

Mechanistic investigation of the oxygen reduction in magnesium ion-containing dimethyl sulfoxide



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ABSTRACT

Mg–O₂ batteries appear to be a promising alternative to Li–O₂ system due to the high abundance and volumetric energy density of Mg. Although much effort has been put into research on Li–O₂ batteries, little is known about the oxygen reduction and evolution in Mg²⁺-containing aprotic electrolytes. In this paper, we present a detailed analysis of the ORR in Mg²⁺-containing DMSO using RRDE and DEMS-techniques and derive a more general reaction mechanism of ORR in aprotic electrolytes using the results for Li⁺, Na⁺ and K⁺-containing DMSO. O₂ first reacts via an initial adsorption step to superoxide which, in the presence of Mg²⁺, is subsequently reduced to peroxide as the main reaction product. However, this product undergoes further reactions leading to a deactivation of the electrode. Regarding the reversibility, unfortunately no OER was observed and reactivation of the electrode proved difficult.

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1. Introduction

The world population's increasing demand for energy combined with scarcity of fossil resources requires an alternative energy production, which relies on renewable resources. One of the current issues concerning the efficiency and attractiveness of renewable energies is the energy storage technology. Since Abraham introduced the concept of the lithium-air battery in 1996, research focused on metal-air batteries in aprotic media as a potential future technology for energy storage [1]. The oxygen reduction reaction (ORR) in aprotic media in the presence of divalent cations like Mg²⁺-ions has attracted little attention [2,3], while there has been a lot of interest in monovalent cations such as Li⁺ [4–15], Na⁺ [4,16–18], K⁺ [4,7,19] and tetrabutylammonium (TBA⁺) [5–7]. Nevertheless, a reversible Mg–O₂ battery appears attractive because of the high energy density, compared to that of Li–O₂, and because of the high abundance of magnesium.

Despite the effort which was put into research on metal-air batteries the exact mechanism of oxygen reduction in aprotic media is still not fully understood. For the ORR in aprotic Li⁺ electrolytes, which is probably the best known system regarding ORR in aprotic solvents, it is generally accepted that the final reduction product is Li₂O₂ with the at least intermediate formation of LiO₂ [4–7,10,11,13,20–23]. In principle two pathways of the

formation of Li₂O₂ have been considered: the *direct* pathway including the direct reduction of superoxide to peroxide at the electrode surface and the *indirect* one proceeding via disproportionation of the initially formed superoxide [4,6,8,14,15,24].

Concerning the detailed mechanism of the direct pathway, Lu *et al.* could show a volcano like correlation between the adsorption enthalpy of O₂ at the electrode material and the potential, which has to be applied in Li⁺-containing electrolytes to supply a certain current density [25]. This directly implies that the ORR takes place via an inner-sphere reaction. More strikingly, Bondue *et al.* showed for the ORR on boron-doped diamond electrodes that even the initial reduction step of O₂ to superoxide proceeds via an inner-sphere reaction [4]. Additionally, the cation as well as the electrode material exerts a catalytic effect by shifting the potential of direct peroxide formation by several hundred millivolts [4]. The effect of the cation on peroxide formation can be observed most strikingly when the ORR in the presence of TBA⁺ is compared to the ORR in the presence of Li⁺: In the former case, peroxide cannot be formed at all [5–7] while in the latter case it is a question of the applied potential and electrode material [4–12,26]. Further kinetic investigations regarding the Tafel-slope in TBA⁺- [7] and Li⁺- [6,25,27] containing DMSO and MeCN yielded values of about 120 mV/dec suggesting a one-electron transfer in the rate determining step. The only study related to the electrochemical reaction order with respect to O₂ in aprotic solvents supports the assumption that O₂ is adsorbed prior to reduction [25] as the reaction order is in between 0 and 1. However, the determination of the reaction order is flawed as discussed later on.

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Preliminary work concerning ORR in Mg^{2+} -containing DMSO has been done by Shiga et al. who presumably identified MgO as the main discharge-product in I_2 -containing DMSO [2]. Additional mechanistic investigations have been conducted by Vardar et al. who could show by examining the thermodynamic potentials that the initial step of the ORR in Mg^{2+} -containing THF involves the intermediate formation of superoxide [3]. Despite the results of Shiga, the authors identified a mixture of $2/3\text{MgO}$ and $1/3\text{MgO}_2$ as the discharge products. However, it remains unclear whether there are possible side-reactions between the electrolyte salt and O_2 and to what extent these reactions could influence the distribution of the products. The aim of the present paper was to elucidate the detailed mechanism of oxygen reduction in DMSO in the presence of Mg^{2+} -ions. Comparison with ORR in the presence of other cations and electrode materials will lead to the derivation of a comprehensive mechanism.

