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Thermoelectric power studies on MgO-stabilized β'' -alumina

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Abstract A study of the temperature dependence of thermopower is known to yield auxiliary information about the electronic conductivity of a mixed conductor. In light of the above, thermoelectric power (TEP) measurements were made on MgO-stabilized β'' -alumina over the temperature range from 773 to 1223 K under conditions of different sodium activities in the ambient in order to substantiate the existing information on the electronic conductivity of sodium beta alumina (SBA). A mixture of $\text{Na}_x\text{Si}_m\text{O}_{2m+x/2}$ and SiO_2 in an environment of fixed P_{O_2} served as electrodes reversible to Na^+ . The heat of transport obtained using the thermopower data at higher temperatures (973–1223 K) was in fair agreement with the activation energy of electrical conduction determined by other studies like impedance measurements and molecular dynamics simulation. It could be inferred from these results that there is negligible electronic conductivity in SBA under the conditions of measurement. The average TEP for SBA was determined to be 700–800 $\mu\text{V}/\text{K}$ and the partial molar entropy of Na^+ in SBA was found to be $\sim 98 \text{ J mol}^{-1} \text{ K}^{-1}$.

Keywords Thermoelectric power · Heat of transport · Sodium beta alumina · Electronic conductivity · Activation energy for electrical conduction

Introduction

Amongst the various methods available to study the transport properties of superionic conductors, ther-

moelectric power (TEP) measurements are known to provide useful information on several aspects of transport, namely the heat of transport of the charge carrier, mechanism of transport and so on. With regard to the thermopower measurements, the conventional oxide-ion conductors (stabilized zirconia and doped thoria) and the silver halides are the most extensively studied materials so far. A careful survey of the literature showed that there are only a few reports of such studies in the case of sodium beta alumina (SBA). The difficulty in the choice of electrodes which are capable of exchanging sodium ions with SBA obviously precludes these measurements in SBA. Kuwamoto and Sato [1] were the first to report TEP data for β - and β'' -alumina using $\text{Na}/\text{Na}_2\text{O}$ as the electrodes. They studied the temperature dependence of the TEP of these materials from room temperature up to 550 K. Schiraldi et al. [2, 3] used the data determined by Kuwamoto and Sato to calculate $\log P_{\text{Na}}$, the sodium vapour pressure which would be in equilibrium with β/β'' -alumina. Subasri and Sreedharan [4] reported TEP data for a composite made up of α -alumina and β -alumina over a wide temperature range (620–1250 K). It is known that the thermopower measurements may also yield auxiliary information on the electronic conductivity of mixed conductors in addition to providing the heat of transport of the mobile species. In this regard, it has to be mentioned here that there have been reports on the existence of a non-negligible electronic conductivity in SBA under the conditions of its use in CO_2 sensors and also in alkali metal thermoelectric converter (AMTEC) cells [5, 6, 7, 8, 9, 10, 11, 12]. Therefore, the prime objective of this work was to substantiate these observations if possible, using thermopower studies on SBA. In addition, there are no reliable reports on TEP data for β'' -alumina. Hence, in order to obtain information on the thermopower of β'' -alumina, the present measurements were performed over the temperature range from 773 K up to 1223 K under different oxygen partial pressures.

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Theory

The thermoelectric power Θ is defined as:

$$\Theta = \frac{d\Phi}{dT} = \frac{\Phi_{\text{hot}} - \Phi_{\text{cold}}}{T_{\text{hot}} - T_{\text{cold}}} \quad (1)$$

It is well known that TEP data can give useful information on the transported entropy of the ionic species in the solid electrolyte when measured as a function of temperature. A comprehensive treatment of the derivation of the expression for the thermoelectric power of mixed conductors under different conditions at the electrodes has been dealt with in the classic paper by Wagner [13]. Consider the situation of a thermocell represented below for a solid electrolyte AX under a temperature gradient:



Here the mobile species is A^+ and let us assume that the material AX exhibits mixed conduction. The electrode is the metal A at unit activity. A potential difference (Φ) develops across cell 2 as a result of the difference in the electrochemical potential of electrons at two different temperatures.

