiation of the sample JBB066.

Conclusions

Chemical sodiation of V_2O_5 is possible by Na_2S in acetonitrile as solvent or dispersion medium. To the best of our knowledge this is the first chemical sodiation of V_2O_5 , while electrochemical sodiation is already known. Simple ball milling for 2 h allows to get a sample of a mean sodium content



of up to 0.3 sodium per molecular formula ($\langle x \rangle_{max} = 0.3$), which is equivalent to a mean composition of Na_{0.3}V₂O₅. This may not be understood as a homogeneous compound but a mixture of fractions of the phase Na_xV₂O₅ with a broad distribution of sodium contents n(*x*).

Higher amounts of sodiation were achieved by stirring powder at room temperature ($\langle x \rangle_{max} = 0.5$) or under reflux ($\langle x \rangle_{max} = 0.6$) for 1 d. If stirring of the suspension was done over 7 d even higher sodium contents could be obtained. If the starting material V₂O₅ was ball milled prior to the reaction with sufficient Na₂S in boiling acetonitrile a more narrow distribution n(*x*) and a composition close to $\langle x \rangle = 1$ was obtained. This is equivalent to a compound NaV₂O₅. The same compound was prepared by a solid state reaction and is already known as α' -Na_xV₂O₅.

In contrast to high temperature processes all values of x within the range of $0 \le x \le 1$ may exist within the α -/ α '-Na_xV₂O₅. Compositions with $x \approx 0.3$ and $x \approx 0.6$ possibly are more preferred than other sodium contents. A nonlinear dependency of the lattice parameters on $\langle x \rangle$ is suggested by Rietveld analysis. Possibly both effects are caused by different types of ordering of sodium. Whether such ordering exists or not is a challenging question. Perhaps further studies aiming for synthesis and characterization of Na_xV₂O₅ with a narrow distribution function n(x) and 0.25 $\langle x \rangle < 0.75$ might allow to answer this question.

The sulfur of Na₂S may be reduced by sodiation of V₂O₅ to the oxidation state S⁻¹ and S⁰, while S⁻¹ as Na₂S₂ seems to be preferred for high amounts of Na₂S as starting material.

Experimental Section

The chemicals used were of the grade "pro analysi" or of a higher grade. V_2O_5 was annealed in a stream of 95 %Ar/5 %H₂ for 16 h at 700 °C. The product was repeatedly ground and annealed in a reducing atmosphere of the same composition until pure V_2O_3 was yielded. NaVO₃ was prepared by calcination of Na₂CO₃ and V₂O₅ at 600 °C for 6 h using a platinum crucible. NaV₂O₅ was synthesized by a high temperature process according to Equation (3):

$$4\text{NaVO}_3 + \text{V}_2\text{O}_5 + \text{V}_2\text{O}_3 \rightarrow 4\text{NaV}_2\text{O}_5 \tag{3}$$

The starting materials were ground in an agate mortar after adding *n*-pentane. The dried mixture was heated to 600 °C for 6 h in a sealed silica tube. In the following the product of this reaction will be called ssr-NaV₂O₅.

Starting materials or mixtures of starting materials were often treated in a ball mill to get fine grained powder, a homogeneous mixture or even a tribochemical reaction. A Fritsch Pulverisette 7 (Fritsch GmbH, Idar-Oberstein, Germany) was used with agate grinding beakers of a volume of about 25 cm³. A beaker was filled with 1 to 2 g of the material, 10 agate balls with a diameter of 1 cm, and 10 mL of solvent. Ball milling was done over 2 h at the speed level 6 to 7 of the Pulverisette. As solvents *n*-pentane and absolute acetonitrile were used. To yield absolute acetonitrile the acetonitrile as received was filtered through a column filled with molecular sieves 3 Å similar to the procedure described in literature^[22] and stored over molecular sieve.

 Na_2S was used to sodiate V_2O_5 acting as sodium source and reducing agent. Commercially available Na_2S ·9H₂O was dried by slowly heat-

ing to 100 $^{\circ}$ C in vacuo over several days and stored in a glove box. The purity of the product was verified by XRD measurements under inert conditions.

Different methods were applied for sodiation:

(1) tcr-method (tribochemical reaction): Different amounts of Na₂S and about 1 g of V_2O_5 were weighed inside the glove box and filled into a beaker of the Pulverisette already containing the balls. After locking out and quick addition of absolute acetonitrile the mixture was ball milled for 2 h. After opening the beaker one or two drops of suspension were dabbed on a low background sample holder for X-ray diffraction. The remaining suspension was dried by allowing the solvent to evaporate at room temperature. Thereafter a standard sample holder was used for X-ray measurements.

