Sodium–Oxygen Batteries

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One- or Two-Electron Transfer? The Ambiguous Nature of the Discharge Products in Sodium–Oxygen Batteries

*Conrad L. Bender, Daniel Schröder, Ricardo Pinedo, Philipp Adelhelm, and Jürgen Janek**

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Rechargeable lithium–oxygen and sodium–oxygen cells have been considered as challenging concepts for next-generation batteries, both scientifically and technologically. Whereas in the case of non-aqueous Li/O_2 batteries, the occurring cell reaction has been unequivocally determined (Li_2O_2 formation), the situation is much less clear in the case of non-aqueous Na/O_2 cells. Two discharge products, with almost equal free enthalpies of formation but different numbers of transferred electrons and completely different kinetics, appear to compete, namely NaO_2 and Na_2O_2. Cells forming either the superoxide or the peroxide have been reported, but it is unclear how the cell reaction can be influenced for selective one- or two-electron transfer to occur. In this Minireview, we summarize available data, discuss important control parameters, and offer perspectives for further research. Water and proton sources appear to play major roles.

1. Introduction

In the past five years, research on sodium–oxygen batteries has intensified, and several fundamental studies of their cell chemistry have been published.[1] In particular, the basic cell reactions and the transport processes at anode and cathode were investigated, but different electrode materials and electrolytes were also tested for cell optimization.[2]

The working principle of a non-aqueous Na/O_2 battery is depicted in Figure 1. During discharge, the sodium metal anode is oxidized to form sodium cations while gaseous oxygen is reduced at the carbon cathode to form reduced oxygen species. Sodium ions combine with the reduced oxygen species and form a solid sodium oxide by precipitation. The charging process proceeds in the opposite direction, and the sodium oxide is converted back into gaseous oxygen and dissolved sodium ions. Oxygen is usually supplied at a defined partial pressure, $p(O_2)$, and may contain a significant amount of water, $p(H_2O)$, amongst other impurities. In addition, the electrolyte may contain impurities, for example, water. As shown below, these impurities can have a decisive influence on the cell reaction. For further details on Na/O_2 batteries, readers are referred to a recent Review.[3]

As in the case of Li/O_2 cells, unwanted side reactions between oxygen species, the organic electrolyte, and the carbon cathode, but also dendrite formation at the alkali metal anode, typically significantly reduce the number of discharge/charge cycles and the charge capacity and prevent the development of commercial battery systems.[4]

Whereas the formation of Li_2O_2 as the only discharge product (two-electron ORR) in non-aqueous Li/O_2 cells is generally accepted,[3] different discharge products have been reported for Na/O_2 cells: Some groups have described the formation of solid NaO_2 in a single-electron electrode

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[*] Dr. C. L. Bender, Dr. D. Schröder, Dr. R. Pinedo, Prof. J. Janek
Physikalisch-Chemisches Institut
Justus-Liebig-Universität Gießen
Heinrich-Buff-Ring 17, 35392 Gießen (Germany)
E-mail: juergen.janek@phys.chemie.uni-giessen.de
Prof. P. Adelhelm
Institut für Technische Chemie und Umweltchemie
Center for Energy and Environmental Chemistry (CEEC Jena)
Philosophenweg 7a, 07743 Jena (Germany)

The ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201510856.

process,[1a,c,d,f,5] whereas others claimed the formation of Na_2O_2 in a two-electron ORR, typically as the dihydrate $Na_2O_2{\cdot}2\,H_2O$.[1e,6] Therefore, a major part of each report on Na/O_2 cells deals with the nature of the discharge product and its characterization by different analytical techniques. As for Li/O_2 cells, the influence of water on the cell reaction has recently been highlighted and will be included in our discussion (see below).[1d,7] It should be noted that the superoxide KO_2 is the sole discharge product in K/O_2 cells,[8] which highlights the change from peroxide to superoxide formation down the alkali metal group, with sodium representing a borderline case as both the peroxide and the superoxide are possible discharge products.

From the thermodynamic point of view, Na_2O_2 is the more stable discharge product at standard pressure and 298 K ($\Delta_fG(Na_2O_2) = -449.7\ \text{kJ mol}^{-1}$).[9] With a free enthalpy of formation of $\Delta_fG(NaO_2) = -437.5\ \text{kJ mol}^{-1}$, the formation of NaO_2 is energetically rather similar to that of Na_2O_2, with a small energy difference of only $12\ \text{kJ mol}^{-1}$.[9] This small difference is also expressed by the quite close standard open cell potentials, $E(NaO_2) = 2.27$ V and $E(Na_2O_2) = 2.33$ V. The free enthalpy difference is probably smaller than the error margins of the thermodynamic data, and thus it is not unequivocally clear whether the peroxide is in fact thermodynamically more stable than the superoxide or not.

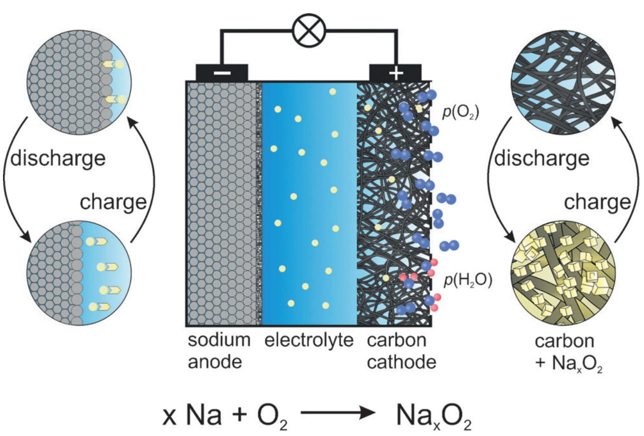

Figure 1. Working principle of a non-aqueous Na/O_2 battery: The sodium anode is stripped during discharge and plated during charge. At the cathode, a sodium oxide is formed during discharge and decomposed during charge. All processes might be affected by water or other impurities.