In the case of a local equilibrium at the phase boundary between A, AX and Pt, the right-hand side of Eq. 1 is determined by the local differences of $\bar{\mu}_e$ within the phases of A, AX and Pt. Then, the total measured TEP (Θ_{measured}) is given by

$$\Theta_{\text{measured}} = \Theta_{\text{AX}} - \Theta_{\text{Pt}} \quad (3)$$

where Θ_{AX} and Θ_{Pt} are the TEP of AX and Pt, respectively. If we assume that the material AX exhibits mixed conduction, then the total non-isothermal e.m.f., E , under a temperature gradient is given as follows:

$$E = -\frac{1}{F} \int_{\mu'_{A,T}}^{\mu'_{A,T+\Delta T}} \left(\frac{t_i}{z_i} d\mu_A + \left[\frac{t_i}{z_i} S^*_{A^+} - t_e S^*_{e,AX} + S^*_{e,Pt} \right] \right) dT \quad (4)$$

where $S^*_{A^+}$ is the total transported entropy of A^+ , $S^*_{e,AX}$ and $S^*_{e,Pt}$ are the same for electrons in AX and Pt, respectively, and $d\mu_A$ is the chemical potential gradient of the mobile species A^+ . The non-isothermal e.m.f. comprises two components, one arising from the temperature gradient and the other due to the chemical potential gradient of the mobile species (the first term in Eq. 4, $d\mu_A$), which is an additional term that becomes evident because of the temperature gradient as μ itself is a function of the temperature:

$$d\mu_A = (-S^{\circ}_A + R \ln a_A) dT + RT d \ln a_A \quad (5)$$

In order to determine the thermopower of the material, we must subtract from the measured non-isother-

mal e.m.f. the contribution arising from the chemical potential gradient. The differential of this corrected e.m.f. with temperature yields the thermoelectric power of the material. If the activity of the neutral species of the mobile ion at the electrodes is independent of temperature (as in the case of pure metals), then the problem is much simplified. In general, for an ionic solid AX (A being the mobile ion in the solid in addition to electrons or holes), the TEP is given by:

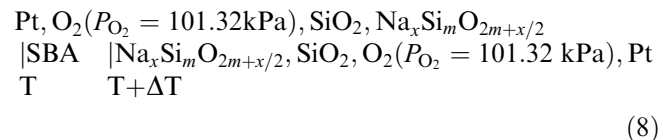
$$\Theta = S(A, e) - S(A, b) - \sum \frac{t_i Q_i^*}{z_i F T} \quad (6)$$

where $S(A, e)$ = entropy of the neutral atom of the mobile species A within the electrode, $S(A, b)$ = entropy of A within the electrolyte, Q_i^* = heat of transport of the charged species i in the solid, t_i = transport number of the species i , z_i = charge carried by the species i and F = the Faraday number.

For a solid electrolyte with predominantly one type of charge carrier (i.e. ionic and $t_{\text{ion}} \geq 0.99$), Eq. 6 reduces to:

$$\Theta = S(A, e) - S(A, b) - \frac{Q_A^*}{z_A F T} \quad (7)$$

Consider a thermocell represented as below where the electrodes are reversible to Na^+ ions and the electrolyte is SBA:



In order to calculate the contribution arising from the chemical potential gradient, one has to consider the following equilibrium that exists at the interface between the electrode and the electrolyte:



Since the chemical potential itself is a function of temperature and composition (or activity):

$$d\mu_{\text{Na}} = \left(\frac{\partial \mu_{\text{Na}}}{\partial \ln a_{\text{Na}}} \right)_T d \ln a_{\text{Na}} + \left(\frac{\partial \mu_{\text{Na}}}{\partial T} \right)_{a_{\text{Na}}} dT \quad (10)$$