2. Experimental

2.1. Chemical reagents

All electrolytes were prepared and stored under an Ar -atmosphere in an *MBraun* glovebox. The freshly prepared electrolytes contained approx. 40 ppm water. The expected error due to the reaction of DMSO with the *Karl-Fischer*-reagents was previously estimated by adding a water standard and is already included in the presented values [4].

Extra dry DMSO (99.7%, over molecular sieve, Acros Organics) was used as received, while magnesium perchlorate ($\geq 99\%$ Sigma-Aldrich) was dried at 245°C under reduced pressure (10^{-2} mbar) before usage. Highly pure Argon (Air Liquid, 99.999 %) and highly pure oxygen (Air Liquid, 99.999 %) were used to purge the vessels and electrolytes. Most of the measurements were performed using a custom made mixture of Ar and O_2 (80:20 = $\text{Ar}:\text{O}_2$) obtained from Air Liquid. The different $\text{Ar}-\text{O}_2$ -mixtures for measuring the oxygen dependence of the current were produced by employing two flowmeters (*Krohne Duisburg*).

2.2. Rotating-Ring-Disc-Electrode (RRDE) measurements

The RRDE-measurements were performed in a classical H-cell which was continuously purged with an $\text{Ar}-\text{O}_2$ mixture to avoid water contamination and keep the electrolyte saturated with O_2 . After finishing the RRDE measurement, a sample of the electrolyte within the working compartment was used to determine the water content, which was approximately 60 ppm for a typical measurement.

2.3. Differential electrochemical mass spectrometry (DEMS) measurements

The dual thin-layer cell used in this work consists of an upper compartment, where the working electrode is placed and a lower compartment, which is connected to the mass spectrometer via a porous Teflon membrane pressed on a steel frit. The electrolyte enters the cell at the upper and leaves it at the lower compartment. The reference electrode is placed at the electrolyte inlet while the main counter electrode, which is connected to a resistance of 1Ω , is placed at the outlet. A second counter electrode connected to a resistance of $1\text{M}\Omega$ is placed at the inlet. This dual counter electrode arrangement suppresses electronic oscillations and the choice of resistances guarantees an optimal current distribution. The dual thin-layer cell used in this work is described in detail in previous papers [28,29]. To correlate faradaic and ionic currents to get information on the number of electrons transferred per oxygen molecule, a calibration of the system is necessary, employing a reaction of known stoichiometry. For this purpose the ORR in KClO_4 -containing DMSO was used, which is discussed in detail elsewhere [5].

2.4. Reference electrode

A silver wire in a solution of 0.1 M AgNO_3 in DMSO was used as a reference electrode. In order to avoid contamination of the working electrolyte with silver-ions during the RRDE-measurement, the reference electrode was connected via a *Luggin* capillary, which had contact to the reference electrolyte through the wet

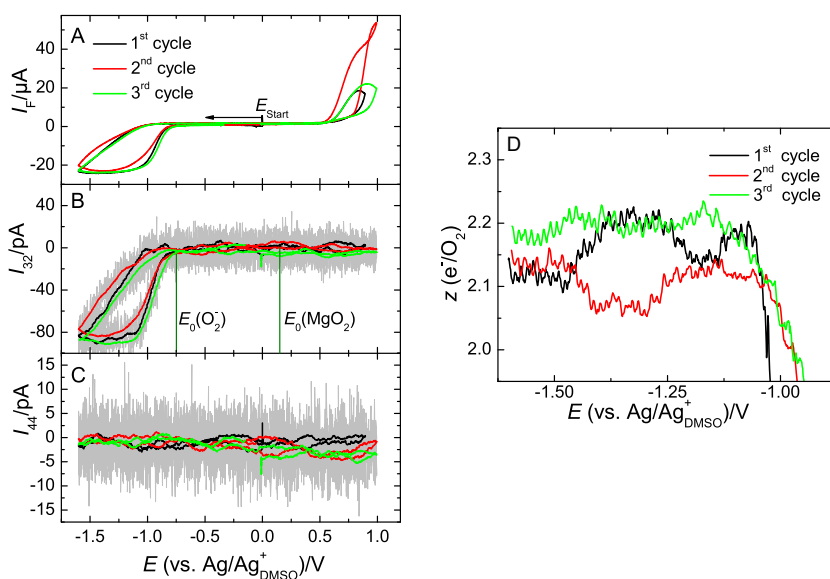


Fig. 1. Subsequent CV (A) and MSCV for mass 32 (B) and mass 44 (C) in DMSO containing $0.4\text{ M Mg}(\text{ClO}_4)_2$ saturated with a mixture (80:20) of Ar and O_2 at a Pt-electrode. Flow rate $u = 5\mu\text{L s}^{-1}$; sweep rate $\nu = 10\text{ mV s}^{-1}$; black: first cycle; red: second cycle; green: third cycle. The arrow indicates the initial sweep direction. The number of electrons transferred per oxygen molecule is shown in (D). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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