**Understanding the charge/discharge mechanisms and passivation reactions in Na-O2 batteries**

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**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-O2 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-O2 cell reactions by combining different electrochemical techniques.

**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 gasoline in electric vehicles [1,2]. Particularly, lithium-oxygen (Li-O2) 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 + O2 → Li2O2) [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-O2 cells, namely; their high overpotentials, low cycling efficiency and side reactions [6-8]. In 2011 Peled *et al*. reported the first sodium-oxygen (Na-O2) 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-O2 battery. The use of cathode materials capable of tailoring the reaction pathway is also considered a promising research field for Na-O2 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 in-situ electrochemical impedance spectroscopy (EIS) study of Na-O2 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-O2 batteries [27]. In their study of Na-O2 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-O2 cells. In addition, electrochemical quartz crystal microbalance (EQCM) experiments are reported for the first time in Na-O2 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 105 – 10-2 Hz frequency range with a perturbation amplitude of 10 mV. Impedance spectra were recorded every 30 minutes 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]:

f = -2 · f02 · ρq-1/2 · μ q-1/2 · m (1)

*Δf* is the frequency change in Hz, A is the piezoelectrically active crystal area, *f0* the resonant frequency in Hz, *ρq* the density of quartz (2.648 g cm-3), μq the Shear modulus of quartz AT-cut crystal (2.947x1011 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:

f = -C · m (2)

*C* is the sensitivity factor for the crystal, namely 56.6 Hz μg-1 cm2 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-O2 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 minutes 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).

**3. Results and discussion**

*3.1. Two-electrode EIS measurements*

The first galvanostatic cycle in a Na-O2 cell was initially analyzed by means of EIS. The cell was first assembled with a 2-electrode set up (Na was used as the counter and reference electrode) and was discharged to 1.5 V at 0.1 mA cm-2 stopping the galvanostatic measurement every 30 minutes in order to perform impedance measurements. After the full discharge, impedance spectra of both the sodium anode and the oxygen electrode were recorded using a sodium reference electrode (3-electrode set up). After that the two electrodes were reassembled in a 2-electrode set up, the cell was charged to 3.0 V and impedance spectra were recorded every 30 minutes. Finally, once the cell was charged, the cell was disassembled again and the anode and the cathode were re-analyzed by impedance using the 3-electrode set up. The galvanostatic cycle and Bode spectra are displayed in Fig 1.

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**Fig. 1.** (a) First galvanostatic cycle of a Na-O2 cell using a 2-electrode set up between 1.5 and 3.0 V at 0.1 mA cm-2. Impedance scans are numbered; measurements during discharge and charge are highlighted by blue and red circles, respectively. Plots of the imaginary impedance component vs. the logarithm of the frequency (Bode plot) as recorded (b) during discharge and (c) during charge are shown. Comparison of the Bode plots obtained using the 2-electrode set up, and the anode and the cathode contribution using a reference sodium electrode after (d) full discharge and (e) full charge are also shown.

Galvanostatic cycling (Fig. 1a) revealed a stable discharge plateau at ~2.1 V. The subsequent charge showed an average potential of 2.55 V with a Coulombic efficiency of 26%. Bode plots recorded during discharge (Fig. 1b) show three main processes taking place in the cell; at high (freq > 102 Hz), mid/low (10-1 < freq < 10 Hz) and very low frequencies (< 10-1 Hz). The lack of symmetry of the curve at high frequency suggests an overlap of two contributions at 103 Hz and ~ 104 Hz. Following the third impedance measurement the contribution in this region was seen to grow with the discharge. As mentioned, a second process was observed at mid/low frequencies (~ 10 Hz). Although its intensity is initially lower than that of the signal at high frequencies it increases during the discharge and clearly surpasses the high frequency contribution. It is worth mentioning that together with this growth the signals peak moves towards lower frequencies, with a maximum at 1 Hz by the end of the discharge. This shift suggests the presence of two overlapping contributions; the contribution at 1 Hz is insignificant compared to that at 10 Hz during the initial stages of the discharge. However, it continually grows as the ORR proceeds, accounting for the dominant contribution by the end of the discharge. Finally, a combination of two processes can be observed at very low frequencies (< 10-1 Hz). In the first stages of the discharge there is an increase recorded in the imaginary impedance close to 10-2 Hz. As the discharge proceeds, however, this contribution disappears and a new one appears with a maximum at 10-1.5 Hz.