Since it can be assumed that there is no local concentration gradient with respect to Na^+ in SBA, the first term in the above equation can be neglected. Accordingly:

$$\begin{aligned} d\mu_{\text{Na}} &= \frac{d\mu_{\text{Na}}}{dT} \cdot dT \\ &= \left[-\Delta_f S^{\circ} (\text{Na}_x \text{Si}_m \text{O}_{2m+x/2}) + m \Delta_f S^{\circ} (\text{SiO}_2) \right. \\ &\quad \left. - \frac{x}{4} R \ln P_{\text{O}_2} \right] \cdot dT \end{aligned} \quad (11)$$

$$E = \frac{1}{xF} \left[\Delta_f S^\circ (\text{Na}_x\text{Si}_m\text{O}_{2m+x/2}) - m\Delta_f S^\circ (\text{SiO}_2) \right. \\ \left. + \frac{x}{4} R \ln P_{\text{O}_2} \right] \cdot dT + \int_{T_1}^{T_2} \left[-\frac{ti}{F} S_{\text{Na}^+}^* + \frac{te}{F} S_{e,NBA}^* \right. \\ \left. - \frac{1}{F} S_{e,Pt}^* \right] \cdot dT \quad (12)$$

where $S_{\text{Na}^+}^*$ is the total transported entropy of Na^+ and $S_{e,SBA}^*$ and $S_{e,Pt}^*$ are the same for electrons in SBA and Pt, respectively. The total transported entropy of a species is a sum of two terms, the partial molar entropy of the species and the entropy of transport of the same:

$$S_{\text{Na}^+}^* = \bar{S}_{\text{Na}^+} + \frac{Q_{\text{Na}^+}^*}{T} \quad (13)$$

Therefore, after subtracting all contributions (due to Pt and electrodes), when the TEP (mV/K) is plotted as a function of inverse temperature ($1000/T$), the slope gives directly the heat of transport (in eV) of Na^+ alone if the material is purely an ionic conductor. The intercept, on the other hand, gives the partial molar entropy of Na^+ , again under the same conditions. Thus, from the results of the temperature dependence of the TEP, the partial entropy of Na^+ in SBA can be determined along with the heat of transport of Na^+ . The heat of transport of solid electrolytes in most cases can be related to the activation energy for electrical conduction. There are three cases which can be possible, i.e. the heat of transport of the mobile species, $Q_{A^+}^*$, can be less than or greater than or equal to the activation energy, E_a . However, in most of the superionic conductors, under the condition of pure ionic conduction, the $Q_{A^+}^*$ is equal to E_a [14, 15, 16]. The thermopower measurements when carried out in two different atmospheres (say pure O_2 and Ar in this case) must yield different values of the thermo e.m.f.s and must vary by a magnitude given by Eq. 14 at a temperature T if all other contributing factors are assumed to remain invariant in the two environments:

$$E_1 - E_2 (\text{mV}) = \frac{R}{4F} \Delta \ln P_{\text{O}_2} dT = 0.2739 dT \quad (14)$$

where E_1 is the e.m.f. obtained in pure O_2 and E_2 in Ar. Equation 14 can be deduced from Eq. 12 by assuming constancy of all other factors except for the P_{O_2} in the surrounding atmosphere.

Experimental

A one end closed beta ($\beta + \beta''$) alumina tube (dia = 25 mm, Asea Brown Boveri, Germany) with an elemental composition of 6.8 wt% Na, 1.9 wt% Mg, 44.7 wt% Al and the rest O was used as the sample. The elemental composition was verified both by AAS and SEM EDX analyses procedures. The material predominantly consisted of the β'' phase, which was revealed by the XRD pattern obtained within the 5 mass % limit of detection of other phases (β).

The tube as supplied was cut to a length of 15 mm in order to remove the closed end. A mixture of $\text{Na}_x\text{Si}_m\text{O}_{2m+x/2}$ (referred to as water glass henceforth) and SiO_2 was used as the electrode. The water glass was prepared by heating highly pure Na_2CO_3 and SiO_2 in a molar ratio of about 1:3 at above 1673 K and dissolving the resultant glass in pressurized water at 473 K. A thin layer of water glass in contact with SiO_2 in an atmosphere of fixed P_{O_2} serves as an electrode reversible to Na^+ in the electrolyte. The layer of water glass was deposited on either sides of the electrolyte tube by dropping the solution and drying with simultaneous addition of grains of SiO_2 over the same. Platinum nets along with platinum wires placed on either side of the sample served as electrodes for the electronic contacts. The sample with the electrodes was held in position between two α -alumina blocks and the whole set-up was spring loaded. Two Pt-10% Rh, Pt pre-calibrated thermocouples were used for measurement of the temperature. The whole assembly was placed in a vertical furnace, thus maintaining a linear temperature gradient of ~ 20 K across the two ends of the sample. A schematic sketch of the thermocell is shown in Fig. 1. The measurements were carried out in different oxygen atmospheres, namely pure O_2 and argon containing 3 vpm O_2 . The gases were dried using traps that contained silica gel as desiccant prior to passing through the experimental assembly. The thermo e.m.f.s and the temperatures were measured using a high impedance voltmeter (Keithley 617). The average temperature of the sample was maintained constant (± 0.5 K) by a temperature controller. The sample was initially heated to 1223 K in order to facilitate faster equilibration. The thermo e.m.f.s were measured after ascertaining constancy of the values (± 0.1 mV for $t > 12$ h). To check whether the e.m.f.s were of reversible nature, a small current was passed through the thermocell and verified that the e.m.f. returned to its original value. The experiment was repeated for the heating as well as cooling cycles. The same experiment was carried out in two different gas atmospheres in order to determine the effect of sodium activity on the heat of transport.