Dr. Conrad L. Bender received his Ph.D. in the field of sodium–oxygen batteries from the Justus Liebig University in Giessen (Germany) in the group of Prof. Jürgen Janek in 2015. He is interested in the fundamental properties of metal–oxygen batteries, and especially in those of non-aqueous sodium–oxygen batteries.

Dr. Daniel Schröder is a process engineer and studied at the Otto-von-Guericke University Magdeburg, Germany. In 2015, he received his doctoral degree in process engineering from TU Braunschweig. He then joined the group of Prof. Jürgen Janek as a research assistant and group leader at the Institute of Physical Chemistry at the Justus Liebig University in Giessen, Germany. His research focuses on model-based analysis and in situ studies of electrochemical cells, aiming to improve our understanding of Li-, Na-, and Zn-based metal–air batteries and developing next-generation systems.

Dr. Ricardo Pinedo received his Ph.D. in the field of solid-oxide fuel cells at the University of the Basque Country (UPV/EHU) in Bilbao (Spain) in 2013 after research stays at the Institute for Solid State Research (IFW) Dresden and the Institute for Crystal Growth (IKZ) Berlin. In 2014, he was a postdoctoral assistant at the UPV/EHU before joining the Institute of Physical Chemistry at Justus Liebig University Gießen (Germany) where he mainly focuses on metal–air batteries, Ni-rich materials for Li-ion batteries, and degradation processes in Na-based systems.

Prof. Philipp Adelhelm is a materials scientist and received his education at the University of Stuttgart, Germany. Afterwards, he joined the Antonietti group at the Max-Planck-Institute for Colloids and Interfaces in Potsdam, Germany. He received his PhD in physical chemistry in 2007 and then became a postdoctoral assistant at the Debye Institute of Nanomaterials Science in Utrecht (The Netherlands) with Petra de Jongh, studying Na- and Mg-based hydrogen storage materials. In 2009, he joined the group of Prof. Jürgen Janek as a research group leader, and in 2015, he was appointed full professor at the Friedrich-Schiller-University Jena, Germany.

Jürgen Janek received his doctoral degree in chemistry from the University of Hannover with Prof. Hermann Schmalzried and was a visiting professor at Seoul National University, Tohuku University/Sendai, and Université d'Aix-Marseille. He is Professor for Physical Chemistry at the Justus Liebig University in Giessen and scientific director of BELLA (Batteries and Electrochemistry Laboratory), a joint laboratory of BASF SE and the Karlsruhe Institute of Technology. His research interests range from fundamental transport studies in mixed conductors, electrode kinetics, and interface phenomena to plasma electrochemistry and in situ studies in electrochemical cells.

Theoretical calculations indicate that the relative thermodynamic stability of NaO_2 and Na_2O_2 depends on the crystallite size; nanosized NaO_2 appears to be more stable than Na_2O_2 of equal size, and nucleation of NaO_2 might thus indeed be favored.[10] In view of the energetic proximity of both product phases, it may thus well be that slight differences in the reaction conditions and kinetics control the reaction product. Additional solids have been reported as side products of the cell reaction: In particular, sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) were identified as discharge products of Na/O_2 cells in rather different amounts, although almost similar cell configurations and setups were used.[3,11] By and large, our current understanding of Na/O_2 cells and their chemistry is far from being complete. NaO_2 is undoubtedly the sole discharge product in a number of studies. In other studies, peroxides (mostly hydrates) were reported as the discharge products under more or less identical conditions, but the reasons for these different observations are currently unclear.

Evaluating these contradictory reports on the major discharge product in Na/O_2 cells, we herein summarize and analyze the existing data and try to answer the major questions that drive research on Na/O_2 cells at the moment: What is the key factor that determines whether the discharge process proceeds by one- or two-electron transfer (oxygen redox reaction, ORR), leading to at least two quite different discharge products? Alternatively, is sodium peroxide not formed within the electrochemical cell but after disassembly during the post-mortem characterization? If so, is the analytical identification of the discharge products reliable? We hope that our analysis will help to better understand the controlling factors during charge and discharge, but also stimulate further research. Owing to the competition of two energetically similar discharge products, we consider Na/O_2 cells to be a highly valuable electrochemical model system that is not yet well understood.

2. Experimental Key Results

2.1. Charge and Discharge Hysteresis

Charge and discharge characteristics (cell potential vs. capacity) contain both thermodynamic and kinetic information. Potential plateaus correspond to specific reaction equilibria between different phases, even if their absolute potential value includes overpotential contributions from different processes. All recently published capacity-potential data is depicted in Figure 2 for comparison of their shapes. The data were digitalized and normalized to the maximum capacity (given by the authors) for improved visualization. However, this normalization “hides” information on the depth of discharge (DOD) and the absolute capacity. It is well known that longer cycle lifetimes can be achieved if only a part of the available charge is cycled (“shallow cycling”). Quantitative differences in the hysteresis may thus be due to different discharge depths, and we will account for these effects in our discussion.