The same signals are found in the Bode diagrams of the impedance measurements during the charge of the cell (Fig. 1c). The high frequency contribution exhibits little changes during charging of the cell; a slight increase in the intensity and a shift to higher frequencies with charge was observed, reinforcing the hypothesis of the presence of two overlapped contributions. It is worth mentioning, however, that intensity values recorded on charge are significantly higher than after a full discharge. The processes at mid/low and very low frequencies remain constant until the last measurement during charging. The processes at very low frequencies, show clear differences between the scans after the full discharge of the cell and those on charge; the contribution at 10-1.5 Hz was not observed and that starting at almost 10-2 Hz was present once again. The shape of these curves in the very low frequency region (< 10-1 Hz) bears a resemblance to those obtained by the mid-end of the previous discharge (Fig. 1b).

The next step in the characterization process was the determination of the origin of each contribution; to this end, impedance of the anode and the cathode was measured separately against a sodium reference electrode. Bode diagrams of the anode and cathode compared to those of the 2 electrode set up after full discharge and full charge are sown in Fig. 1d and Fig. 1e, respectively. This revealed that the processes at very low and low/intermediate frequencies originated in the oxygen electrode, while those at high frequencies were related to the sodium anode. In both figures at high frequencies, the impedance of the anode (from 3-electrode measurements) overlaps quantitatively with the impedance of the 2-electrode cell. The agreement at mid/low frequencies is not so good, fact that we attribute to small variations in the oxygen electrode during the impedance measurements, as discussed below.

Based on the Bode plots it is not possible to propose a unique equivalent circuit that allows adjusting and explaining the changing scenario observed during the galvanostatic cycle and consequently, different equivalent circuits (shown in Fig. S2) are adopted in this work depending on the stage of the cycle. Some examples of Nyquist plots fitted with the equivalent circuits proposed in Fig. S2 are shown in Fig. S3. Impedance data recorded at half discharge (Fig. S3a, 5th measurement during discharge) and at full discharge (Fig. S3b, 11th measurement during discharge) reveal the presence of two main semicircles that could consist of one or two overlapped minor semicircles each due to their depressed shape.

The evolution of the resistance values, obtained by fitting the Nyquist plots, along with the galvanostatic cycle data is displayed in Fig. 2. The analysis of the resistance values and their evolution towards the discharge-charge cycle allows the identification of each contribution.

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**Fig. 2.** Analysis of the evolution of the resistances with the galvanostatic cycle.

Resistance R1 is constant throughout the measurements and is related to the ohmic losses generated by the connections in the system. From the comparison of the Bode diagrams of the 2- and 3-electrode measurements we can conclude that R2 and R3 resistances are related to anodic processes (charge transference and anode/electrolyte interface). In the fitted Nyquist plot for the first stage of the discharge the equivalent circuit shown in Fig. S2a, in which a sole anode process is included, was used (in good agreement with the Bode plots in Fig. 1b). However, from the second measurement during discharge a second anode resistance R3 (Fig. S2b) has been included. Although it is significantly smaller than R5 it continuously grows matching its value at the 4th measurement. After that it remains almost constant around 200 ohm during the rest of the discharge. Both R2 and R3 were adjusted using constant phase elements (CPE) in parallel that facilitate the simulation of heterogeneities in the system and can be related to the double-layer capacitance in the electrode surface. The capacitance values associated to such CPEs point out the type of processes taking place; both CPE2 and CPE3 show values between 10-6 and 10-7 F and can therefore be assigned to double-layer charging processes at the anode surface. R2 can be assigned to the charge transfer resistance at the electrolyte/anode interface (solid electrolyte interphase, SEI) [32]. It remains almost constant during the discharge and increases when the charge of the cell takes place. This is in good agreement with the dendrite formation reported by Bi *et al*. [33]. On the other hand, the continuous growth of R3 with time until a limiting value of ~ 200 ohms could indicate the reaction of the Na electrode with O2. Alternatively, it may be due to the O2- crossover from the cathode as reported by Bi *et al.* [33]; once the SEI and passivating layer are stabilized, however, the reaction between the oxygen-based compounds is stopped and the resistance remains almost constant.