Results and discussion

The non-isothermal e.m.f. of the sample was measured as a function of temperature in the temperature range

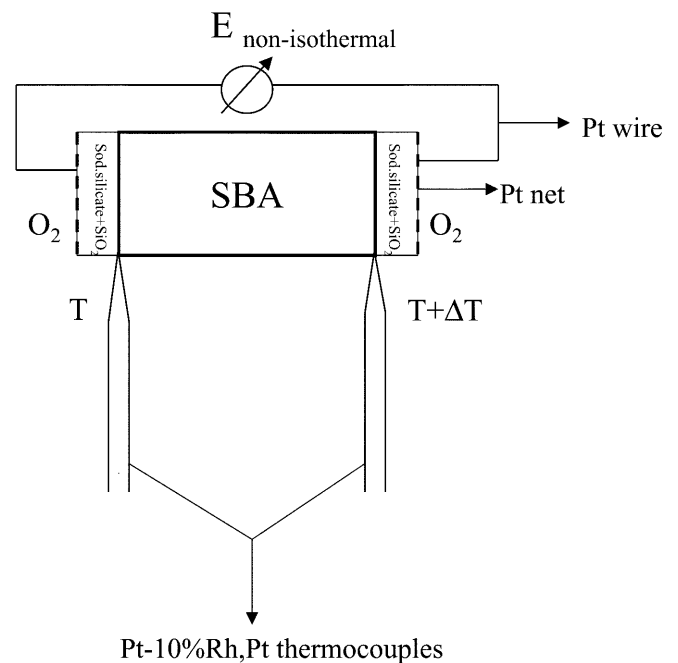


Fig. 1 Schematic diagram of the thermocell

from 773 to 1223 K in two different gas atmospheres. The thermopower at each temperature was determined by subtracting from the measured data the contribution due to the sodium activity difference caused by the thermal gradient. For this purpose, the activity of sodium in the water glass has to be known. Since activity of sodium (a_{Na}) in the glass is unknown and has to be determined by an independent set of measurements, the Gibbs energy data on a sodium silicate having a composition close to that of the glass will be considered for the present measurements. There are only five ternary oxides in the $\text{Na}_2\text{O}-\text{SiO}_2$ system for which the Gibbs energy data are available in the literature. Of these, the compound $3\text{Na}_2\text{O}\cdot 8\text{SiO}_2$ is the ternary oxide having a composition close to that of the glass that was determined using elemental analysis procedures. The contribution to the total e.m.f. due to the electrodes essentially contains the entropy of formation of the oxide $3\text{Na}_2\text{O}\cdot 8\text{SiO}_2$ and that of SiO_2 , as already discussed above. The Gibbs energy data for the compound $3\text{Na}_2\text{O}\cdot 8\text{SiO}_2$ was taken from Zaitsev et al. [17] and is given below:

$$\Delta_f G^\circ(\text{Na}_6\text{Si}_8\text{O}_{19}, \text{kJ mol}^{-1}) = -9152.6 + 1.7527T(\text{K}) \quad (974 - 1071 \text{ K}) \quad (15)$$

The contribution due to the electrodes in case of the sample being in an O_2 atmosphere was calculated to be:

$$E_{\text{electrode}}(\text{mV}) = 0.5902\Delta T(\text{K}) \quad (16)$$

and the same for the sample in an argon atmosphere was:

$$E_{\text{electrode}}(\text{mV}) = 0.3162\Delta T(\text{K}) \quad (17)$$

The contribution from the electrons in platinum to the total thermo e.m.f. is given by Eq. 18, which gives the inverse temperature dependence of the TEP of Pt:

$$\Theta(\text{Pt}, \text{mV/K}) = -0.0697 + 0.1111x - 0.0850x^2 + 0.0303x^3 - 0.0040x^4 \quad (373 - 1873 \text{ K}) \quad (18)$$

where $x = 1000/T$.