We divided the available data into three groups based on the major discharge products that were identified by the respective authors (Figure 2 a–c):

1) Figure 2 a: Sodium superoxide (NaO_2), formed by one-electron transfer to O_2
2) Figure 2 b: Sodium peroxide (Na_2O_2), formed by two-electron transfer to O_2
3) Figure 2 c: Hydrated sodium peroxide and other hydrated oxides, such as NaOH

In general, the reported capacity–voltage plots vary significantly in shape and the observed voltage plateaus. All groups that claimed the formation of NaO_2 reported a flat voltage plateau for both the discharge and the charge processes, with slight voltage differences mainly being ascribed to different current densities (Figure 2 a). The

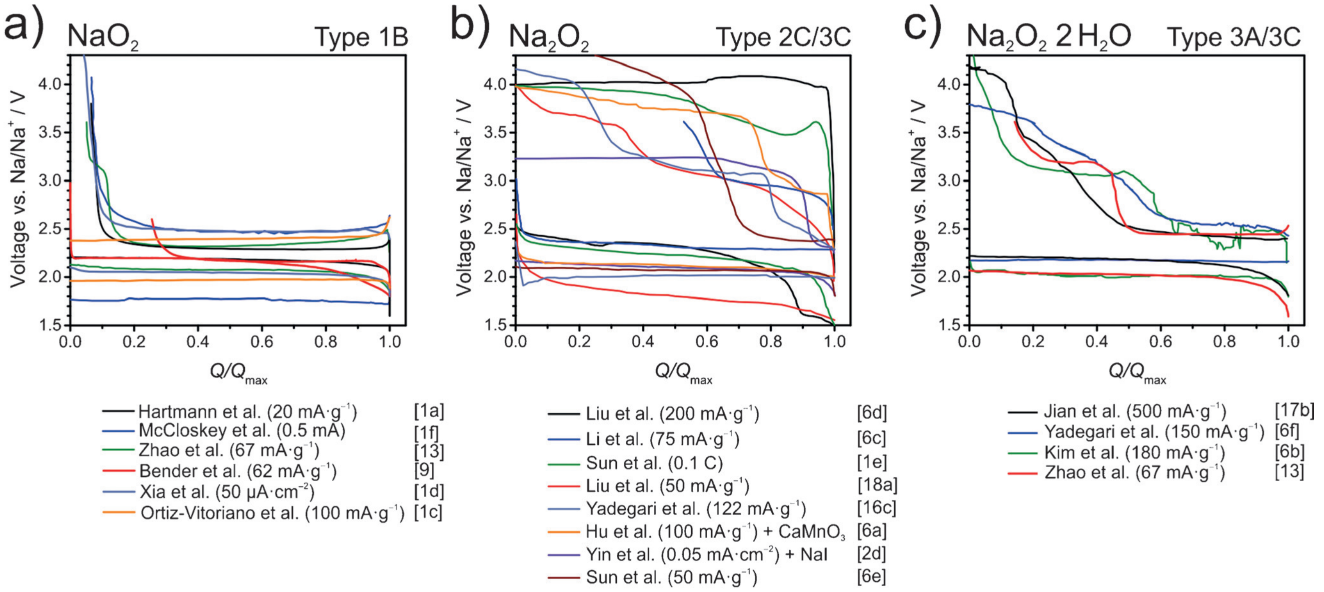

Figure 2. a–c) Comparison of various reported voltage–capacity hystereses (discharge/charge). The hystereses are grouped according to the claimed discharge product. The type of discharge/charge hysteresis was classified as proposed in Ref. [3].

beginning of the charge process is characterized by a short voltage peak, which may be attributed to a small reaction surface area after the discharge product has covered the available surface in the previous discharge run.[1b] In all cases, the end of the charge process is indicated by a sharp increase in the voltage without any further plateau-like regions, indicating that no other charging reactions, such as electrolyte decomposition, take place beyond the decomposition of NaO_2. As recently shown by Lee et al., the solvation energy of NaO_2 is very low, which leads to the reported small overpotential during the charge process. Moreover, the large overpotential for the oxidation of sodium peroxide can be attributed to the slow OER kinetics and the low conductivity of Na_2O_2.[12] These results support our observations on the discharge and charge hysteresis.

Reports on pure Na_2O_2 as the reaction product show completely different shapes for the capacity–voltage hystereses (Figure 2b). Some results are well comparable to reports on $Na_2O_2{\cdot}2\,H_2O$ as the discharge product (Figure 2c; type 3A/3C); others are comparable to the results of typical Li/O_2 cells with type 2C hysteresis and high overpotentials.[1f]

Authors that obtained $Na_2O_2{\cdot}2\,H_2O$ as the discharge product (Figure 2c) reported a charge process that is characterized by multiple voltage plateaus. Beginning with a low overpotential close to the values observed for NaO_2, the voltage increases with time, that is, with capacity. At the end of the charge process, relatively large overpotentials of up to 1 V are observed. Depending on the upper potential cut-off, another plateau is observed, indicating additional electrochemical reactions. Qualitatively, these charge curves differ not much from the charge curves of cells for which Na_2O_2 was reported as the primary discharge product.

Obviously, the shape of the charge/discharge hysteresis can be used as a first indicator for the composition of the discharge product. All results for NaO_2 forming cells are in good agreement, showing minor overpotentials during charge and discharge. Cells forming Na_2O_2 or $Na_2O_2{\cdot}2\,H_2O$ show a more complicated charge behavior that is similar to that of Li/O_2 cells: Aside from the plateau at low voltage, at least two plateaus are observed, which most probably correspond to the decomposition of NaOH and Na_2CO_3.

Various factors, such as the applied potential window, the current density, the solvent and conducting salt, the water content in the cell, and the cell design itself, can have a significant impact on the capacity–voltage hysteresis, and are discussed in detail in Section 3. First, we want to critically discuss the experimental identification of the discharge products as the experimental evidence is not always convincing.

2.2. Product Identification

The choice of suitable analytical techniques for determining the reaction products of alkali metal/oxygen batteries is critical and must fulfill the following requirements:

1) Inert-gas conditions during sample handling as NaO_2 is converted into $Na_2O_2{\cdot}2\,H_2O$ upon air exposure[1c]
2) Stability of the sample during the measurement
3) Unambiguous differentiation between superoxide and hydrated/non-hydrated peroxide species.