(2a) strt1-method (stirring at room temperature, 1 d): Different amounts of Na_2S and about 1 g of V_2O_5 were weighed inside the glove box and filled into a two necked round-bottomed flask. After locking out of the glove box the flask was connected to an argon supply and absolute acetonitrile was added under a counter flow of argon. The mixture was stirred for about 24 h at room temperature in an argon atmosphere. Subsequently, the solvent was removed under inert condition and the product dried in vacuo. For X-ray powder diffraction (XRD), a small fraction of the product was transferred to a "dome" sample holder in the glove box.

(2b) strf1-method (stirring under reflux, 1 d): Like method strt1, but refluxing the solvent by heating the flask in an oil bath.

(2c) bmrf1-method (balled milled V_2O_5 , stirring under reflux, 1 d): Like method strf1, but the V_2O_5 was ball milled in *n*-pentane for 2 h prior to locking in into the glove box.

(3) strt7, strf7, and bmrf7: Stirring for about 7 d instead of about 24 h.

For XRD three different sample holders were used. Samples expected to be sensitive to air were characterized using special sample holders, which allow fixing of a "dome" above the sample and prevent the sample from exposure to air. Because of the amorphous scattering of the "dome" itself, which is made of PMMA, and a less effective shielding of scattering by air for a "dome" sample holder the background radiation is more intense than for the standard open top loading sample holder. For other materials standard sample holder could be used, consisting of a round plate with a deepening milled into. Additionally, a low background sample holder containing a specifically cut silicon slice, such that no Bragg reflection arises from the holder, is used. This is especially suitable if only a small amount of material is prepared. To prepare such a sample, one or two drops of a suspension were dabbed to the middle of the silicon crystal and allowed to dry in air.

X-ray patterns were recorded on a D8 Advance diffractometer (supplier Bruker AXS, Karlsruhe, Germany) with focusing Bragg-Brentano geometry and a fine focus X-ray tube with Cu anode in a 2θ range from 7 to 120° , scantime 2 h usually. Samples in an inert atmosphere were measured in a 2θ range from 7 to 80° instead. No monochromator was attached, but low energy radiation was removed by discriminating the detector. A fast Lynxeye detector and variable divergence slits were used.

The program Topas was used for Rietveld analysis. Modeling width and shape of the peaks and correcting peak positions was done according the fundamental parameters approach,^[23] as implemented in Topas. The instrumental function was determined by a scan of LaB₆. For standard Rietveld refinement the following parameters were refined: lattice

parameters, sample height displacement, microstructural parameters, coordinates of the atomic sites, isotropic temperature parameters constraining the temperature factors of the same type of atoms to a single parameter, and parameters of preferred orientation. Severely textured samples were modeled by two March Dollase distributions with different orientation vectors as implemented in Topas. According to properties of the structure the main preferred orientation is (001). (100) may be selected as the second preferred orientation.

Because the sodiated samples often showed severely broadened peaks an extended model was used. The Na_xV₂O₅ α - and α' -phase was modeled with 34 fractions with $-0.12 \le x \le 1.20$, equidistant in x with $\Delta x = 0.04$. If a lower number of fractions with $0 \le x \le 1$ was applied then often a waved fit curve was obtained. A higher number of fractions would demand for additional constraints to avoid "noise" within the scaling factors and would cause a more complex model. The value of $\Delta x = 0.04$ was a compromise between quality of the fit and simplicity and stability of the model. The fractions with x < 0 and x > 1imply occupation densities for Na with no physical meaning, but were added as "resource" fractions enabling recognition of special effects and fitting of other broadening effects, like microstrain. V2O5 and ssr-NaV₂O₅ were used as external reference samples for position of the atoms and values of the lattice parameters. In the case of V₂O₅ the hypothetical coordinates of the site of Na were estimated with a site occupation factor of 0. The reference data were handled as "additional phases" with a scaling factor of 0. The coordinates of the sites, the parameters of preferred orientation, the site occupation factor of the Na site, and the lattice parameters of the 34 fractions of Na_xV₂O₅ were calculated by linear interpolation and extrapolation according to the data of both the reference samples. The microstructural parameters and the parameters of isotropic thermal vibration were refined but constrained to be the same for the reference phases and all fractions of $Na_{r}V_{2}O_{5}$.

To improve the fit finally a third "reference" was defined to have the composition $Na_{0.5}V_2O_5$ and to have the average volume of V_2O_5 and ssr-NaV₂O₅. Nevertheless, the lattice parameters *a* and *b* could be refined for this "reference". Together with phases like Na₂S typically about 40 "phases" were used for refinement of sodiated samples.