The impedance spectra relating to the cathode process was fitted using a single semicircle (R5CP5) until the final stages of the discharge. However, it is likely that a second contribution could be present after the 7th discharge measurement due to the observed electrochemical response at low/intermediate frequencies (10-1 < freq < 10 Hz). R5 gradually increases until the 7th-8th measurement in good agreement with the formation of discrete nucleation points that continuously grow in a solution-mediated mechanism as demonstrated by Xia *et al*. [34]. This will be further discussed later. The capacitance value associated to this contribution is ~ 10-4 F and consequently can be attributed to the diffusion of oxygen through the porous carbon electrode coupled to oxygen adsorption and electrochemical reactions of oxygen species within the carbon electrode pores, in good agreement with the results reported by Knudsen *et al.* [26]. By the end of the discharge it is necessary to include a second cathode contribution. This contribution exhibits a capacitance value of 10-6 F and can be assigned to an increase in the resistance associated with the charge transference in the cathode/electrolyte interface, due to the formation of insulating or poor electronic conducting products in the interface. Both processes are highly overlapped and it is difficult to accurately separate each contribution. During charge the contribution from the 4th process (R4) disappears and resistance associated to the 5th process (R5) is remarkably decreased. This is as expected for the removal of the discharge products during the OER. R5, however, was seen to slightly increase at the end of the charge, this may be related to passivation reactions, as suggested by Knudsen *et al*. [26].