For the investigation of the discharge products in Na/O_2 cells, the following analytical techniques have been applied thus far: In most cases, X-ray diffraction (XRD) is used, often complemented by Raman spectroscopy. Further methods include transmission electron microscopy (TEM) analysis despite the fact that it has already been confirmed that NaO_2 is reduced to Na_2O_2 by electron beam irradiation.[13] Fourier transform infrared spectroscopy (FTIR) analyses are hampered by the lack of NaO_2 references, together with the difficult differentiation between NaOH, Na_2CO_3, and Na_2O_2. For XRD measurements, although the lack of reliable crystallographic data hinders the refinement of the dihydrated peroxide, other discharge and side products, namely NaO_2, Na_2O_2, $Na_2O_2{\cdot}8\,H_2O$, Na_2CO_3, NaOH, and the hydrated forms of the two latter ones, can be unequivocally identified. Nevertheless, most authors fail to correctly identify the obtained phases by XRD, as the intensity ratios between different reflections of a phase are often neglected, above all for peroxide phases. In contrast, Raman spectra of the commonly reported discharge products NaO_2 and Na_2O_2 are well known and enable the unequivocal identification of the discharge products, even at low volume fractions and/or with poor crystallinity (first stages of the discharge processes). Interestingly, no references for $Na_2O_2{\cdot}2\,H_2O$ have been made available to date, and therefore, the Raman band assignment of this compound is only possible after first identifying the product by means of XRD—which itself appears to be a doubtful approach.[1c] As stated above, the crystallographic data of the dihydrated peroxide $Na_2O_2{\cdot}2\,H_2O$ are not fully reliable, and therefore, the identification of this phase as a discharge product must be considered with care. X-ray photoelectron spectroscopy (XPS) is particularly useful for the detection of side products, such as carbonates or fluorides. However, the clear identification of sodium superoxide or peroxide is not possible as various sodium compounds have similar binding energies for the Na 1s spectral line. Moreover, the presence of Auger peaks (O 1s spectral line) further complicates the analysis.

Whereas XRD, Raman spectroscopy, XPS, and TEM provide direct chemical/structural information, differential electrochemical mass spectrometry (DEMS) and pressure monitoring have emerged as very useful methods for the quantitative and phenomenological evaluation of cell reactions. Both are important diagnostic methods that enable the evaluation of the number of electrons transferred during oxygen reduction or oxidation. However, the direct correlation of electron-transfer reactions with the number of transferred electrons is sometimes challenging for both methods owing to side reactions.[1f,14] Unfortunately, neither pressure monitoring nor DEMS are widely used, and results for Na/O_2 systems have only been reported by two groups; in both cases, the formation of NaO_2 in a one-electron process was clearly proven.[1d,f,5,15] To facilitate the correct identification and comparison of discharge products in future studies, we evaluated the reliability of the product identification in previous reports. The results are summarized in Table 1 and marked with an asterisk (★), a question mark (?), and a cross (†) to indicate reliable, ambiguous, or incorrect data, respectively.

In most studies that suggested the formation of NaO_2, reliable product-identification methods such as XRD or Raman spectroscopy were applied. However, in two studies where mixed discharge products with NaO_2 as the main component were reported, the main reflections at 37° were incorrectly assigned to NaO_2.[6f,7] Nevertheless, we conclude that the identification of sodium superoxide is reliable in most studies. In contrast, the identification of sodium peroxide is less straightforward in every study published thus far, which has mostly been due to the methods chosen (Table 1). The commonly employed selected area electron diffraction (SAED) and FTIR are not sufficient for product identification in sodium–oxygen cells as they fail to fulfill the aforementioned conditions. Although problems that are due to the amount and the partially amorphous character of the peroxide can be encountered during Raman spectroscopy and/or XRD, these difficulties can be overcome by increasing the depth of the discharge and/or the current density as well as by adjusting the experimental conditions of both methods.

In conclusion, identification by XRD must be conducted with a special focus on the intensity ratios and the selected reference. Peroxide formation can lead to various phases (amorphous or crystalline, hydrates) and requires particular attention. It appears necessary to revisit the structures of various sodium peroxide phases to enable the unequivocal identification of products in Na/O_2 cells.

3. Influencing Parameters

3.1. Cell Setup and Cell Components

An overview of selected experimental parameters of all studies on laboratory-scale Na/O_2 cells that have been published thus far is given in Table 1.

3.1.1. Cell Setup

Studies on metal–oxygen cells were mostly conducted with in-house-built cell setups. A setup that is based on ready-made components (e.g., Swagelok), which are modified for the individual requirements, is often used.[1a,5,6b,c,e,f,7,9,13,16] Coin cells,[6a,17] self-made pot cells[2b,17a] with different sizes, and various other designs[1e,2d,6d,18] have also been reported aside from commercial cell types, but these are hardly used.[1d] Every cell setup differs in the electrode diameter and contact pressure of the electrodes, the volume of the oxygen gas reservoir, and the tightness of the cell. Apart from the cell components themselves, it is crucial to be aware of the cell design and related issues for comparable experiments.[9,19] Thus far, detailed information on the cell setup is missing in most cases, and therefore, we cannot exclude that the cell design influences the cell reaction.

3.1.2. Cell Components

To date, most authors have reported on the influence of the anode, electrolyte, or cathode materials on the cell reaction. Thus far, sodium metal has always been applied as the anode, so we can exclude the anode as the origin of different cell reactions. In a very recent study, we used a non-metal anode and obtained NaO_2 as the reaction product as well.[20]

The cathode material and the electrolyte are the cell components that have been varied and studied most extensively, and various carbon-based materials were applied as cathode materials. Interestingly, different discharge products were obtained even when the same carbon material was used. For example, Ketjenblack, Super PLi, and carbon nanotubes were used and yielded NaO_2 as well as Na_2O_2 after the discharge process.

