Detection of Electrochemical Reaction Products from the Sodium–Oxygen Cell with Solid-State $^{23}$Na NMR Spectroscopy

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Supporting Information

ABSTRACT: $^{23}$Na MAS NMR spectra of sodium–oxygen (Na–O$_2$) cathodes reveals a combination of degradation species: newly observed sodium fluoride (NaF) and the expected sodium carbonate (Na$_2$CO$_3$) as well as the desired reaction product sodium peroxide (Na$_2$O$_2$). The initial reaction product, sodium superoxide (NaO$_2$), is not present in a measurable quantity in the $^{23}$Na NMR spectra of the cycled electrodes. The reactivity of solid NaO$_2$ is probed further, and NaF is found to be formed through a reaction between the electrochemically generated NaO$_2$ and the electrode binder, polyvinylidene fluoride (PVDF). The instability of cell components in the presence of desired electrochemical reaction products is clearly problematic and bears further investigation.

However, NaO$_2$ has proven to be elusive and potentially unstable, as the electrochemical production of pure NaO$_2$ has not been unequivocally confirmed in more recent studies. Instead, a variety of reaction products including sodium peroxide (Na$_2$O$_2$), sodium peroxide dihydrate (Na$_2$O$_2$·2H$_2$O), and a mixture thereof have all been reported as constituent discharge products. Undesirable side products (i.e., sodium acetate, sodium formate, and NaF) have also been reported as minor reaction products. Results vary with cell chemistry and the method of detection: PXRD, Raman, IR, TEM, SEM, X-ray absorption near edge structure (XANES), and X-ray photoelectron spectroscopy (XPS). The relative ratios and stabilities of these reaction products are not well determined.

We demonstrate here that solid-state nuclear magnetic resonance (ssNMR) spectroscopy; particularly, $^{23}$Na NMR, is a valuable diagnostic tool for investigating the Na–O$_2$ battery. ssNMR is an appealing characterization approach for this purpose as it is restricted neither to the surface nor the degree of crystallinity of the electrochemical particles. Instead ssNMR is sensitive to the bulk material and offers element-specific information.

ssNMR has previously been used to investigate Li–O$_2$ batteries. In that system, $^{17}$O NMR was shown to be a valuable tool for monitoring the discharge products, whereas direct 1D $^6$Li NMR spectra were not informative. Unfortunately, $^{17}$O NMR studies require expensive and cumbersome isotopic enrichment owing to the low natural abundance of $^{17}$O (0.04%), making the widespread use of such a research strategy unlikely. In contrast, $^{23}$Na NMR spectra are straightforward to acquire, as the $^{23}$Na isotope is 100% naturally abundant and has a favorable magnetogyric ratio, making it an ideal candidate for the characterization of the sodium–oxygen electrochemical reaction products.

$^{23}$Na magic-angle-spinning (MAS) ssNMR is a well-established technique for studying the molecular structure of inorganic salts and sodium oxide species. Sodium ($^{23}$Na I = $^{3}/2$) NMR spectra are influenced by not only their chemical shift but also the quadrupole coupling constant. $C_q$ provides structural information as it reflects the environment at the nucleus of interest. This can be appreciated by measurable

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differences in the NMR line shapes. It should be noted that the quadrupole interaction causes a field dependence in both the line shape itself and the location of its center of gravity. The 23Na NMR spectra can also be influenced by the paramagnetic interaction, which can add a large frequency shift when unpaired electrons are present in the system, as is the case in NaO2. Here, a combination of NMR techniques are required to fully characterize the Na–O2 electrochemical reaction products, due to the differences in local symmetry and electron configuration among these materials. Complementary data from 23Na chemical shifts, relaxation properties, and the quadrupolar interactions of the 23Na nuclei are utilized to identify the electrochemical reaction products produced in Na–O2 cells.

The 23Na MAS NMR spectra of the relevant electrochemical reaction products are shown in Figure 1. It is immediately apparent that there is good spectral resolution between these species. Additionally, NaO2 has a 23Na T1 relaxation time of 7 ms compared to those of >5 s for sodium peroxide and carbonate. Details of the spectral features and relaxation properties are provided in the Supporting Information and are consistent with previous reports of these phases.

For simplicity, 23Na resonances from compounds with multiple crystallographic sites are labeled from high- to low-symmetry Na environments, as re

![Figure 1. 1D 23Na NMR spectra of (a) sodium peroxide, with a small sodium oxide impurity, (b) sodium superoxide, with residual NaOH, and (c) sodium carbonate. All spectra were collected at room temperature under an MAS frequency of 20 kHz and an 11.7 T applied field. O atoms, gray; C, black; and Na, various colors.](image)

An unanticipated species, which we have identified as NaF, is observed at 9 ppm in the 1D 23Na NMR spectra of the cycled electrodes (Figure 2a). The unexpected phase is assigned to NaF owing to the similarity of its 23Na chemical shift to that of pristine NaF (7.4 ppm, Supporting Information). The assignment is additionally supported by filtering out of this new signal in the 3QMAS experiment, as would only be expected for a very high symmetry Na environment such as the cubic salt NaF.