*3.2. Three-electrode EIS measurements*

In order to determine the processes occurring in each electrode the cell was turned to a 3-electrode set up. The impedance measurements were performed, after discharge/ charge, on the anode and cathode separately for comparison with those obtained using the 2-electrode set up (Fig. S4). Anodic processes estimated using the 2-electrode set up and measured in the 3-electrode set up fit after both full discharge and charge. However, R4 was not observed in the 3-electrode set up. This fact could be also observed in the Bode plots when comparing the 2- and 3-electrode set up after a full discharge (Fig. 1d). Rinaldi *et al*. [35] suggest the formation of a thin film of discharge products on the electrode surface by the end of the discharge coinciding with the end of the plateau and the potential drop in Li-O2 batteries. In addition, re-dissolution of the discharge products of Na-O2 cells has previously been reported by our group [28], in good agreement with Kim *et al*. [36]. Considering that both the 2-electrode and 3-electrode measurements were performed on the same cell, resulting in approximately 10 minute measurements, it is possible that the thin film could be easily re-dissolved during the course of the measurements. The signal at 1 Hz observed by the end of the discharge in the 2-electrode set-up (Fig. 1b), disappeared after the set-up change (Fig. 1d), and was not observed during the charge of the cell (Fig. 1c). This would also support the hypothesis and can be assigned to the formation of a thin discharge product layer by the end of the discharge. In fact, if we assume that the deposition of the discharge products gradually turns from discrete particles to a thin film that passivates the electrode/electrolyte interface between these nuclei. We can then analyze the evolution of R5 throughout the discharge and estimate the moment at which the formation of the layer is initiated. This suggests that the film formation occurs prior to the 7th measurement, as the value of R5 measured with the 2-electrode set up during discharge at the 8th point and after full discharge with the 3-electrode set up are in agreement. Fig. S5 shows a comparison of the Nyquist plots obtained by the 2-electrode set up during discharge at the 8th and the 11th point and those using the 3-electrode set up. The anodic contribution in the 3-electrode set up closely matches that recorded at high frequencies in the 11th measurement using the 2-electrode set up. While the cathode contribution measured using the 3-electrode set up resembles that in the 8th measurement rather than the 11th measurement with the 2-electrode set up. In fact, the growth of R5 is altered after the 8th measurement, turning from a linear (before) to an exponential (after) increase. This may be due to the formation of a thin film. This thin film is then re-dissolved before the charge of the cell, while different impedance measurements are performed. Consequently, SEM images of the oxygen electrode after full discharge can only show a notable accumulation of the usually reported cubic-shaped NaO2 (Fig. S6) [10,17]. After charge R5 is similar for both 2- and 3-electrode set up which is in good agreement with our hypothesis. Finally, passivation reactions reported by other authors support the incomplete removal of the discharge products and, consequently, persistence of R5 despite the cell being fully charged [28,37]. In order to separate the contributions from cathodic and anodic processes, the charge and discharge of a Na-O2 cell was measured in a 3 electrode configuration. Galvanostatic cycling using the 3-electrode set up was slightly longer than the cycle with the 2-electrode set up (Fig. 3). This difference, however, is within the reproducibility of the measurements; it is well-known that it is difficult to accurately reproduce galvanostatic cycles in non-aqueous metal-oxygen batteries [38]. Nevertheless, it should be noted that the cycle overpotential is reduced by approximately 200 mV; this behavior was also observed by Knudsen *et al*. [26] and is indicative of side reactions in the sodium counter electrode (anode) that influence the cell potential.

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**Fig. 3.** (a) Galvanostatic cycles carried out with the 2-electrode (purple line) and 3-electrode set up (black line).

When using a 3-electrode setup the reference Na electrode does not undergo these reactions as electrochemical oxidation and reduction reactions are not continuously occurring on its surface. This results in more reliable measurements of the processes taking place at the oxygen electrode. As expected, no evidence of anodic processes (at high frequencies) were observed in the Bode plots recorded during discharge (Fig. 4a) and charge (Fig. 4b) with the 3-electrode set up.

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**Fig. 4.** Bode plots of the oxygen electrode recorded during (a) discharge and (b) charge.

At low frequencies, when using the 3-electrode set up, a sole contribution at 10 Hz can be observed during the first stages of the discharge. The signal peak is shifted to lower frequencies as the second contribution in the cathode-region grows. The disappearance of the signal at ~1 Hz was also observed. As previously discussed it is believed that this is due to the re-dissolution of the thin film of discharge product. A similar trend was observed during the charge of the cell with a single signal that moves to lower frequencies during charging. Two different equivalent circuits (displayed in Fig. S7) were necessary to fit the Nyquist diagrams. Fig. S8a and S8b show some examples of Nyquist plots of the recorded data and their corresponding fittings. R1 is again assigned to the ohmic resistance and has negligible differences through the cycle. R with a capacitance value of 10-6 F is related to the side reactions that take place in the Na counter electrode. Moreover, the frequency at which these contributions are observed was similar to those for the anode processes in the 2-electrode cell. Consequently, although imperceptible in the Bode diagrams and negligible compared to the resistances associated with the oxygen electrode and of the anode (when using a 2-electrode set up), the reference electrode also has a small contribution in the impedance spectra. Finally, both CP4 and CP5 have capacitance values of around 10-4 - 10-6 F. This allows us to identify R4 and R5 resulting from the oxygen diffusion from outer atmosphere to the oxygen-electrode surface and oxygen adsorption together with the charge-transfer resistance from the electrochemical reduction of oxygen species. As previously mentioned R4 was not used in the fittings of the first discharge measurements. On the contrary, it was necessary for obtaining a successful fitting following the 8th measurement. Nevertheless, it must be considered that the significant overlapping of R4 and R5 may hide the presence of R4 in the impedance measurements prior to this 8th scan. The evolution of resistance during the galvanostatic cycle is shown in Fig. 5.

