Article:

Mudenda, S and Kale, GM orcid.org/0000-0002-3021-5905 (2017) Electrochemical determination of activity of Na2O in Na2Ti6O13-TiO2 two phase system between 803–1000 K. Electrochimica Acta, 258. pp. 1059-1063. ISSN 0013-4686

https://doi.org/10.1016/j.electacta.2017.11.158

Electrochemical determination of activity of Na_2O in $Na_2Ti_6O_{13}$ - TiO_2 two phase system between 803 - 1000 K

Steven MUDENDA[a,b], Girish M. KALE[b]

(a) Department of Physics, University of Zambia, P.O Box 32379, Lusaka, Zambia

(b) Institute for Materials Research, University of Leeds, LS2 9JT, Leeds, UK

Abstract

Sodium oxide (Na_2O) activity in NT6-TiO_2 was measured using the EMF method with test electrode Pt,$Na_2Ti_6O_{13}$+TiO_2(NT6-TiO_2). NASICON ($Na_2Zr_2Si_2PO_{12}$) was used as the solid electrolyte in conjuction with a biphasic mixture of alpha alumina and sodium beta alumina Al_2O_3, $Na_2O.xAl_2O_3$ ($8.5 \leq x < 11$) as the reference electrode and measurements taken over the temperature range of $803 \leq T \leq 1000$ K. Internal consistency of the cell was ensured by approaching the equilibration target temperature from both sides, during cooling and heating. EMF measurements showed linear dependency with temperature in the temperature range under study. The activity of Na_2O in NT6-TiO_2 in the temperature range under study was determined. This was found to be $\log a_{\mathrm{Na_2O}(NT6-\mathrm{TiO_2})} = 1.20 - \frac{13211}{T}$. This data is important in the determination of theoretical EMF for the calibration electrochemical sensors employing NT6-TiO_2 electrode. Furthermore, it was found that, $a_{\mathrm{Na_2O}(NT6-\mathrm{TiO_2})} > a_{\mathrm{Na_2O}(NASICON)}$ indicating chemical stability when in contact with NASICON at higher temperatures.

Email address: `g.m.kale@leeds.ac.uk` (Girish M. KALE[b])

Keywords: NT6-TiO_2, $Na_2Ti_6O_{13}$+TiO_2, EMF method, thermodynamics, thermodynamic stability, NT6, NASICON, sodium beta alumina, sodium oxide activity.

---

1. Introduction

For high temperature applications, sodium metal oxide (Na-M-O) ternary systems are most probable materials for reference electrodes in solid-state potentiometric gas sensors[1, 2, 3, 4]. To ascertain for phase constitution constancy in a binary mixture, determination of the thermodynamic stability of the heterogeneous phase equilibria is often compulsory. Whilst calorimetric measurements can accurately give information on enthalpies, the electrochemical method is considered as the most accurate method as far as the determination of partial Gibbs energy is concerned[5, 6, 7, 8, 9]. Measurement of surface energy and entropy of nano sized anatase using EMF method has also been reported[8].

Thermodynamic data on NT6-TiO_2 system, that is, a_{Na_2O} in NT6-TiO_2 is vital for assessing its compatibility and stability against a variety of solid electrolytes in solid-state electrochemical cells working at high temperatures.

The electrochemical determination of the thermodynamic stability of the heterogeneous phase equilibria comprising sodium containing compounds therefore and usually dependent on the determination of the sodium (or sodium oxide) activity of these phase mixtures[10] is commonly accomplished by means of potentiometric measurements on galvanic cells using a sodium ion conductor such as sodium beta alumina (NBA) or NASICON.

Although there are few investigations already reported in literature employing calorimetry[11, 12] and the EMF method[10, 12] the magnitude of scatter of the thermodynamic data makes another independent investigation necessary[13]. In addition, although the Gibbs energies have been reported[14], the temperature dependence of the activity of sodium oxide ($a_{\mathrm{Na_2O}}$) in the biphasic mixture which is needed for accurate characterisation of potentiometric gas sensor operations, is yet not reported.

