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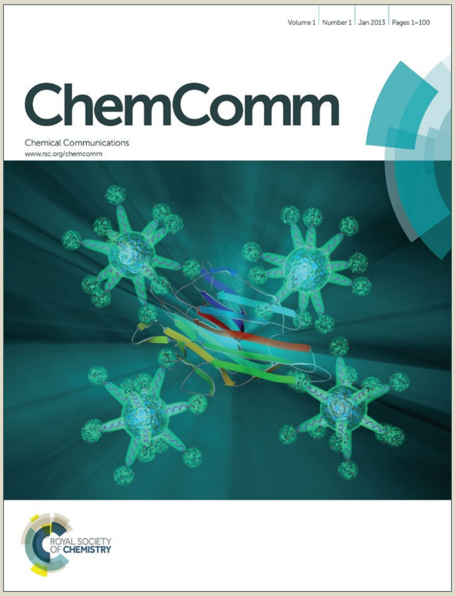

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Na^+ mobility in sodium strontium silicate fast ion conductors

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We present the first direct evidence of Na-ion mobility in sodium strontium silicate fast ion conductors, based on variable temperature ^{23}Na solid state NMR spectroscopy and spin-lattice relaxation measurements.

Solid oxide fuel cells (SOFCs) are a promising technology for clean and efficient energy generation.[1] The main obstacles to the widespread use of these devices, namely their cost and reliability, result from the high operating temperatures of current SOFCs. This has prompted a significant research effort into new materials for intermediate temperature SOFCs, operating in the temperature range between 500 and 650 °C. Recent initial reports of excellent oxide ion conductivity in a series of K- and Na-doped $SrSiO_3$ materials (1.79×10^{-2} S cm^{-1} at 550 °C for $Sr_{0.55}Na_{0.45}SiO_{2.775}$) therefore created much excitement in the field.[2, 3] Subsequent studies, based on variable temperature X-ray and neutron diffraction, electron microscopy, ^{29}Si solid state NMR and time-of-flight secondary ion mass spectroscopy, however, have found no evidence of significant Na incorporation and O^{2-} vacancy creation in $SrSiO_3$ and have demonstrated that the samples consisted of two phases, with an amorphous phase (identified as $Na_2Si_2O_5$) being primarily responsible for the high conductivity observed.[4-6] Careful recrystallisation experiments demonstrated that the observed conductivity degradation in these materials on prolonged heating occurred due to crystallisation of α-$Na_2Si_2O_5$ in the sample.[7] While the most recent investigation of Na-doped $SrSiO_3$ appears to agree with these findings, it concludes that the nature of ionic conduction in terms of the prevalent charge carrier has not been established.[8] Here we report the first direct evidence of Na^+ mobility in sodium strontium silicate fast ion conductors, based on variable temperature ^{23}Na solid state NMR spectroscopy and spin-lattice relaxation (T_1) measurements.

The work reported here was carried out on a sample of nominal composition $Sr_{0.60}Na_{0.40}SiO_{2.80}$, prepared by a conventional solid state route and previously characterised by laboratory powder X-ray diffraction (including amorphous content quantification), variable temperature neutron diffraction, scanning electron microscopy, impedance spectroscopy and room-temperature ^{29}Si solid state NMR.[5] Solid-state ^{23}Na NMR spectra acquired under magic-angle spinning (MAS) showed a single broad peak, which would be expected for Na^+ ions in a distribution of local environments (see Figure S7 and associated discussion in the Supplementary Information). As MAS was not providing site resolution, and could affect the observation of dynamics on a similar timescale, further experiments were conducted on non-spinning samples using a non-spinning probe capable of high-temperature operation.[9, 10] Solid state ^{23}Na NMR spectra were recorded at temperatures from 30 to 350 °C at 105.85 MHz using a Bruker Avance III HD spectrometer and wideline (non-spinning) probe accommodating samples packed into 5 mm o.d. glass tubes. These spectra were obtained using a solid-echo (i.e., 90° – delay – 90° – acq) with a 0.5 s recycle delay, a 30 μs delay between pulses, and 90° pulses of 2 μs in duration. 512 transients were accumulated for each temperature point. Spectra were referenced to an external sample of aqueous 0.1 M NaCl. For the T_1 measurements only, experiments were carried out for temperatures ranging from 25 to 150 °C at 132.18 MHz using a Bruker Avance III HD spectrometer and a 4 mm (rotor o.d.) magic-angle spinning probe. The saturation-recovery method using a train of 20 saturation pulses was used on a non-spinning sample.