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**Fig. 5.** Analysis of the evolution of the resistances measured with the 3-electrode set up during the galvanostatic cycle.

R1 remains relatively constant throughout the galvanostatic cycle. This is in good agreement with its assignment to the ohmic losses of the measurement system. The resistance of R was seen to gradually increase during the experiment, therefore, it can be attributed to charge transfer at the electrolyte/RE interface. Nevertheless, R is between 10 and 50 ohms throughout the cycle, and consequently variations recorded may not be significant, or may be attributed to the fitting. The evolution of the resistances, R4+R5, is similar in shape to the inverted discharge plateau which remained constant while the potential plateau was flat, and increased significantly as the discharge came to an end. R4+R5 then decreased during the first stages of the charge, but increased by the end of the charge. Knudsen *et al*. [26] attributed this fact to the side reactions that can occur on the oxygen electrode surface and on the discharge products. This leads to the formation of species that cannot be eliminated at these low working potentials, such as carbonates, in good agreement with the results reported elsewhere [28]. During the first stages of the discharge the electronic insulator NaO2 is generated and stored in the electrode limiting the O2 accessibility to its surface. Consequently, R5 can be assigned to the resistance of deposited NaO2 that accumulates on the electrode. Fig. 5 shows that R5 increases gradually reaching a maximum of approximately 400 ohms although there are slight deviations that can be attributed to an overlapping of the cathode contributions. On the other hand, after the 7th/8th measurement R4 grows exponentially until the end of the discharge. This can be related to an inhibition of the electrochemical reactions at the cathode/electrolyte interface due to the formation of a thin film (~ nm) of NaO2 that ultimately leads to the end of discharge. This film is rapidly solubilised and consequently it is not detected in the first measurement during the charge. Instead R5 remains the sole contribution during charge. It can therefore be concluded that some discharge products remain accumulated in the electrode and cannot be eliminated during charge. The increase in the cathode contribution, also observed in the 2-electrode set up, is reproducible and can be related to the formation of insulating species that cannot be eliminated at these low working potentials, such as carbonates.

*3.3. EQCM and CV characterization*

In order to shed some light into the discharge product accumulation and removal on the oxygen electrode EQCM measurements were carried out. Fig. 6a shows the frequency variation associated with a CV measurement in an EQCM cell. The accumulation of discharge products during the cathodic scan led to a negative frequency variation (f) (in good agreement with EQCM experiments in Li-O2 literature) [39-47] that continued increasing during the whole potential region where a reductive current was recorded. The variation in the frequency was then reversed, and a positive variation of f was observed between 2.1 and 2.6 V, evidencing OER activity and, therefore, confirming the release of some of the ORR products that were previously accumulated in the cathodic scan. However, not all the products were removed, and a significant mass associated with passivating products was accumulated by the end of the cycle.

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**Fig. 6**. (a) Plot of the cyclic voltammogram (CVs) and variation of frequency as measured by the EQCM cell. (b) Mass gain in the electrode calculated using Sauerbrey’s equation using the experimental variations in frequency. Mass change based on the ideal formation of NaO2 (red) and Na2O2 (blue), as calculated from the CV curves.