The purpose of this study therefore is to measure the activity of Na_2O in the NT6-TiO_2 system as a function of temperature, using a solid-state EMF technique with NASICON as the solid electrolyte. Among other uses this data is desirable for the calculation of the theoretical EMF and interpretation of the measured EMF of CO_2 sensors[15] employing NT6-TiO_2 as reference electrodes.

2. Experimental Methods

2.1. Materials

In this investigation, NASICON ($x \simeq 2$), developed in our laboratory[16] was used as a solid electrolyte for the galvanic cell. The powder was then pressed into a pellet uniaxially using a load of 5 tonne and then isostatically pressed to a pressure of 300 MPa. The pellet was then sintered at 1423 K for 6 h. Sintering of pellet was done on alumina tiles. Firstly, powder of the same material was placed on the tile to act as sacrificial material to prevent any potential reaction between NASICON and alumina. The pellet was then placed on top of the sacrificial powder, then covered completely with the powder of same composition and finally the whole material (powder and pellet) were covered with an alumina lid. This was also to prevent any volatisation of Na_2O and P_2O_5 which easily occurs at high temperatures[4, 17].

The reference electrode was a biphasic mixture of α - Al_2O_3(Sigma Aldrich, 99.7 %) and Na - β - Al_2O_3 denoted in this research as ($\alpha + \beta$ - Al_2O_3 or simply $\alpha + \beta$ in the calculations). It was used because the sodium oxide activity in this mixture is well known [9, 18] and recently critically assessed by Spear and Allendorf [19].

The biphasic mixture was synthesised by mechanical mixing through a 12 h ball milling of γ-Al_2O_3 and Na_2CO_3(Acros Organics, >99.6 %). Firstly, Na_2CO_3 was dried in a convectional oven at 423 K to remove any moisture. It was then weighed and stoichiometric amounts of the two precursors were mixed. The amounts mixed was corresponding to $Na_2O : xAl_2O_3$ where $x = 9.5$. The mixture was then calcined at 1543 K for 5 h. The product was then reground in an agate mortar, and XRD confirmed formation of the sodium beta alumina. Further, about 11.8 wt% of α-Al_2O_3 was then added to form the biphasic mixture. A 5 tonne load was used to press the pellet after which it was sintered at 1873 K for 15 h. The pellet was not very well sintered but could be used as electrode nevertheless as long as the electrolyte was well sintered.

NT6 was synthesised by mixing appropriate amounts of Na_2CO_3 and TiO_2(Sigma Adrich, > 99.5%, 21 nm particle size) and milled for 12 h. The phase was obtained by calcining in air at 1223 K for *ca* 5 h. XRD analysis confirmed the phase. The biphasic mixture was obtained by mixing 6:1 molar ratio of NT6 and TiO_2. The mixture (NT6-TiO_2) was milled overnight. The slurry was then dried and the powder pelletised. The pellets were then sintered at 1323 K for *ca* 2 h.

Platinum ink was used for electroding. After the ink was painted as illustrated in Figure 1, it was dried at 343 K for 30 minutes. It was then fired for a further 30 minutes at 1123 K.

For phase analysis of the samples before and after the measurements, XRD was performed using the P'Analytical X'Pert MPD (using Cu K_α radiation).