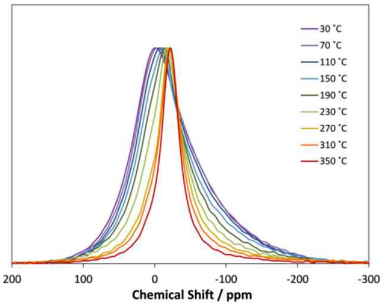

Figure 1: ^{23}Na solid state NMR spectra recorded at temperatures from 30 to 350 °C in 40 °C increments for a sample of nominal composition $Sr_{0.6}Na_{0.4}SiO_{2.8}$. Peak heights have been normalised.

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Figure 1 shows the ^{23}Na solid state NMR spectra collected over the temperature range of 30 °C to 350 °C. At lower temperatures, each spectrum contains a single broad asymmetric peak. This is consistent with an overlapping distribution of resonances caused by the wide range of Na^+ environments present in the amorphous phase identified in previous work.[5, 11, 12]. The contributions to the static lineshape are discussed further in the Supplementary Information (cf. Figure S7). As the temperature increases, the distribution narrows, and becomes more symmetrical around the (weighted) mean chemical shift. This can be most readily attributed to exchange phenomena[13] and indicates that the Na^+ ions in the material become increasingly mobile as the temperature increases. If the Na^+ ions themselves were not dynamic, the progression of spectra depicted in Figure 1 would imply that the complete surrounding environment would have to be dynamically averaged, essentially corresponding to a melting of the glass at approximately 200-300 °C, which we know does not occur.[3, 5-8] Quantitative analysis of the lineshape is difficult, since it is not possible to identify the coalescence point beyond which the linewidth is determined purely by this exchange rate. In addition, the temperature limitations of the probe mean that the fast exchange limit, required to determine the limiting non-exchanging linewidth, may not have been reached at the maximum temperature used. It is actually likely that the fast exchange limit is not directly observable in this material, since differential scanning calorimetry (DSC) measurements suggest an onset of crystallisation of α-$Na_2Si_2O_5$ in the sample at 490 ˚C, i.e. the Na^+ ions segregate between the original glassy phase and the newly formed crystalline one, in which they are not as mobile, as evidenced by a reduction in conductivity.[8]

Having established the presence of Na^+ dynamics from the NMR spectra, ^{23}Na T_1 relaxation times were measured and used to provide a quantitative determination of the activation energy (E_{act}) for the dynamics of the Na^+ ions in the material. The T_1 relaxation times were determined over a range of temperatures from 25 to 150 °C.

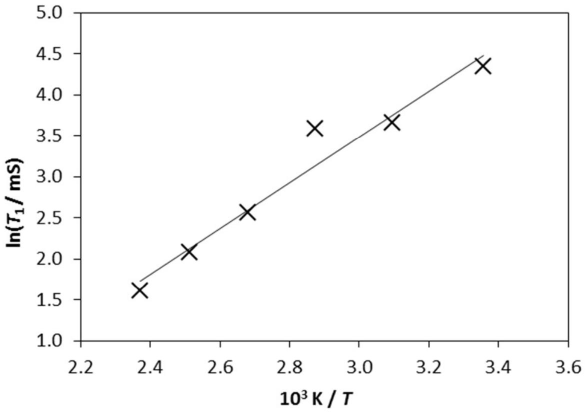

Figure 2: Arrhenius plot of T_1 relaxation times of ^{23}Na recorded at temperatures from 25 to 150 °C in 25 °C increments for a sample of nominal composition $Sr_{0.6}Na_{0.4}SiO_{2.8}$. The one-standard deviation uncertainties associated with random noise are of the order of the size of the symbols used.