The thermoelectric power data for Pt has been taken from Landolt-Bornstein [18]. After correcting for the chemical potential difference due to the temperature difference at the two electrodes and the contribution due to the TEP of platinum, the TEPs of SBA were calculated and plotted as a function of inverse temperature. The temperature here was the lower temperature at which one end of the sample was placed. The difference in temperature (ΔT) was taken as $T_{\text{hot}} - T_{\text{cold}}$. During the measurements the hot electrode determined the sign of the thermo e.m.f. The plots of the TEPs of SBA versus $1000/T$ in the two atmospheres (pure O_2 : $P_{\text{O}_2} = 101.32 \text{ kPa}$; and in argon: $P_{\text{O}_2} = 0.303 \text{ Pa}$) are shown in Figs. 2 and 3, respectively. It can be seen from the plots that there is a sudden change in the sign of the slope in both cases around 1000 K. The coefficients of the linear fit of the thermopower data are presented in

Table 1. As already mentioned, if the material under consideration has only one ionic charge carrier, then the slope directly gives the heat of transport of the single species. However, if there is more than one charge carrier in the material, then the slope is a sum of more than one term and therefore bears a contribution from all charge carriers. In the temperature range from 1000 to 1223 K, the magnitude of the slope of the expression for the TEP corresponds to 0.245 eV in O_2 ($\sim 24 \text{ kJ mol}^{-1}$) and 0.306 eV in Ar ($\sim 30 \text{ kJ mol}^{-1}$). In most of the cases of supercationic conductors, the heat of transport is identical to the activation energy of conduction of the mobile species and this is valid provided there is exclusive ionic conduction in the material. In order to compare the activation energy for conduction with the heat of transport obtained from the present studies, a survey of the conductivity data on SBA in the literature was made and the activation energy obtained only at high temperatures are considered here for comparison (cf.

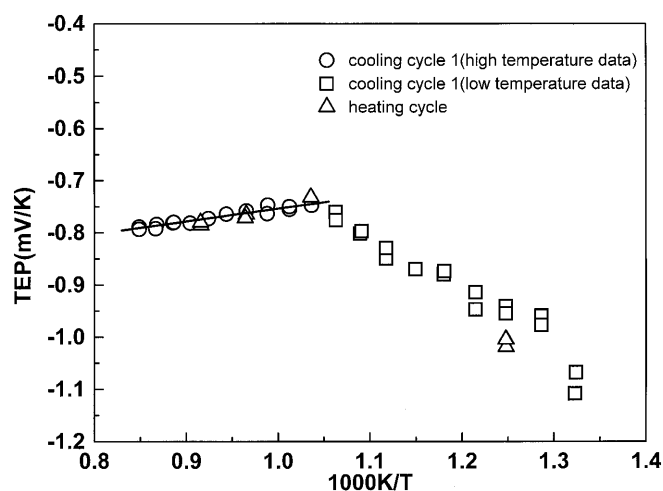


Fig. 2 Inverse temperature dependence of the TEP of SBA in pure O_2

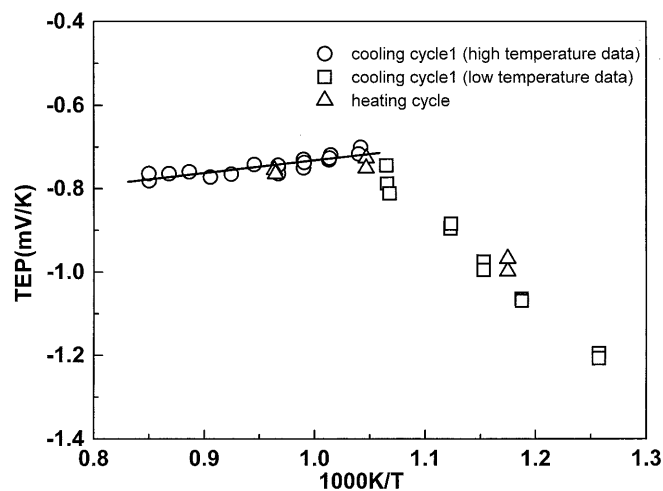


Fig. 3 Inverse temperature dependence of the TEP of SBA in Ar

Table 1 Coefficients of the linear fit of the thermopower data in two different atmospheres