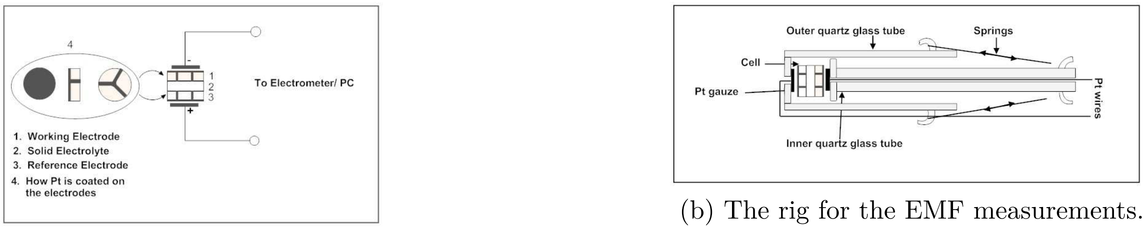
2.2. Measurement cell set-up

The pellet based cell was connected according to the notation in (1)

$$(-)\mathrm{Pt}, \mathrm{NT6}-\mathrm{TiO_2}|\mathrm{NASICON}|(\alpha+\beta)-\mathrm{Al_2O_3}, \mathrm{Pt}(+) \tag{1}$$

The polarity of the electrodes is indicated in the parentheses

Figure 1 shows the cell arrangement and the measurement rig. Platinum was used both as contact and leads. On one side of the pellet, platinum was fully painted while on the other side which would interface with the electrolyte pellet, thin strips of platinum were painted and then connected to the outer coated side. This was to ensure that the leads were directly connected to where the electrode reactions were actually taking place, at the interface between the electrode and the solid electrolyte. This is shown in Figure 1a. The measurement rig is shown in Figure 1b. The cell is sandwiched with two Pt-wire gauzes on either sides and then spring loaded to hold it in place in a quartz rig. The rig was inserted in the Faraday cage within a horizontal tube furnace. This was to shield from any induced Faraday EMFs.



(a) Cell assembly based on pellets.

(b) The rig for the EMF measurements.

Figure 1: Measurement setup of the galvanic cell including the rig. For the electrode pellets, one of the parallel sides was coated while the other side in contact with the electrolyte was just partially coated with strips of platinum.

2.3. Measurements

The EMF of the solid cell was measured as a function of temperature in the range of interest $803 \leq T \leq 1000$ K using a high impedance Keithley 6517A electrometer. The cell electrodes were connected to the Keithley electrometer which digitized the data and LabVIEW installed on the computer ensured real time data capture and display. A K-type thermocouple was placed close to the sample to ensure real time temperature measurement.

EMF reproducibility and internal consistency was checked by approaching the target temperature from higher and lower values. The first measurement point was at 1000 K and then decreased with a step of *ca.* 50 K. The equilibration time during the cooling run was 12 h while in the second cycle of measurement in the heating run, the equilibration time was 6 h. Starting measurements from the higher values is in fact advantageous as it rules out any irreversible reaction which would affect the EMF during heating.

2.4. Theoretical Considerations

Electrode conductivity has a role in the kinetics of the reactions at the interface as well as the transfer of charge carriers within the system of phases(electrodes and electrolyte). This results in a difference between electrical and chemical potential of the charge carriers within the phases in contact. With regard to electro-conductivity of the electrodes, NT6-TiO_2 is a mixed conductor (ion + p-type) with activation energy of about 0.9 eV [20], while there is scanty information in literature on the conductivity of the biphasic mixture of α+β-Al_2O_3. However, a single phase Na-β-Al_2O_3 is highly conductive with activation energy ranging from 0.12 to 0.27 eV [21]. But this conductivity is obviously damped down by the presence of alumina in the biphasic mixture.

According to Nafe[22], the electronic conductivity in Na-β-Al_2O_3 is very prominent in high and pure oxygen environment which can affect the stability of the cell as well as warranting the Nernstian law invalid. However, and importantly, in this research, electronic conductivity should not affect the activity of Na_2O in either α+β-Al_2O_3 or NT6-TiO_2 according to the phase diagram of Na_2O-Al_2O_3 and Na_2O-TiO_2 binary systems[23] as they are two phase equilibrium mixtures and would therefore act as a buffer to maintain constant thermodynamic activity of Na_2O in both the mixtures. Hence the results in this paper can be relied up and the use of the Nernstian law applied is valid.