NaF is proposed to result from a reaction between the electrochemically generated superoxide and the polyvinylidene fluoride (PVDF) binder, which acts as a support for the electrode. An analogous reaction, resulting in LiF, is

In sodium peroxide, the two unique crystallographic Na positions have extremely similar environments, as reflected by their similar NMR parameters. Previously the 23Na NMR data of Na2O2 reported a single Na site. 3QMAS provides resolution of the sites; however, they are not definitively assigned due to the similarity of the environments. (See the Supporting Information)

The electrochemical reaction products are determined by examining the extracted Na–O2 electrodes with 1D and 2D solid-state 23Na MAS NMR. The electrolyte system investigated is a 0.5 M solution of sodium triflate in a standard ether electrolyte, diethylene glycol dimethyl ether (DEGDME). A representative electrochemical curve illustrating the first discharge profile is shown in the Supporting Information. Two samples were selected for the ex situ 23Na NMR study: one early and one later in the discharge process, where the specific capacities were limited to either 100 mAh/g (D100) or 750 mAh/g (D750).

The 1D 23Na NMR spectra of the cycled Na–O2 electrodes (Figure 2a) illustrate that there is no signal in the sodium superoxide (Na(sup-1)) region at -23 ppm for either discharge capacity. This signifies that NaO2 is not produced in an appreciable quantity, or, more likely, that NaO2 is unstable and has not been consumed by subsequent reactions. The absence of NaO2 was confirmed with T1 filtering experiments, where no evidence of the NaO2 species was detected, even with many scans at short recycle delays (conditions which enhance the NaO2 signal while suppressing those of the other species).

Rather, one of the sodium peroxide resonances, (Na(per-1)) and one of the sodium carbonate resonances, (Na(carb-3)) are resolved in the 1D NMR spectrum (Figure 2a) at D100 and D750. The signal strength increases from D100 to D750 as an increasing amount of Na-containing reaction products are formed.

Spectral overlap in the multicompont electrochemical samples can be rectified through 2D 23Na-3QMAS spectroscopy (Figure 2b). 23Na-3QMAS provides spectral resolution of the individual chemical shifts in the indirect (isotropic) dimension and separates the quadrupole lineshapes of each in the direct (isotropic + quadrupolar) dimension (labeled as δc in Figures 2b). For example, the 2D 23Na-3QMAS spectrum of D750 (Figure 2b) shows clear resolution of all of the five crystallographic Na sites in Na2O2 and Na2CO3. This 2D 3QMAS spectrum demonstrates that we will be able to successfully separate and identify the electrochemical reaction products and track their presence and quantity as we iterate cell designs. We note sodium has a Cq of 0 in the superoxide, due to the cubic symmetry at the sodium site, and is therefore easily identified via its absence in 3QMAS experiments.

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NaF is proposed to result from a reaction between the electrochemically generated superoxide and the polyvinylidene fluoride (PVDF) binder, which acts as a support for the electrode. An analogous reaction, resulting in LiF, is
documented in the Li–O2 literature. It was unexpected in this case, as the stability of NaO2 is generally accepted as greater than that of LiO2, though that fact is called into question by these results.

In order to determine the stabilities directly, components of the composite cathode were exposed to the electrochemical reaction products (sodium oxides) and investigated with 23Na NMR; see the Supporting Information for full details. Figure 3a reveals the breakdown products formed by aging a mixture of NaO2 and Na2O2 and a mock cathode (i.e., Super-C65 carbon mixed with PVDF binder) for a week under argon: Na2CO3 and NaF are produced, while all NaO2 and nearly all Na2O2 are gone.

The presence of Na2CO3 and NaF is confirmed with powder X-ray diffraction of the composite cathode, as discussed in the Supporting Information. We also note that a mixture of NaO2 and Na2O2 aged without the cathode present, as shown in Figure 3b, shows no sign of any reaction. This confirms that NaF and Na2CO3 can be generated from solid-state reactions involving the discharge products of the Na–O2 cell and the electrode itself, rather than with the electrolyte as traditionally assumed. Both PVDF and Super-C65 carbon are shown to react individually with NaO2. Details are given in the Supporting Information. Relative roles of electrolyte stability and amorphous carbon/binder stability must therefore be addressed in future studies.

We have shown that 23Na ssNMR is a sensitive probe for unveiling the complex Na–O2 electrochemistry. With 23Na MAS NMR of Na–O2 electrodes, expected reaction products Na2O2 and Na2CO3 are observed in addition to an unanticipated phase, NaF. Both NaF and Na2CO3 are observed to result from parasitic reactions involving the carbon electrode and a Na2O2/NaO2 mixture. This demonstrates the reactivity of the Na–O2 reaction products with the cell components and highlights that Na2CO3 may be produced from alternative processes other than degradation of the organic electrolyte.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11333.

Experimental procedures and supporting data, including 23Na NMR and MQMAS of reference phases, PXRD data, and details of composite electrode reactivity (PDF)

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Notes
The authors declare no competing financial interest.
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