Partial electronic conductivity of nanocrystalline Na$_2$O$_2$

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Abstract

Understanding charge carrier transport in Na$_2$O$_2$, being one of the possible storage materials in the non-aqueous Na–O$_2$ battery, is key to the development of this type of energy storage system. The electronic and dynamic properties of Na$_2$O$_2$ are expected to greatly influence the overall performance and reversibility of the discharge process. Thus far experimental studies on this topic are rare. To measure the extremely low conductivities setups with sufficiently high sensitivity are needed. Here we studied the partial electronic conductivity $\sigma_{eon}$ of nanocrystalline Na$_2$O$_2$ by potentiostatic polarization measurements which we carried out at room temperature. $\sigma_{eon}$ turned out to be in the order of $8.8 \times 10^{-14}$ S cm$^{-1}$; with a very poor total conductivity of $\sigma_{total} = 17 \times 10^{-14}$ S cm$^{-1}$ we obtained $\sigma_{total}/\sigma_{eon} \approx 2$ clearly showing that ionic transport of Na ions is strongly coupled to electronic dynamics.

1. Introduction

Future energy storage technologies benefiting from extraordinary energy densities are currently attracting tremendous attention from both academic and automotive industry [1–3]. Since a couple of years Na–oxygen batteries [4] are discussed as an alternative to the non-aqueous lithium–air system [6]. The efficiency and long-term behavior of the batteries is expected to significantly depend on the electric and dynamic properties of the discharge products formed [7]; the same holds for the Li–oxygen system. Such information is, however, rarely available so far [8–10]. To our knowledge, the electric conductivity of defect-rich nanocrystalline Na$_2$O$_2$ at room temperature has not been reported as yet.

In a sodium–oxygen battery the Na metal of the anode reacts during discharge with (atmospheric) oxygen and may form different discharge products such as NaO$_2$ or Na$_2$O$_2$ or Na$_2$O$_2$·2H$_2$O [7, 11, 12]. Which product is finally formed depends on a number of influencing parameters such as the cell setup, the components used as well as the presence of water or other proton sources [7]. The reversibility, and thus the overall performance of the battery, is expected to significantly depend on the electric properties of the discharge products. Only little information is, however, available about the Na$^+$ and e$^-$ partial conductivities, particularly at ambient temperature.

Here we used potentiostatic polarization measurements to record the partial electronic conductivity of nanocrystalline Na$_2$O$_2$ at room temperature. A recent study [10] has shown that the overall conductivity of nanocrystalline Na$_2$O$_2$, which was prepared by high-energy ball-milling of coarse-grained Na$_2$O$_2$, is by one order of magnitude higher than that of Na$_2$O$_2$ with $\mu$m-sized crystallites, see also [13]. It has been demonstrated that in nanostructured Na$_2$O$_2$, for which we expect a large number of defects introduced during mechanical treatment, the total conductivity approached an upper limit [10]. This peak value, which is much lower than for mechanically treated oxides [14, 15], was almost reached after the sample had been ball milled in Ar atmosphere for 60 min [10]. It is expected to be governed by (i) the defect chemistry, (ii) the increased volume fraction of (locally) disordered interfacial regions [14–17] as well as (iii) by the non-negligible effect of overlapping space charge zones known to play a pivotal role in nanostructured systems [18].

2. Experimental details

Nanocrystalline Na$_2$O$_2$ was prepared from the coarse-grained material (97%, Sigma Aldrich, No. 223417) using a high-energy planetary mill (Fritsch Pulverisette 7 (premium line)) operated at a rotation speed of 500 rpm.
We used a ZrO2 beaker equipped with 180 balls; the milling time was set to 1 h. For the conductivity measurements pellets, 10 mm in diameter, ca. 1 mm in thickness, were prepared by cold-pressing the powders with a uniaxial force of 15 kN. Au electrodes, 100 nm in thickness) were applied by means of evaporation (MBraun MB-EVAP). All preparation steps were done in an inert Ar or N2 atmosphere with O2 and H2O contents below 1 ppm. The samples were characterized by x-ray powder diffraction (Bruker D8 Advance), scanning electron microscopy (Tescan VEGA3) as well as 23Na magic angle spinning (MAS) NMR (Bruker Avance III, 11 Tesla (132 MHz), 30 kHz spinning frequency, 2.5 mm rotors). Polarization measurements were performed with a Parstat MC potentiostat (Princeton Applied Research) equipped with a low current interface. A Faraday cage was employed to suppress any electromagnetic influences.

3. Results and discussion

3.1. Characterization via x-ray powder diffraction and 23Na MAS NMR

\( \text{Na}_2\text{O}_2 \) crystallizes with the hexagonal space group \( P\bar{6}2m \) (see figure 1(a)). The peroxide anions occupy the positions 2e and 4h; they are arranged along the c-axis; Na ions reside on 3f (Na1) and 3g (Na2). The cations are surrounded in a distorted trigonal prism by the oxygen ions. The closest Na1–Na2 distance is given by 3.06 Å.

X-ray powder diffraction revealed that the starting material is of high purity, the pattern recorded as well as the lattice constants extracted (\( a = 6.207(1) \), \( b = 4.471(1) \)) fully agree with literature data (see figure 1(b)). The tiny reflection at ca. 35° most likely stems from Na2O; the reflection at ca. 38° represents a still unknown marginal impurity; it might be sodium bicarbonate, see below. After mechanical treatment for 60 min nanocrystalline \( \text{Na}_2\text{O}_2 \) is obtained in high purity. X-ray diffraction neither indicates any decomposition processes having taken place nor a mechanically induced formation of new phases; according to Rietveld analysis the mean lattice parameters remain essentially the untouched (\( a = 6.207(1) \), \( b = 4.472(1) \)). Significant broadening of the reflections is attributed to the generation of nm-sized crystallites and strain introduced. Taking instrumental broadening into account, see figure 1(b), with the relation introduced by Scherrer we estimated the average crystallite size to be ca. 20 nm. This result agrees well with sizes usually obtained through ball milling of oxide ceramics [19].