The anodic reaction at the NASICON /NT6-TiO_2 in the galvanic cell shown in (1) is given by

$$\mathrm{Na_2O(NT6 - TiO_2)} \rightarrow 2\,\mathrm{Na^+} + 2\mathrm{e} + \frac{1}{2}\mathrm{O_2}. \tag{2}$$

The $\mathrm{Na^+}$ ions migrate through the NASICON/$\alpha + \beta{-}\mathrm{Al_2O_3}$ interface where they react with oxygen in the cathodic reaction as

$$2\,\mathrm{Na^+} + 2e + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{Na_2O}(\alpha + \beta). \tag{3}$$

Because the oxygen gas ($P_{\mathrm{O_2}}$) atmosphere is common to both electrodes of the cell, the net cell reaction from (2) and (3) is

$$\mathrm{Na_2O}(\mathit{NT6} - \mathrm{TiO_2}) \rightarrow \mathrm{Na_2O}(\alpha + \beta). \tag{4}$$

also equivalent to the overall virtual cell reaction

$$\mathrm{Na_2Ti_6O_{13}} + 9.5\,\mathrm{Al_2O_3} \rightarrow 6\,\mathrm{TiO_2} + \mathrm{Na_2O \cdot 9.5Al_2O_3}. \tag{5}$$

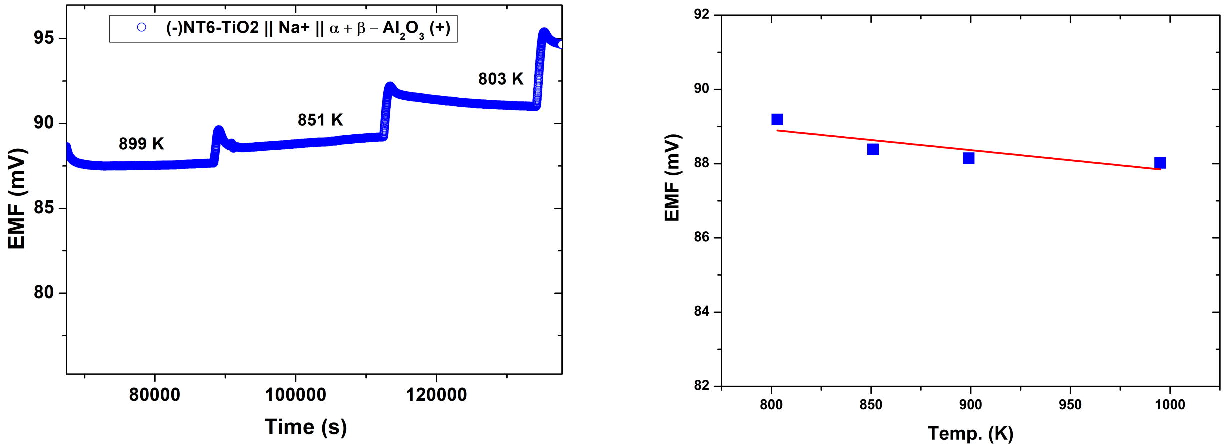
The EMF generated due to the electrode reactions is related to the Gibb's free energy or activity as

$$\Delta G = -zFE = RT \ln \frac{a_{\mathrm{Na_2O}}(RE)}{a_{\mathrm{Na_2O}}(WE)} \tag{6}$$

at constant temperature, where z and F are the electrons transfered and Faradays constant (96485 C/mol) respectively. The acronyms RE and WE denote Reference Electrode and Working Electrode respectively.

3. Results and Discussions

The variation in EMF of the cell with time and temperature is shown in Figures 2a and 2b respectively. Figure 2b is the average of heating and cooling runs. The temperature of interest is the high temperature (HT) range ($755 \leq T < 1073$ (K)). Low temperature range is discarded because of the associated resistivity interference between the electrodes and the instrument.



(a) Typical equilibration of the cell during EMF measurements.

