Understanding the charge/discharge mechanisms and passivation reactions in Na-O$_2$ batteries

CrossMark

Imanol Landa-Medrano [a], James T. Frith [b], Idoia Ruiz de Larramendi [a], Iñigo Lozano [a], Nagore Ortiz-Vitoriano [c, d], Nuria Garcia-Araez [b], Teófilo Rojo [a, c, *]

[a] Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Barrio Sarriena s/n, 48940, Leioa, Bizkaia, Spain
[b] Department of Chemistry, University of Southampton, SO17 1BJ, Southampton, UK
[c] CIC EnergiGUNE, Albert Einstein 48, 0150, Miñano, Spain
[d] IKERBASQUE, Basque Foundation for Science, 48013, Bilbao, Spain

HIGHLIGHTS

- Electrochemical quartz microbalance is for the first time used in Na-O$_2$ batteries.
- Solution-mediated product growth in the beginning of the discharge is evidenced.
- A film-like discharge product is detected by the end of the discharge.
- Discharge product accumulation, passivation and removal model has been proposed.

GRAPHICAL ABSTRACT
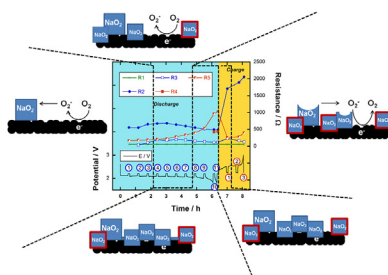
ARTICLE INFO

ABSTRACT

Sodium-oxygen batteries are becoming of increasing interest in the research community as they are able to overcome some of the difficulties associated with lithium-oxygen batteries. The interpretation of the processes governing the discharge and charge of these batteries, however, has been under debate since their early development. In this work we combine different electrochemical methods to build up a model of the discharge product formation and decomposition. We initially analyze the formation and decomposition of the discharge products by means of electrochemical impedance spectroscopy. After that, and for the first time, oxygen electrode processes in Na-O$_2$ cells are analyzed by means of electrochemical quartz crystal microbalance experiments. Based on the combination of these two techniques it is possible to evidence the stabilization of the discharge products in the electrolyte prior to their precipitation. The deposition of passivating products that cannot be stripped off during charge is also demonstrated. Cyclic voltammetry experiments at different potential limits further confirm these passivation reactions. In conclusion, this work provides an accurate picture of the mechanism of the Na-O$_2$ cell reactions by combining different electrochemical techniques.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Many research groups have focused their interest on metal-oxygen batteries, due to their high theoretical energy density, in an effort to develop energy storage devices capable of replacing

* Corresponding author. Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Barrio Sarriena s/n, 48940, Leioa, Bizkaia, Spain.
E-mail address: trojo@cicenergigune.com (T. Rojo).

gasoline in electric vehicles [1,2]. Particularly, lithium-oxygen (Li-O$_2$) batteries with non-aqueous electrolytes have received much attention due to their high theoretical energy density, 3485 W h kg^{-1} based on the reduction of dioxygen to lithium peroxide (2 Li + O$_2$ → Li$_2$O$_2$) [3,4]. However, 20 years after first being proposed by Prof. Abraham's group [5], these batteries are still far from becoming commercially available. Many researchers are now seeking alternative systems in order to overcome the difficulties associated with Li-O$_2$ cells, namely; their high overpotentials, low cycling efficiency and side reactions [6—8]. In 2011 Peled et al. reported the first sodium-oxygen (Na-O$_2$) battery that worked at 105 °C, above the melting point of sodium [9]. In the following years, Janek's group led the research of such systems discussing the identity of the oxygen reduction products [10—13], its deposition mechanism [14,15] and the influence of oxygen pressure [16]. In these studies they demonstrated that the superoxide radical was generated by the reduction of oxygen and stabilized in the electrolyte, being precipitated in cubic-shaped deposits after supersaturation of the electrolyte. Many groups have since reported results in good agreement with this mechanism [17—21].

In parallel to fundamental electrochemistry other groups have focused their research on developing cathode materials to improve the electrochemical performance of the Na-O$_2$ battery. The use of cathode materials capable of tailoring the reaction pathway is also considered a promising research field for Na-O$_2$ batteries. A recent work by Ma and Zhang [22] reported an enhancement of the discharge capacity and cycling life of the cell through the use of an oxygen electrode consisting of nitrogen-doped carbon with a hierarchically porous structure. Moreover, this group has successfully eliminated the binder from the carbon electrode [23,24] as its inclusion can lead to parasitic reactions as evidenced by Reeve et al. [25].