Another important parameter that defines the charge/discharge characteristics of Na/O_2 cells to a large extent is the used electrolyte. In Table 2, we provide an overview of different electrolytes used in Na/O_2 cells. For a given solvent and conducting salt concentration, the resulting discharge product is indicated with the charge/discharge hysteresis obtained. Cells with carbonate electrolytes, such as propylene carbonate (PC) and ethylene carbonate/dimethyl carbonate (EC/DMC), gave mostly Na_2CO_3 as the reaction product as they undergo decomposition during cycling. Cells with ether-based electrolytes yielded various sodium oxides, irrespective of the conducting salt. Up to now, NaO_2 has solely been reported for cells with ether-based electrolytes and NaOTf as the conducting salt. Interestingly, this combination is no guarantee for the formation of NaO_2 as the reaction product, and the formation of Na_2O_2, hydrated Na_2O_2, and Na_2CO_3 has been reported as well. As no other conducting salt has been tested in combination with diglyme thus far, the influence of the electrolyte composition on the discharge product is not clear yet, implying that more research is needed in this field.

Most studies use 0.5 M NaOTf in diglyme as the electrolyte. The reported discharge products differ, and no clear reason for their formation has been provided. Considering the aforementioned facts, we strongly believe that another parameter is key to controlling the electron-transfer reaction and the resulting discharge products in Na/O_2 cells.

3.2. The Role of Water

The role of water in alkali metal/oxygen cells (primarily in Li/O_2 cells) has recently been intensively studied.[22] In most of these studies, the amount of water in the electrolyte was determined by Karl-Fischer titration, and values below 5 ppm water in the electrolyte were obtained. Xia et al. demonstrated that the water concentration in the electrolyte is crucial for high discharge capacities as well as for the overall functionality of the NaO_2-forming Na/O_2 cell.[1d] Presumably, small amounts of water are essential to operate the Na/O_2 cell, as water might act as catalyst in the formation of NaO_2. Higher concentrations of water (≤ 100 ppm) lead to a significant increase in the discharge capacity. Irrespective of the

Table 1: Summary of all experimental cell parameters published to date.

Author	Oxygen electrode	Hysteresis	Electrolyte		Methods for analysis
NaO_2					
Hartmann[1a]	GDL H2315	1B	0.5 M NaOTf in diglyme		Raman★, XRD★
Hartmann[5]	GDL H2315	1B	0.5 M NaOTf in diglyme		Raman★, XRD★
Hartmann[16a]	GDL H2315	1B	0.5 M NaOTf in diglyme		pressure monitoring★
McCloskey[1f]	P50 Avcarb carbon paper	1B	0.2 N NaOTf in DME		DEMS★
Bender[9]	GDL H2315, Ketjenblack, and others	1B	0.5 M NaOTf in diglyme		XRD★
Zhao[13]	vertically aligned carbon nanotubes (VACNTs)	1B/3B	0.5 M NaOTf in tetraglyme		SAED?, XRD★
Bender[2a]	different CNTs	1B	0.5 M NaOTf in diglyme		XRD★
Bi[2c]	P50 Avcarb carbon paper	1B	0.5 M NaOTf in DME or diglyme		Raman★, XRD★
Xia[1d]	GDL Freudenberg	1B	0.5 M NaOTf in diglyme		DEMS★, XRD★
Ortiz-Vitoriano[1c]	vertically aligned few-walled CNT carpets	1C	0.1 M $NaClO_4$ in DME		Raman★, SAED★, XRD★
Na_2O_2					
Peled[17a]	E-TEK air electrode, 10% Pt support, XC72 coated with Na_2CO_3	2C	0.1 M calixpyrrole, 1 M $NaClO_4$ in PEGDME/PC (90:10) +1 wt%Al_2O_3		–
Sun[1e]	diamond-like carbon thin film	2C	1 M $NaPF_6$ in EC:DMC 1:1		FTIR?, SAED?
Das[21]	Super P	-	1 M $NaClO_4$ in tetraglyme, 0.75 M NaOTf in EMIM OTf		FTIR?, XRD†
Liu[6d]	graphene nanosheets	2C	0.25 M $NaPF_6$ in DME 0.25 M $NaClO_4$ in DME		SAED?
Li[6c]	graphene nanosheet and N-doped graphene nanosheets	3B	0.5 M NaOTf in diglyme		XRD?
Liu[18a]	$NiCo_2O_4$ nanosheets on Ni foam	3B	1 M $NaClO_4$ in DME		FTIR?, SAED?
Yin[2d]	CNT on Ni foam	2C	1 M $NaClO_4$ in DME and 0.001 M NaI		Raman?, SAED?
$Na_2O_2{\cdot}2H_2O$					
Kim[6b]	Ketjenblack	2C	1 M $NaClO_4$ in PC 1 M $NaClO_4$ in tetraglyme		FTIR★, Raman, XRD★
Jian[17b]	CNT paper	3B	0.5 M NaOTf in diglyme 0.5 M NaTFSI in tetraglyme		XRD★
Mixed discharge products				**Discharge product**	
Sun[6e]	N-doped CNT and CNT on polypropylene + PVDF	2C	0.5 M NaOTf in diglyme	NaO_2* Na_2O_2	XRD†
Yadegari[16c]	N-doped CNTs on carbon paper	3C	0.5 M NaOTf in diglyme	NaO_2* Na_2O_2 Na_2CO_3	FTIR?, XANES, XRD†
Hu[6a]	$CaMnO_3$/Super P/PVDF 30:60:10	3C	1 M NaOTf in tetraglyme	NaO_2 Na_2O_2*	Raman?, XRD?
Yadegari[6f]	carbon black N330/NH_3 or treated with CO_2	3C	0.5 M NaOTf in diglyme	NaO_2 Na_2O_2 $2H_2O$*	FTIR?, XRD†, Raman†
Sun[7]	CNTs	3C	0.5 M NaOTf in diglyme	NaOH H_2O Na_2O_2 NaOH NaO_2 Na_2CO_3	FTIR?, XRD†