(b) EMF as a function of temperature. The high temperature(HT) range is the range of interest.

Figure 2: EMF measurements of the cell: NT6-TiO_2 | NASICON | $\alpha + \beta$ which includes heating and cooling runs.

Based on the linear regression analysis, the measured EMF is given by Equation (7)

$$E(\text{mV}) = (93.27 \pm 2.12) - (0.00545 \pm 0.00239)T. \tag{7}$$

In order to obtain the sodium oxide activity in the two phase mixture of NT6 and TiO_2, Equation (6) is employed and rearranging it gives the relationship

$$\ln a_{\text{Na}_2\text{O}(NT6-\text{TiO}_2)} = \frac{2E_IF}{RT} + \ln a_{\text{Na}_2\text{O}(\alpha+\beta)} \tag{8}$$

The only unknown in Equation (8) is the sodium oxide activity in the biphasic mixture NT6-TiO_2 since the sodium oxide activity in the reference electrode α-Al_2O_3 + Na-β-Al_2O_3 denoted as $Na_2O(\alpha+\beta)$ is known from earlier measurements by Jacob et al. [18] and is given by

$$\log a_{\text{Na}_2\text{O}(\alpha+\beta)} = \left\{ \begin{array}{ll} 1.255 - \frac{14148}{T} & \text{for} \quad 798 \leq T < 980(K) \end{array} \right. \tag{9}$$

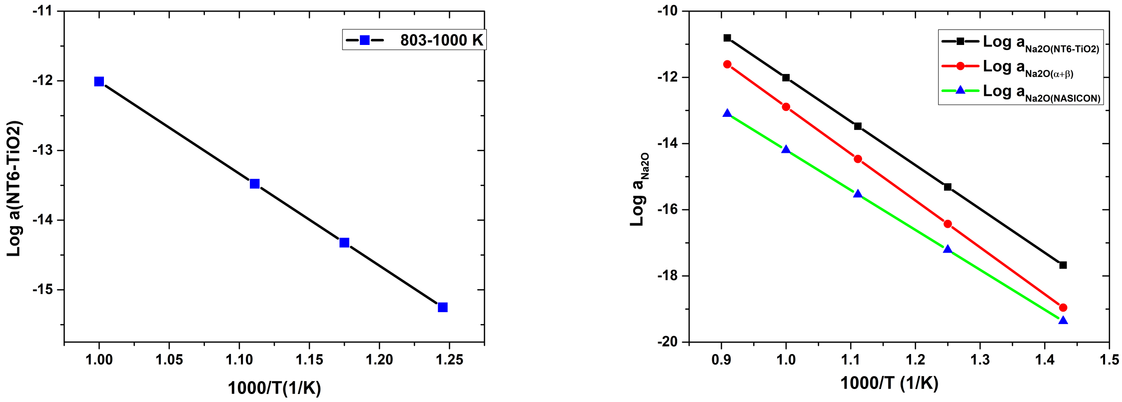
Note that this temperature range is within our measured range and based on the data presented by Spear [19] on the activity of Na_2O in α+β-Al_2O_3, the extrapolation of the data outside the temperature range range is also acceptable.

Combining Equations (7), (8) and (9) gives

$$\log a_{\text{Na}_2\text{O}(NT6-\text{TiO}_2)} = \left\{ \begin{array}{ll} 1.20 - \frac{13211}{T} & \text{for} \quad 803 \leq T < 1000(K) \end{array} \right. \tag{10}$$

Figure 3a is the sodium oxide activity in NT6-TiO_2 according to the relation in

Equation (10) while Figure 3b compares the variation of sodium oxide activity in NT6-TiO_2, NASICON [24] and $\alpha + \beta$-alumina [18] as a function of reciprocal of absolute temperature.



(a) Activity of Na_2O in NT6-TiO_2 vs temperature

(b) Comparison of sodium oxide in NT6-TiO_2 with that in NASICON and $\alpha + \beta$

Figure 3: Variation of activity of sodium oxide in NT6-TiO_2 as a function of temperature. It is higher than that in NASICON and $\alpha + \beta$ confirming its stability.