Θ (mV/K) = $A + 1000B/T$		Temperature range (K)	Ambient atmosphere
A	B		
-0.9979 (± 0.0174)	0.245 (± 0.0188)	974–1189	Pure O ₂
0.3637 (± 0.0852)	-1.064 (± 0.0722)	762–950	Pure O ₂
-1.038 (± 0.0388)	0.306 (± 0.041)	972–1187	Argon
1.625 (± 0.106)	-2.254 (± 0.093)	760–950	Argon

Table 2) [1, 19, 20, 21, 22, 23]. The E_a depends to a large extent on the nature of the conducting ions and the thickness of the conducting slab. It can be seen from Table 2 that the high-temperature E_a value for β'' -alumina ranges from 0.09 eV to 0.2 eV. According to a recent paper by Beckers et al. [24], the E_a itself is a function of temperature and is higher for higher temperatures. The values given in Table 2 give the E_a measured up to a maximum temperature of 1000 K. Since there are no data reported for conductivity at higher temperatures ($T > 1000$ K), it can be considered that the heats of transport (slopes) obtained from the present studies (0.245 eV and 0.306 eV in the temperature range 1000–1223 K) which can be identified with the activation energy for electrical conduction are comparable (± 5 kJ mol⁻¹) to the reported values for E_a (at 1000 K, the highest temperature for which data are reported) using conductivity measurements, whereas the magnitude of the slopes in the lower temperature regions (773–1000 K) are very high and are opposite in sign compared to those obtained at higher temperatures. In order to verify whether the contributing factors have the same weighting in both the atmospheres, the e.m.f. values obtained at the same temperature of the sample under each atmosphere were subtracted and are presented in Table 3 and compared with the expected value given by Eq. 14. It can be seen that at higher temperatures the difference is as expected. This could mean that at lower temperatures the material may not be purely ionic conducting and there could be some contribution to the conductivity from other charge carriers as well. Also, it can be seen that, at higher temperatures, on thermal cycling there is a better consistency in the measured values compared to those measured at lower temperatures. There seems to be a scattering of values in

the heating and cooling cycles at lower temperatures. This could be due to a large contribution from the electronic conduction at lower temperatures at such values of the sodium activities at the electrodes, which could be a cause for the sudden change in the sign and increase in the magnitude of the slope. If there were more than one charge carrier, then the homogenous contribution to the thermoelectric power becomes a sum of terms given as:

$$\Theta_{\text{hom}} = \sum_i \frac{t_i Q_i^*}{z_i F T} = t_{\text{Na}} Q_{\text{Na}} / FT - t_e Q_e / FT \quad (19)$$

Accordingly, at higher temperatures, since the slope obtained from the TEP measurements agrees fairly well with the E_a values reported from conductivity measurements, it can be considered that there is only a single charge carrier, i.e. Na⁺, and hence nearly negligible electronic conductivity in the material. On the other hand, at lower temperatures, since the magnitude of the slope is very high and opposite to that obtained at higher T , it can be seen from Eq. 19 that the second term must be greater in magnitude and opposite in sign to the first term so that the overall sum is a negative quantity. This means that there is a significant contribution from the electronic conduction in β'' -alumina at lower tem-