Recently, Knudsen et al. [26] reported, for the first time, an insitu electrochemical impedance spectroscopy (EIS) study of Na-O$_2$ batteries, in order to identify the capacity limitation of such systems, using a 2-electrode configuration. This technique was also used by our group to analyze the processes during the first galvanostatic cycle of Li-O$_2$ batteries [27]. In their study of Na-O$_2$ batteries, Knudsen et al. proposed a discharge product deposition model based on the potential evolution and impedance data recorded [26]. One of the most significant conclusions of their work was that the surface of the discharge products becomes passivated in the cell environment, this is in good agreement with the results reported by our group [28]. In this work we have utilized EIS and cyclic voltammetry experiments to further elucidate the chemistry of Na-O$_2$ cells. In addition, electrochemical quartz crystal microbalance (EQCM) experiments are reported for the first time in Na-O$_2$ batteries; this allows the monitoring and quantification of the deposits on the oxygen electrode. By combing the electrochemical techniques it is possible to analyze the accumulation, removal and passivation of the discharge products allowing us to propose mechanisms for the ORR and the OER.

2. Experimental

A 3-electrode cell similar to that reported by Janek et al. was used for the galvanostatic and electrochemical impedance spectroscopy measurements [11]. Sodium metal (99.9%, Sigma-Aldrich) was used as the counter and reference electrode. Experiments were performed assembling the cell in a 2- and 3-electrode set up; in the 3-electrode set up a small piece of Na was used as the reference electrode. Oxygen (working) electrodes consisted of 11 mm diameter carbon paper electrodes (H2315, Freudenberg). A stainless steel mesh (Alfa Aesar) served as the current collector. Two microfiber filters (Whatman) were placed as separators between

sodium and oxygen electrodes and soaked with 150 μL of 0.5 M sodium trifluoromethanesulfonate (NaOTF, 98%, Sigma- Aldrich) in diethylene glycol dimethyl ether (DEGDME, anhydrous, 99.5%, Sigma-Aldrich). Prior to use, the electrolyte was dried using 3 Å type molecular sieves (Sigma-Aldrich). The electrochemical cells were assembled inside an argon filled glovebox (<1 ppm water content, < 10 ppm oxygen content). The cell was purged with pure oxygen for 1 min before the electrochemical measurements and cycled between 1.8 and 3.0 V at room temperature at a current density of 0.1 mA cm^{-2}, using a Biologic-sas VMP-2 potentiostat. The impedance spectra were recorded in the 10^5—10^{-2} Hz frequency range with a perturbation amplitude of 10 mV. Impedance spectra were recorded every 30 min and analyzed using Scribner Associates' Zview software.

The deposition and decomposition of discharge products in the oxygen electrode was analyzed by means of an EQCM. A 5 MHz, 1 inch diameter AT-cut Au-covered quartz crystal (Stanford Research Systems) was used as the oxygen electrode. Na foil pressed onto a stainless steel mesh piece served as the counter and reference electrode. A cathode-containing holder was connected to a QCM 200 Quartz Crystal Microbalance Digital Controller (Stanford Research Systems) and ultimately to the potentiostat in order to record both the frequency variation and voltammetry concurrently. Some pictures of the electrochemical set up are displayed in Fig. S1. The deposition of ORR products leads to a decrease in the resonance frequency that can be used to determine the amount of discharge product deposited on the electrode, based on Sauerbrey's equation [29]:

$$\Delta f = -2 \cdot f_0^2 \cdot \rho_q^{-1/2} \cdot \mu_q^{-1/2} \cdot \Delta m \tag{1}$$

Δf is the frequency change in Hz, A is the piezoelectrically active crystal area, f_0 the resonant frequency in Hz, ρ_q the density of quartz (2.648 g cm^{-3}), μ_q the Shear modulus of quartz AT-cut crystal (2.947 × 10^{11} g cm^{-1} s^{-2}) and Δm the mass variation per electrode area (g cm^{-2}). This equation can be reformulated in order to group together all the parameters associated to the quartz resonator:

$$\Delta f = -C \cdot \Delta m \tag{2}$$

C is the sensitivity factor for the crystal, namely 56.6 Hz μg^{-1} cm^2 for a 5 MHz crystal. It is worth mentioning that the Sauerbrey equation is only strictly applicable to uniform, rigid, thin-film deposits [30]. It is accepted that the discharge products in Na-O$_2$ oxygen electrodes are accumulated as cubic-shaped deposits. However, it has recently been reported [31] that as the discharge current increases the morphology of the discharge product turns from the classic cubic morphology to a thin-film morphology. It can be assumed that at the limiting current conditions achieved in this experiment the discharge product is accumulated as a thin-film.

Cyclic voltammetry (CV) experiments were performed using a cell consisting of two glass compartments separated by a glass frit. A glassy carbon electrode and Na foil pressed onto a stainless steel mesh were used as the oxygen (working) electrode and sodium (counter and reference) electrode, respectively.

In both the CV and EQCM experiments, oxygen was bubbled through the electrolyte for 10 min to produce a saturated solution. CVs were performed at a scan rate of 10 mV s^{-1} with varied anodic scan limits of 3.5, 3.8 and 4.2 V. EQCM experiments were also carried out at 10 mV s^{-1}, limiting the anodic scan to 4.2 V. In both cases the cathodic scan was limited to 1.5 V.

Finally, discharge product morphology and deposition on the oxygen electrode surface was analyzed using a Quanta 200 FEG scanning electron microscope (SEM).