It can be seen that $\log a_{Na_2O(\text{NT6}-TiO_2)}$ as a function of temperature is higher than that of NASICON and the biphasic mixture of α-alumina and sodium beta alumina. This implies that it is more thermodynamically stable when in contact with any of these materials, which is essential in obtaining reliable thermodynamic equilibrium data.

Furthermore, it also implies that at any fixed temperature, the decrease in concentration of Na_2O in the working electrode corresponds to the decrease in Na_2O activity, leading to a corresponding decrease in cell EMF because the gradient of the chemical potential of Na_2O across the NASICON decreases[25]. The stability of working electrode composition was also confirmed by examining the sample using XRD before and after the high temperature thermodynamic measurements. This is shown in Figure 4.

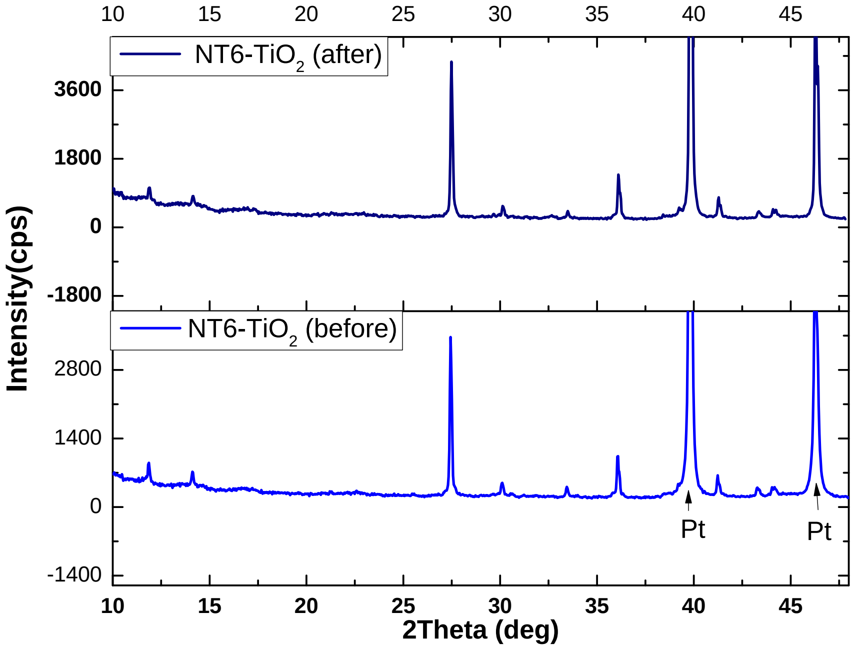


Figure 4: NT6-TiO$_2$ before and after the EMF measurements. The side analysed was one that was in contact with NASICON pellet.

Generally, all electrochemical cells have a concentration gradient of conducting species across the solid electrolyte. A semi-permeability flux of the conduction ions can result when there is a large chemical potential gradient resulting in mass transport across the electrolyte from one electrode to another subsequently resulting in a small composition change in the electrode and electrolyte interface. However, in this research, the cell is buffered by the presence of the two phase mixture in the reference and working electrode.

On the basis of Equation (10), the relative chemical potential of sodium oxide in the phase mixture NT6 - TiO$_2$ ($\Delta\mu = RT \ln a_{Na_2O}$) is also the standard Gibbs energy of formation from the component oxides according to the reaction ,

$$Na_2O(s) + 6TiO_2(s) \rightarrow NaTi_6O_{13}(s) \tag{11}$$

which yields

$$\Delta G^{\circ}_{f,\mathrm{NT6}}(\mathrm{J/mol}) = \left\{ -252,952.89 + 22.98T \quad \text{for} \quad 803 \leq T < 1000(K) \right. \tag{12}$$

Table 1 is a comparison of the Gibbs energies of formation in this investigation with literature values for the reaction (11).