Table 1: (Continued)

Author	Oxygen electrode	Hysteresis	Electrolyte		Methods for analysis
Xu[17c]	Super P-Li/VDF 9:1 on Toray paper or aluminum mesh	3C/2C	1 M NaTFSI in PC, 10 vol% SiO_2, 1-methyl-3-propylimidazolium bis(trifluoromethanesulfone)-imide	$NaHCO_3$	FTIR, XRD
Kwak[17d]	ordered mesoporous carbon (OMC)/PVDF on GDL SGL-35BC and SuperP	3C	0.5 M NaOTf in PC/0.5 M NaOTf in diglyme, tetraglyme, and monoglyme	Na_2CO_3	SAED, XRD
Zhang[2b]	Graphene nanosheets + Pt nanoparticles + PVDF	2C	1 M $NaClO_4$ in PC	Na_2CO_3	FTIR, SAED

[a] The reports were grouped according to the major discharge product and are arranged in the order of publication date. The type of charge/discharge hysteresis is classified as in Ref. [3]. In the section "mixed discharge products", an asterisk (*) denotes the main discharge product. DME = 1,2-dimethoxyethane, EMIM = 1-ethyl-3-methylimidazolium chloride, OTf = trifluoromethanesulfonate, PEGDME = polyethylene glycol dimethyl ether, PVDF = polyvinylidene fluoride, TFSI = bis(trifluoromethane)sulfonimide.

Table 2: All previously used electrolyte compositions with the reported discharge product. The conducting salt concentrations are given in brackets.

	NaOTf	$NaPF_6$	$NaClO_4$	NaTFSI
DME/monoglyme	NaO_2 (0.2 N,[1f] 0.5 M)[2c] Na_2CO_3 (0.5 M)[17d]	Na_2O_2 (0.25 M)[6d]	NaO_2 (0.1 M)[1c] Na_2O_2 (0.25 M,[6d] 1 M)[18a]	
diglyme	NaO_2 (0.5 M)[1a,d, 2a,c, 5, 6e,f, 9, 16a,c] Na_2O_2 (0.5 M)[6c,e, 16c] $Na_2O_2{\cdot}2\,H_2O$ (0.5 M)[6f, 17b] Na_2CO_3 (0.5 M)[16c, 17d]			
tetraglyme	NaO_2 (0.5 M)[13] Na_2O_2 (1 M)[6a] Na_2CO_3 (0.5 M)[17d]		$Na_2O_2{\cdot}2\,H_2O$ (1 M)[6b]	$Na_2O_2{\cdot}2\,H_2O$ (0.5 M)[17b]
PC	Na_2CO_3 (0.5 M)[17d]		Na_2CO_3(1 M,[6b] 1 M)[2b]	
EC/DMC 1:1		Na_2O_2 (1 M)[1e] Na_2CO_3 (1 M)[1e]		
EMIM·OTf	Na_2O_2 (0.75 M)[21]			

water amount, the discharge product was identified to be NaO_2. In view of the thermodynamic driving forces, high water concentrations must lead to the formation of NaOH[9] or $Na_2O_2{\cdot}2\,H_2O$ as the major reaction product. It appears that the water concentrations in the electrolyte reported by Xia et al. and also by our group were too low to lead to the formation of NaOH or $Na_2O_2{\cdot}2\,H_2O$. Interestingly, Ortiz-Vitoriano et al. prepared cells with up to 6000 ppm of water in the electrolyte and also identified NaO_2 as the sole discharge product by XRD.[1c] They suggested that NaO_2 cannot be converted into $Na_2O_2{\cdot}2\,H_2O$ solely by water in the electrolyte.

Sun et al. made comparable observations when testing the influence of humidity on the cell reaction.[7] When discharged in dry air, NaO_2 and Na_2O_2 were formed. With a relative humidity of 30%, only hydrated sodium hydroxide ($NaOH{\cdot}H_2O$) was formed. At even higher relative humidities, NaOH reacted with CO_2 from the atmosphere to form Na_2CO_3. The identification was carried out by XRD. In contrast to the report by Ortiz-Vitoriano et al., the diffraction patterns showed only low resolution and small reflections and are thus less conclusive. It is surprising that hydrated peroxide was not observed, as this compound would be expected to be formed during the reaction of NaO_2 with water.

Zhao et al. found different discharge products when they varied the gas supply (static or flow conditions). Cells with closed, static oxygen atmosphere yielded NaO_2 whereas cells with actively supplied oxygen yielded $Na_2O_2{\cdot}2\,H_2O$. The authors ascribed this difference to the substantial amount of humidity supplied with the O_2 flow, supposedly leading to the hydration of NaO_2, so that the reaction $2\,NaO_2 + 2\,H_2O \rightarrow Na_2O_2{\cdot}2\,H_2O + O_2$ is favored. For long discharge times, water might accumulate and could be responsible for the formation of the hydrated peroxide phase.

Detailed information on the gas supply is often missing, and therefore, it is not possible to extract a correlation between the properties of the gas phase and the discharge product obtained in Na/O_2 cells. Some groups used a static gas reservoir,[1a,c,d, 2a,c, 5, 6c, 9, 16a, 17c,d] and others used an active gas supply.[1e, 6b,f, 16b, 17a, 21] In both cases, the water concentration in the gas phase might have been higher than expected and/or measured. The effect of this underestimation will be much more severe for the active gas supply. In any case, the amount of water brought into the cell when using a flow of gas is several orders of magnitude larger than the amount of water brought into the cell via the electrolyte.