Table 3 Comparison of the thermo e.m.f. values obtained in O₂ and Ar atmospheres

T (K)	E_1 (mV) in O ₂	ΔT (K)	E_2 (mV) in Ar	ΔT (K)	$E_1 - E_2$ (mV) (measured)	$E_1 - E_2$ (mV) (theoretical)
1223	-3.9	21.4	-9.9	23.2	6.0	6.1
1198	-3.9	22.5	-10.0	23.4	6.1	6.3
1173	-3.7	21.7	-10.0	23.5	6.3	6.2
1148	-3.5	20.4	-9.9	22.7	6.4	5.9
1123	-3.3	20.2	-9.5	22.1	6.2	5.8
1098	-3.2	20.3	-9.2	22.6	6.0	5.9
1073	-3.0	20.1	-8.9	21.0	5.9	5.6
1048	-2.8	19.3	-8.6	21.2	5.8	5.5
1023	-2.8	19.0	-8.1	20.7	5.3	5.4
998	-2.6	18.6	-8.0	21.4	5.4	5.5
973	-2.8	17.6	-9.1	20.2	6.3	5.2
923	-4.0	17.0	-10.7	19.2	6.7	5
898	-4.4	16.7	-11.8	18.0	7.4	4.8
873	-4.6	16.8	-13.6	18.5	9.0	4.8
823	-4.8	14.0	-14.8	17.0	10.0	4.3
948	-3.4	17.7	-7.5	20.4	4.1	5.2

Table 2 Comparison of the E_a values for β'' -alumina determined by various methods

Method used	E_a (eV)	Temperature range (K)	Remarks/ref
Conductivity	0.09–0.12	423–773	[19]
Conductivity	0.2	573–973	[20]
Conductivity	0.17	523–923	[21]
Conductivity	0.165	300–1000	Unquenched sample [22]
Molecular dynamics simulation	0.09	$T > 600$	[23]
TEP measurements	0.188	300–550	Using Na/Na ₂ O electrodes [1]
TEP measurements	0.245 (1 atm O ₂); 0.306 (Ar)	973–1190	Using Na _x Si _m O _{2m+x/2} /SiO ₂ /O ₂ electrodes; present work

peratures at such activities [5]. However, unless the transference numbers of each of the charge carriers are known, nothing can be said about the heat of transport of Na^+ at lower temperatures from the thermoelectric power measurements. The advantage of using reversible electrodes is that the partial molar entropy of Na^+ could be determined from the intercept of the plot. Accordingly, from Table 1 the intercepts are 0.998 and 1.038 in case of pure O_2 and Ar, respectively. The partial molar entropy of Na^+ in SBA could be calculated as $96.4 \text{ J mol}^{-1} \text{ K}^{-1}$ and $100.3 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively, which values are reported for the first time in the literature. However, in order to obtain further insight into this aspect, the TEP has to be measured in a wide range of sodium activities as well as a function of temperature, in order to find out at what values of sodium activities the electronic conduction becomes substantially contributing. Also the activity of sodium (a_{Na}) in the water glass has to be determined by an independent set of measurements in order to calculate exactly the partial molar entropy of Na^+ in SBA. The magnitude of the TEP of β'' -alumina over the temperature range 1000–1223 K varies from 700 to 800 $\mu\text{V/K}$.

Conclusions

The TEP of MgO-stabilized β'' -alumina in the temperature range 1000–1223 K was found to vary from 700 to 800 $\mu\text{V/K}$. The partial molar entropy of Na^+ as well as the heat of transport of Na^+ for the same material has been determined under different sodium activities. In both cases, at higher temperatures the heat of transport agrees fairly well with the reported values of activation energies determined by conductivity measurements, as is normally expected for supercationic conductors. Hence, it can be concluded that at higher temperatures there is no electronic conductivity occurring in β'' -alumina. However, at temperatures lower than 1000 K, a sudden change in the magnitude and sign of slope in the plot of the temperature dependence of the TEP was observed in both cases. This was attributed to the onset of electronic conduction at lower temperatures. The partial molar entropy of Na^+ in β'' -alumina was determined to be $\sim 98 \text{ J mol}^{-1} \text{ K}^{-1}$ in the higher temperature range from the measured data. Further investigations are necessary, however, to determine accurately the sodium activities and temperatures at which the electronic conduction

occurs. This could be accomplished by using other reversible electrodes in which the a_{Na} could be varied by manipulating the surrounding atmosphere. The thermoelectric power is a useful tool to detect electronic conduction in solid electrolytes. The need to find reversible electrodes in order to make meaningful measurements, however, preclude the use of this technique in the case of materials like sodium beta alumina. Nevertheless, this could be solved by using electrodes as in the present studies. Further measurements are in progress to gain a better insight.

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