Table 1: Thermodynamic data for $Na_2O(s)$ + $6TiO_2(s) \rightarrow NaTi_6O_{13}(s)$

T/K	ΔG°_{f}**(J/mol)** **Ferrante [11]**	ΔG°_{f}**(J/mol)** **This study**	**% diff.**
700	-252,124	-236,866	6.1
800	-255,186	-234,568	8.1
900	-256,743	-232,270	9.5
1000	-258,149	-229,972	10.9
1100	-259,387	-227,674	12.3

160 The values are in reasonable agreement with literature from Ferrante [11] for the Gibbs energy of formation calculated using his experimental data and supplemen-

tary data, S°_{298}, ΔH°_{298} obtained from Stuve [26] and Bennington and Brown [27] respectively.

4. Conclusions

The standard Gibb's free energy of formation of NT6 from component oxides (or sodium oxide chemical potential change) for the working electrode cell reaction $\mathrm{Na_2O} + 6\mathrm{TiO_2} \rightarrow \mathrm{NaTi_6O_{13}}$ was found to be

$$\Delta G^\circ_{f,\mathrm{NT6}}(\mathrm{J/mol}) = \left\{ \; -252,952 + 22.98T \quad \text{for} \quad 803 \leq T(K) < 1000 \right.$$

whilst the activity of sodium oxide in the biphasic NT6-$\mathrm{TiO_2}$ system determined as

$$\log a_{\mathrm{Na_2O}(NT6-\mathrm{TiO_2})} = \left\{ \; 1.20 - \tfrac{13211}{T} \quad \text{for} \quad 803 \leq T < 1000(K) \right.$$

Contrary to the findings by Amin [10] for the possible NT6/electrolyte reactions which hindered the thermodynamic equilibrium in his findings, the present study has shown that actually NASICON and sodium beta alumina have much lower $\mathrm{Na_2O}$ activity than that in NT6-$\mathrm{TiO_2}$ electrodes indicating good stability when in contact with each other. Furthermore, XRD conducted before and after the EMF measurements showed no change in the phases confirming the stability of NT6-$\mathrm{TiO_2}$ phase assemblage between 803 - 1000 (K) .

References

[1] H.Y. Dang and X.M. Guo. Characteristics of NASICON-based thick-film CO_2 sensor attached with integrated auxiliary electrode. *IEEE Sens. J.*, 12(7):2430–2434, July 2012.

[2] M. Holzinger, J. Maier, and W. Sitte. Fast CO_2 - selective potentiometric sensor with open reference electrode. *Solid State Ionics*, 86-88:1055, 1996.

[3] M. Holzinger, J. Maier, and W. Sitte. Potentiometric detection of complex gases: Application to CO_2. *Solid State Ionics*, 94:217, 1997.

[4] T.Kida, Y. Miyachi, K. Shimanoe, and N. Yamazoe. NASICON thick film-based CO_2 sensor prepared by a sol-gel method. *Sens. Actuators, B*, 80(1):28 – 32, 2001.

[5] Zbigniew Moser and Krzysztof Fitzner. The use of Experimental Thermodynamic Data in the Phase Equilibria Verification. *Thermochimica Acta*, 332: 1–19, 1999.

[6] Herbert Ipser, Adolf Mikula, and Iwao Katayama. Overview: The emf method as a source of experimental thermodynamic data. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.*, 34:271–278, 2010.

[7] R. Subasri, T. Mathews, K. Swaminathan, and O.M. Sreedharan. Thermodynamic Stability of Na_2ZrO_3 using the Solid Electrolyte Galvanic Cell Technique. *Journal of Nuclear Materials*, 300:237–241, 2002.

[8] P. Balaya and J. Maier. Thermodynamics of nano- and macrocrystalline anatase using cell voltage measurements. *Phys. Chem. Chem. Phys.*, 12:215–219, 2010.