Another important, often neglected, and scarcely investigated factor is the sodium metal anode: Sodium metal will act as a water trap, forming NaOH, which may severely influence the cell reaction. Even if a protecting solid electrolyte interphase forms, it will break up during deep cycling, and so the sodium metal anode will continuously consume water.

In essence, the reported results on the role of water are not consistent, and the formation of peroxide hydrates—which has been suggested by some authors—requires relatively large amounts of water.

3.3. Other Impurities

Aside from water, other (yet unknown) impurities in the electrolyte may additionally impact the cell chemistry in Na/O_2 cells. Even though solvents and conducting salts are usually purchased in the highest available purity, small amounts of impurities are always present. To minimize their impact on cell performance, distillation, recrystallization, or synthesis were applied in some of the studies cited above, but not in the majority of these studies. Our own first studies with Na/O_2 cells were conducted with dried electrolyte,[1a] without any further purification. Later experiments that used electrolytes without water or any detectable impurity yielded comparable results and the same discharge product.[9] This observation implies that impurities more likely result in slight improvements of the cell performance owing to the reduction of potential side reactions than in changes in the chemical nature of the discharge products.

4. Theoretical and Thermodynamic Considerations

4.1. Sodium Superoxide or Sodium Peroxide?

Two theoretical studies addressed the relative stability of the sodium oxides in Na/O_2 cells: Lee et al. focused on the phase stability as a function of $p(O_2)$.[10b] They concluded from their calculated surface energies that NaO_2 is the favored product under standard conditions as the oxygen reduction reaction (ORR) for the transfer of one electron is kinetically favored over the two-electron transfer.

The second theoretical study of the surface energies was carried out by Kang et al.[10a] In contrast to Lee et al., they found Na_2O_2 to be more stable under standard conditions in the bulk phase. However, considering a variation in the crystal size, the authors concluded that NaO_2 becomes more stable for crystals with a diameter smaller than approximately 6 nm. Thus these two theoretical studies provide strong support for the predominant formation of NaO_2, irrespective of its metastable character relative to Na_2O_2 in the bulk phase.

As already mentioned above, the accuracy of the thermodynamic data reported in the literature is probably not high enough to clearly decide whether NaO_2 or Na_2O_2 is thermodynamically more stable. The difference in the free enthalpies of bulk NaO_2 and Na_2O_2 is less than 3%, which is probably smaller than the errors of the thermodynamic quantities of these less common phases. Consequently, calculations based solely on thermodynamic data can lead to incorrect results.

4.2. The Impact of Water on the Thermodynamic Landscape

Considering reactions of sodium with oxygen in the presence of water (see Section 3.2) from the thermodynamic point of view, the product will always be NaOH, as its free enthalpy of formation is even larger than for the oxides. Thus the reaction of different sodium oxides with water should also lead to the unwanted formation of NaOH. Figure 3 depicts the thermodynamic landscape for the reaction of sodium and sodium oxide species with water, based on the free energies of the reaction.

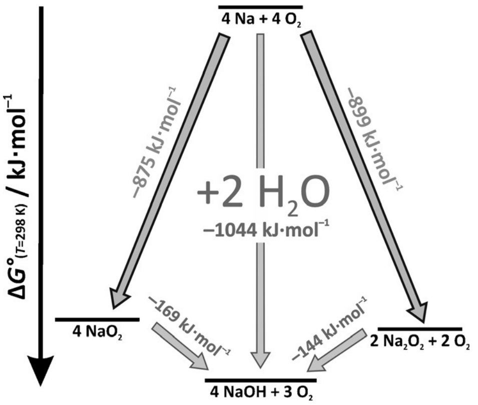

Figure 3. Thermodynamic relations for reactions of sodium and sodium oxides with water.

All in all, small changes in the thermodynamic landscape can determine whether NaO_2 or Na_2O_2 is formed. Furthermore, if water is present, even further reaction products can be formed and might influence the cell performance. We therefore would like to emphasize the importance of maintaining dry conditions or at least minimal water concentrations in the cell (see Xia et al.).[1d]

5. Prospective/Perspective Thoughts

We have found that up to now, no conclusive and consistent model for the competing formation of NaO_2 and Na_2O_2 has been proposed. To stimulate further discussion, we depict possible reaction paths for the formation of sodium oxides in Na/O_2 cells in Figure 4. Based on the experimental identification (see Section 2.2) of discharge products in Na/O_2 cells, we highlight three possible pathways.

First of all, superoxide anions will be formed during the electrochemical discharge reaction at the cathode (sodium cations are formed at the anode) because their formation is favored owing to simple/fast one-electron charge transfer kinetics. As only NaO_2 has been identified without doubt, we assume that NaO_2 will subsequently precipitate from solution as recently published by Hartmann et al.[1b] Based on these