As shown in Figure 2, the T_1 times decrease with increasing temperature, implying that the jump rate of the ions (which modulates the local NMR interactions, predominantly the quadrupolar couplings, hence driving the relaxation) is steadily increasing towards the ^{23}Na Larmor frequency (i.e. 132 MHz) as the temperature approaches 150 °C. The data contained in this Arrhenius-type plot behave linearly over this temperature range, allowing a value of 0.24(3) eV to be calculated for the activation energy, where the uncertainty is derived from the residuals between the experimental data points and the fitted line. In comparison, the value measured for the activation energy of conduction in this material using impedance spectroscopy was 0.324 eV.[14] The activation energy values obtained using impedance spectroscopy and solid state NMR differ, but the differences are consistent with those found for the ionic mobility in a variety of materials (including alkali metal, oxide and fluoride ion conductors) using these two techniques.[15] Selected examples of activation energies determined by impedance spectroscopy and solid state NMR for different types of Na^+ ion conductors are given in Table 1. It has been suggested that the lower activation energies observed using solid state NMR are due to the local motion of the sodium and the surrounding atoms, which contribute to the NMR relaxation in addition to the longer-range diffusional motion of the Na^+ ions.[16, 17] In other words, these differences are likely to reflect different averaging of the underlying distribution of dynamic processes in glassy materials by the different techniques.

Table 1: Activation energies for a range of sodium ion conductors reported in the literature, determined using both electrochemical impedance spectroscopy (EIS) and solid state NMR techniques.

	E_{act} (EIS) / eV	E_{act} (NMR) / eV	Ref.
$NaAlSi_3O_8$	0.88	0.46(2)	16, 18
$Na_{0.8}In_{0.8}Sn_{0.2}S_2$	0.56	0.36	19
$Na_3Zr_2Si_2PO_{12}$	0.29	0.135	17
Na_3InCl_6	0.735(5)	0.48(3)	20
$Na_2B_{10}H_{10}$	0.47	0.19	21
"$Sr_{0.6}Na_{0.4}SiO_{2.8}$"	0.324	0.24(3)	14, this work

In summary, the narrowing of the broadband signal in the ^{23}Na solid state NMR spectra and the decrease of the corresponding T_1 times with temperature, in conjunction with the impedance measurements and other characterisation methods reported in the literature, indicate that the Na^+ ions in the material with nominal composition $Sr_{0.6}Na_{0.4}SiO_{2.8}$ are mobile, and that this mobility is a thermally activated process. The consistency in the activation energy values found for the thermally activated process responsible for the averaging of the Na^+ ion environments by solid state NMR and the conduction process probed by impedance is strong evidence that the dominant charge carriers in the nominally Na-doped $SrSiO_3$ materials are in fact sodium ions in an amorphous $Na_2Si_2O_5$ phase. This conclusion is also consistent with previous findings based on high-resolution powder neutron diffraction and tracer diffusion measurements[4, 5], which show that although a very low level of oxygen vacancy creation in $SrSiO_3$ cannot be ruled out, the oxide ions are not responsible for high conductivity measured in these samples.

Note added during manuscript revision: While our communication was under review, we became aware of an *ab-initio* molecular dynamics (AIMD) simulation of the ionic mobility in amorphous and crystalline $Na_2Si_2O_5$.[22] This simulation suggests that amorphous $Na_2Si_2O_5$ is a good Na^+ ion conductor and gives the activation energy of 0.17 eV at lower temperatures, which is in very good agreement with the activation energy of 0.24(3) eV we determined from our T_1 measurements. The small discrepancy can be accounted for by a relatively low accuracy of the quantitative parameters obtained in this AIMD simulation due to a relatively short run time and size of the simulation box); the authors of the AIMD study specifically comment that this can lead to an overestimate of the diffusion coefficients (and hence lower E_{act}) in this temperature range.

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