[9] G.M Kale. $Na_2O-AI_2O_3$ System Activity of Na_2O in $(\alpha+\beta)$ and $(\beta+\beta")$ − Alumina. *Metall. Trans. B*, 23B:839, 1992.

[10] Md. Rahul Amin. *Solid state electrochemical characterization of thermodynamic properties of sodium-metal-oxygen systems.* PhD thesis, University of Stuttgart, 2005.

[11] M. J. Ferrante. High Temperature Relative Enthalpies and Related Thermodynamic Properties of $Na_2Ti_6O_{13}$. Technical report, US Department of Interior Bureau of Mines, 1986.

[12] M. Holzinger, A. Benisek, W. Schnelle, E. Gmelin, J. Maier, and W. Sitte. Thermodynamic properties of $Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$: Electrochemical and calorimetric determination. *J. Chem. Thermodyn.*, 35:1469–1487, 2003.

[13] Steven Mudenda. *Development of a Solid State Planar Carbon Dioxide Sensor.* PhD thesis, University of Leeds, 2015.

[14] G. Eriksson and A.D. Pelton. Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the MnO-TiO_2, MgO-TiO_2, FeO−TiO_2, Ti_2O_3-TiO_2, Na_2O-TiO_2, and K_2O-TiO_2 systems. *Metall. Trans. B*, 24B:795–805, 1993.

[15] G.M Kale, A.J Davison, and D.J. Fray. Investigation into an improved design of CO_2 sensor. *Solid State Ionics*, 86-88:1107, 1996.

[16] Steven Mudenda and Girish M. Kale. New insight into the electrical properties and ion dynamics of screen printed NASICON thick films. *Journal of Materials Chemistry A*, 3:12268–12275, 2015.

[17] G. Collin and J.P Boilot. *Superionic solids and solid electrolytes.* Academic Press, 1989.

[18] K.T Jacob, K. Swaminathan, and O.M. Sreedharan. Potentiometric determination of activities in the two-phase fields of the system Na_2O - $(\alpha)Al_2O_3$. *Electrochimica Acta*, 36:791–798, 1991.

[19] Karl E. Spear and Mark D. Allendorf. Thermodynamic analysis of alumina refractory corrosion by sodium or potassium hydroxide in glass melting furnaces. *J. Electrochem. Soc.*, 149:B551–559, 2002.

[20] A.L Sauvet, S. Baliteau, C. Lopez, and P. Fabry. Synthesis and characterisation of sodium titanates $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$. *J. Solid State Chem.*, 177:4508–4515, 2004.

[21] X. Lu, G. Xia, J. Lemmon, and Z. Yang. Advanced materials for sodium-beta alumina batteries: Status, challenges and perspectives. *J. Power Sources*, 195: 2431–2441, 2010.

[22] H Nafe. Thermodynamic stability and electronic conductivity of Na-beta-Alumina. *J Electrochem. Soc.*, 143:943–948, 1996.

[23] Robert S. Roth, Taki Negas, and Lawrence P. Cook. *Phase Diagrams for Ceramists*, volume IV. American Ceramic Society, INC, 1981.

[24] G. M. Kale and K.T Jacob. Thermodynamic partial pressures of Na_2O in NASICON solid Solution, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$. *J. Mater. Res.*, 4:417, 1989.

[25] G.M Kale and S. Srikanth. Electrochemical determination of the activity of

Na_2O in the pyrochlore phase of the Sb_2O_4-$NaSbO_3$ system. *J. Am. Ceram. Soc.*, 82(8):2161–2165, 1999.

[26] J. M Stuve. Low-temperature heat capacities of sodium hexatitanate. *Journal of Chemical Engineering data*, 27:391–392, 1982.

[27] K.O Bennington and R. R Brown. Thermodynamic properties of three sodium titanates. Technical report, US Department of Interior Bureau of Mines, 1973.