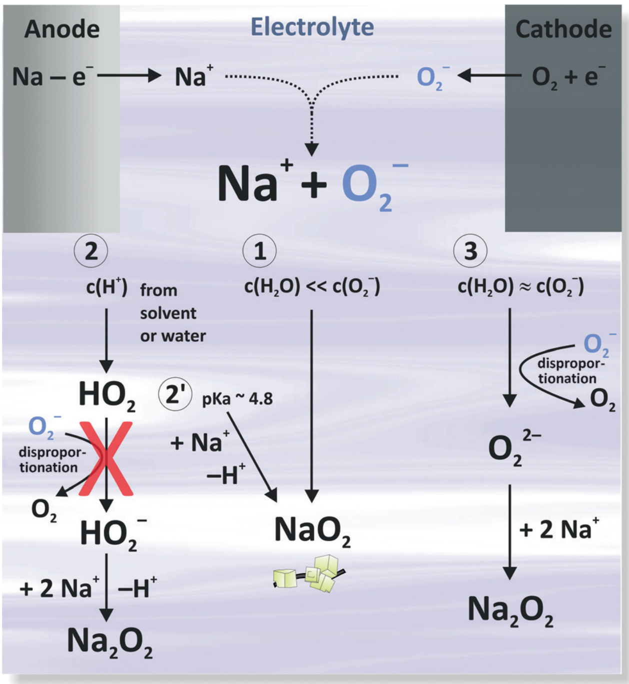

Figure 4. Suggested reaction pathways for the formation of sodium superoxide and sodium peroxide as discharge products in Na/O_2 cells.

findings, the solubility product, which is given by the product of the concentrations of Na^+ and O_2^- in the solution, plays an important role for this pathway. Thus the solubility product of Na^+ and O_2^- should be subject of further investigations.

For pathway 1, we assume that even a small concentration of water affects the solubility of O_2^- and also the solubility of NaO_2. Considering all studies reported thus far, this pathway is most likely to occur when the concentration of water in the electrolyte is rather small—but not too small (see Xia et al.).[1d]

If, on the contrary, intermediate water concentrations are present that are almost equal to that of O_2^-, direct peroxide formation might occur (pathway 3). We speculate that high water concentrations directly increase the solubility of O_2^-, kinetically favoring the disproportion of two O_2^- ions into O_2^{2-} and O_2 in a second-order reaction. Subsequent association with two Na^+ ions might finally yield Na_2O_2 as a precipitate.

As discussed in Sections 3.2 and 4.2, water plays an important role as a proton source, but organic compounds (solvent molecules)[23] may also supply protons, which can initiate another pathway towards the formation of Na_2O_2 (pathway 2). As shown by the results that were recently obtained by Xia et al. and by Hartmann et al., the solvated superoxide might enable homogeneous reactions with protons, forming hydroperoxyl HO_2.[1b,d] However, HO_2 has a relatively small pK_a value ($pK_a = 4.8$ in aqueous environment),[24] resulting in small HO_2 concentrations. Further reactions, including the reduction to HO_2^-, are thus not likely to occur. Precipitation of NaO_2 would then be a reasonable step (pathway 2′), once the solubility product has been exceeded.

We admit that these mechanisms are based on hypotheses and have not been experimentally confirmed. Thus far, there is no explicit experimental evidence for the intermediate species in the pathways proposed. Future work has to identify the most influential parameters for these pathways, such as proton concentration and water concentration, as well as the solubility product of Na^+ and O_2^-. We would also like to emphasize again that the experimental evidence for the formation of NaO_2 is sound and unequivocal, whereas experimental confirmation for the formation of the difference peroxide phases is hampered by analytical ambiguities.

6. Conclusions

In conclusion, for the discharge of a Na/O_2 cell, both NaO_2 and Na_2O_2 (mostly as hydrates) have been reported as the product phase in roughly the same number of studies. However, only NaO_2 has been identified without doubt as the discharge product in Na/O_2 cells by means of Raman spectroscopy and X-Ray diffraction, and the steps that lead to its formation have been unequivocally determined.

In the case of Na_2O_2, product identification appears to be less reliable, and even the mechanism of formation is unclear. Therefore, we proposed a potential reaction scheme and elucidated conditions under which peroxide formation is possible. As shown in Figure 4, a certain concentration of water or other impurities might affect the nature of the discharge products in Na/O_2 cells.

Furthermore, based on previous studies and thermodynamic calculations, the formation of hydrated peroxide ($Na_2O_2{\cdot}2H_2O$) can occur in Na/O_2 cells through the reaction $2NaO_2 + 2H_2O \rightarrow Na_2O_2{\cdot}2H_2O + O_2$. As a significant (stoichiometric) amount of water is required for this reaction, minor water traces in the electrolyte are not sufficient to explain the formation of the hydrated peroxide. Thus the formation of hydrated peroxide can only be explained by the presence of a large amount of water or by decomposition of the solvent in stoichiometric amounts.

In essence, at the moment, it remains unclear which factors favor the two-electron reaction to form pure Na_2O_2. One problem is that hardly any information on the crystal structures of peroxides and especially of the hydrated peroxide phases has been reported. Thus the basis for the proper identification of all oxides by X-Ray diffraction is missing. Therefore, we strongly recommend using Raman spectroscopy for the unequivocal identification of discharge products in Na/O_2 cells.

The decisive factors that determine whether NaO_2 or Na_2O_2 is formed remain unknown, and more research efforts, both experimentally and by model-based considerations, are needed to identify these factors. Answers to the following questions may help to determine the reasons for the occurrence of one- or two-electron transfer step by step:

1) How does the solubility product of Na^+ and O_2^- change under various conditions (e.g., for various solvents, temperatures, conducting salts)? The solubility product could yield valuable insight into the reaction pathways for discharge product formation.

2) What is the morphology of Na_2O_2? The cubic shape of NaO_2 crystallites has been reported several times, but the morphology of Na_2O_2 was only analyzed in TEM images under strong electron exposure.
3) Are the discharge products stable in the long term? Owing to the small energy differences, a slow reaction from the initial (metastable) product may occur.
4) What is the reason for the sudden death of Na/O_2 cells? A passivating layer of discharge or decomposition products may be responsible for this observation, as well as hindered oxygen diffusion in the electrolyte.

In the end, the answers to these questions and to the question of one- or two-electron transfer will help to significantly improve our understanding of further non-aqueous metal–oxygen systems and facilitate their optimization.

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