The weight fractions (calculated by the program Topas), the volumes of the unit cells, and the assumed values of *x* for the 34 fractions of $Na_xV_2O_5$ were transferred to an EXCEL sheet. This was used to calculate the relative molar fractions of the phase fractions and $\langle x \rangle$, the mean value of *x*.

Supporting Information (see footnote on the first page of this article): Details of the structures of the reference phases V_2O_5 , $Na_{0.5}V_2O_5$, and NaV_2O_5 as used for Rietveld refinement.

Acknowledgements

Robert Haberkorn wants to thank the Universität des Saarlandes for financial support of the project "Anschubfinanzierung – Batteriewerkstoffe auf der Basis von Na-Ionenleitern". Jessica Bauer wants to thank the Landesgraduiertenförderung Saarland for financial support.

References

- A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, J. Electrochem. Soc. 1997, 144, 1188.
- [2] O. Clemens, R. Haberkorn, M. Springborg, H. P. Beck, Z. Anorg. Allg. Chem. 2014, 640, 173.
- [3] G. Pistoia, S. Panero, M. Tocci, Solid State Ionics 1984, 13, 311.
- [4] R. K. B. Gover, P. Burns, A. Bryan, M. Y. Saidi, J. L. Swoyer, J. Barker, *Solid State Ionics* 2006, 177, 2635.
- [5] V. Palomares, P. Serras, I. Villaluenga, K. B. Hueso, J. Carretero-Gonzalez, T. Rojo, *Energy Environ. Sci.* 2012, 5, 5884.
- [6] J.-M. Savariault, J.-L. Parize, D. Ballivet-Tkatchenko, J. Galy, J. Solid State Chem. 1996, 122, 1.
- [7] T. Chatterji, K. D. Liß, G. J. McIntyre, M. Weiden, R. Hauptmann, C. Geibel, *Solid State Commun.* 1998, 108, 23.
- [8] M. Pouchard, A. Casalot, J. Galy, P. Hagenmuller, Bull. Soc. Chim. Fr. 1967, 11, 4343.
- [9] K. West, B. Zachau-Christiansen, T. Jacobsen, S. Skaarup, Solid State Ionics 1988, 28–30, 1128.
- [10] S.-Y. Bae, M. Miyayama, H. Yanagida, J. Am. Ceram. Soc. 1994, 77, 891.
- [11] H. R. Bak, J. H. Lee, B. K. Kim, W. Y. Yoon, *Electron. Mater. Lett.* 2013, 9, 195.
- [12] C. Cheng, Z. H. Li, X. Y. Zhana, Q. Z. Xiaoa, G. T. Lei, X. D. Zhou, *Electrochim. Acta* **2010**, *55*, 4627.
- [13] J. Dai, S. F. Y. Li, Z. Gao, K. S. Siow, J. Electrochem. Soc. 1998, 145, 3057.
- [14] J. Farcy, R. Messina, J. Perichon, J. Electrochem. Soc. 1990, 137, 1337.
- [15] A. Hammou, A. Hammouche, Electrochim. Acta 1988, 33, 1719.
- [16] N. C. Chaklanabish, H. S. Maiti, J. Mater. Sci. 1986, 21, 2850.
- [17] R. J. Cava, A. Santoro, D. W. Murphy, S. M. Zahurak, R. M. Fleming, P. Marsh, R. S. Rot, *J. Solid State Chem.* **1986**, 65, 63.
- [18] S.-H. Ng, N. Tran, K. G. Bramnik, H. Hibst, P. Novak, Chem. Eur. J. 2008, 14, 11141.
- [19] S. Bach, J. P. Pereira-Ramos, B. N, R. Messina, J. Electrochem. Soc. 1990, 137, 1042.
- [20] A. Meetsma, J. L. d. Boer, A. Damascelli, J. Jegoudez, A. Revcolevschi, T. T. M. Palstra, *Acta Crystallogr., Sect. C* 1998, 54, 1558.
- [21] S. Jouanneau, A. Verbaere, D. Guyomard, J. Solid State Chem. 2005, 178, 22.
- [22] G. Brauer, Handbuch der Präparativen Anorganischen Chemie, 3rd Ed., Ferdinand Enke Verlag, Stuttgart, 1975.
- [23] R. W. Cheary, A. A. Coelho, J. P. Cline, J. Res. Natl. Inst. Stand. Technol. 2004, 109, 1.

Received: August 8, 2014 Published Online: October 9, 2014