The \( 23\text{Na} \) MAS NMR spectrum is clearly composed of two well-resolved lines showing up at 7.0 ppm and 11.6 ppm when referenced to an 1 M aqueous solution of NaCl. The lines represent the Na1 and Na2 sites in \( \text{Na}_2\text{O}_2 \) and are in very good agreement with a recent study by Goward and co-workers [12]. The spectrum of non-milled, microcrystalline \( \text{Na}_2\text{O}_2 \) is shown for comparison. The line at 55.6 ppm has to be assigned to \( \text{Na}_2\text{O} \) as also noticed through x-ray diffraction. Interestingly, this signal almost vanishes after ball milling. Most likely, residual \( \text{Na}_2\text{O} \) of the starting material reacts with traces of oxygen to eventually form the thermodynamic more stable \( \text{Na}_2\text{O}_2 \). The signal at −4.7 ppm seems to reflect a tiny amount of sodium bicarbonate [12]. Fortunately, the contaminations are small enough not to influence the electronic and overall conductivity of our sample.
the thickness of the tablet, and
I keep in mind that also electric contacts do not behave in their usual manner at such low currents. Nevertheless,
and that any disturbances may result in noticeable effects that may easily explain the noise observed. We have to
measurement. The lowest current value ($3.6 \times 10^{-13}$ A) was taken for the calculation of the electronic conductivity which results in a value of $1 \times 10^{-13}$ S cm$^{-1}$. For pellet B we obtain $2.9 \times 10^{-13}$ A which yields
$\sigma_{\text{eon}} = 7.6 \times 10^{-14}$ S cm$^{-1}$. The average value is given by $8.8 \times 10^{-14}$ S cm$^{-1}$, $\sigma_{\text{eon}}$ exceeds the theoretical values $[^{21}, ^{22}]$ by 6 to 8 orders of magnitude. Since the theoretical values refer to an ordered single crystalline state it is evident that the much higher values probed experimentally are chiefly affected by defect sites. Importantly, the electronic conductivity turned out to be very similar to the ionic one determined by AC impedance measurements. At ambient temperature the ratio $\sigma_{\text{total}}/\sigma_{\text{eon}}$ is given by $\sigma_{\text{total}}/\sigma_{\text{eon}} \approx 2$. This ratio is also obtained when we look at the initial current $I(t = 0) \approx 8 \times 10^{-13}$ A; it is indeed twice the final one and hence in good agreement with our earlier AC impedance data. With $I(t = 0) = 0.8$ pA (pellet A) we end up with $\sigma_{\text{total}} = 2.2 \times 10^{-13}$ S cm$^{-1}$ at 293 K, see also $[^{10}]$. For pellet B the same ratio $I(t = 0)/I(t \to \infty) \approx 0.6/0.29 \approx 2$ can be estimated.

Similarly to our study Gerbig $[^{13}]$ has investigated ionic and electronic conductivities of microcrystalline
Na$_2$O$_2$ and a ball-milled sample (60 min, Pulverisette 5) but at higher temperatures than ambient. Some of

Figure 2. (a) Scanning electron micrograph of nanocrystalline Na$_2$O$_2$ prepared by high-energy ball-milling. (b) $^{23}$Na MAS NMR spectrum of nano-Na$_2$O$_2$, collected with room temperature bearing gas and under a spinning frequency of 30 kHz. The magnetic field applied (11.7 T) corresponds to a Larmor frequency of 132.25 MHz. For comparison, the spectrum of the source material is also shown.
the results are shown in the inset of figure 3. Keep in mind that $\sigma_{\text{eon}}$ will depend on the measuring conditions (Ar atmosphere (this work) versus oxygen atmosphere [13]); thus, they are not directly comparable to each other. Furthermore, the samples are expected to differ in morphology as well as the number and type of ionic and electronic defects, e.g. (isolated) superoxide defects as suggested in [13]. Despite of these differences our value is not in contradiction with the high-$T$ data; quite the contrary, it supports the results presented recently. By analyzing measurements carried out as a function of oxygen partial pressure Gerbig concluded that sodium interstitials, $\text{Na}_i$, are involved in ionic transport; for electronic conduction p-type behavior was found [13]. The calculations mentioned above discussed the transport behavior of several ionic and electronic charge carriers; for electronic conduction hole polarons have been identified as the most important charge carriers in crystalline $\text{Na}_2\text{O}_2$. Note, however, that the activation energies probed experimentally (ca. 1 eV) significantly differ from calculated values, most of them are well below 1 eV, see [20, 21].

4. Conclusion

We investigated the poor electronic conductivity in nanocrystalline, defect-rich $\text{Na}_2\text{O}_2$ that was prepared by high-energy ball milling. The sample turned out to be a mixed conductor with the ionic and electronic conduction contributing in equal shares when measured under $\text{O}_2$-free atmosphere. While the partial electronic conductivity was in the order of only $8.8 \times 10^{-14} \text{ S cm}^{-1}$, the total one is given by ca. $22 \times 10^{-14} \text{ S cm}^{-1}$. The results indicate a strong coupling of the ion movements with electronic dynamics. Modifying the electric properties of the discharge products might be a not unreasonable strategy to overcome the current limitations in reversibility.

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