Between 2.8 and 3.8 V a slight mass accumulation was registered, providing interesting information. Based on the work by Pinedo *et al*. [13], if there were leaks in the cell we would expect the formation of Na2O2·2H2O in the cathodic sweep, leading to the formation of NaOH:

2NaO2 + 2H2O → H2O2 + 2NaOH + O2 (3)

2NaO2 + H2O → Na2O2·2H2O + O2 (4)

Na2O2·2H2O → H2O2 + 2NaOH (5)

NaOH is eliminated between 2.8 and 3.5 V, and thus, its presence in our cell would be seen as a decrease in the mass recorded in this potential range together with the appearance of a peak in the CV [13]:

2NaOH → 2Na+ + H2O2 + 2e- (6)

2H2O2 → 2H2O + O2 (7)

An electrochemical oxidation peak was not observed and a small mass gain (f decrease) was observed at this potential window. This demonstrates that the cell is leak free and that NaOH is not formed under these conditions. This small mass gain could be associated with the accumulation of passivation products, which is in good agreement with the resistance increase observed in the last stage of the impedance measurements. In fact, as the potential approached 4.2 V an increase in f was observed, revealing a decrease in mass that can be attributed to the elimination of carbonates. Furthermore, it is worth noting that f did not return to the initial value, indicating that some products remained on the oxygen electrode after the complete cycle, this is in good agreement to the passivation of the oxygen electrode discussed above and with the last results reported by Liu *et al*. [21].

Further information on the discharge mechanism can be obtained by comparing the EQCM data with calculations of the mass of discharge product expected for the 1 and 2 electron reduction reactions:

O2 + e- + Na+ → NaO2 (8)

O2 + 2e- + 2Na+ → Na2O2 (9)

The calculations are done considering that each electron in the cathodic scan is used in the formation of the discharge product and accumulated on the electrode surface. Comparison of the calculated curves with the experimental mass accumulation on the electrode, obtained from f using the Sauerbrey equation (equation 2) [29,39], reveals some interesting differences (Fig. 6a). During the first 160 s of the cathodic scan the registered mass was lower than the theoretical mass for both a 1 and 2 electron reduction process, this indicates that although electrons were being transferred this did not result in the accumulation of discharge products on the electrode surface. This suggests that these discharge products were instead accumulating in the electrolyte. On the other hand, at longer times, a significant increase in mass was observed, due to deposition of products on the electrode surface. By the end of the ORR the experimental mass accumulation exceeded that of the ideal 1 and 2 electron reduction processes. Chemical reaction of the superoxide with the electrolyte may result in the formation of “heavy” carbonates and could account for this unexpected mass gain and the resulting passivation [21].

Although it was not possible to identify the discharge product generated during ORR two main conclusions were obtained from this experiment:

1. It is demonstrated that ORR is solution mediated in good agreement with the literature [15,18,34].
2. It is confirmed that a passivating discharge product is accumulated on the oxygen electrode surface, which has also been observed by other authors [28,36,37].

Passivation of the electrode by discharge products was further analyzed using a glassy carbon (GC) electrode. CV measurements were carried during which the anodic scan limit was varied between 4.2, 3.8 and 3.5 V in order to investigate the ability of the cell to retain the cathodic current depending on the anodic limiting potential (Fig. 7).

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**Fig. 7**. Cyclic voltammetry carried out at 10 mV s-1 limiting the anodic sweep to 4.2 (black line), 3.8 (red line) and 3.5 V (blue line). The first 3 cycles are shown in all cases.

When the anodic scan of Na-O2 cells was limited to 4.2 V it was possible to retain similar charges during the first three ORR cycles (0.51, 0.53 and 0.52 mC in the first, second and third cycle, respectively). However, when the anodic sweep limit was decreased to 3.8 V the ORR charge was decreased from 0.47 to 0.39 mC in the second cycle and to 0.38 mC for the third cycle. The inability to retain the ORR charge was enhanced when the anodic sweep was limited to 3.5 V, decreasing from 0.43 mC in the first cycle to 0.26 and 0.21 mC in the second and the third cycle, respectively.

Based on the impedance, EQCM and CV data it is possible to postulate a discharge product formation and removal model, schematized in Fig. 8. In the initial stages of the discharge (Fig. 8.a) superoxide is formed at the oxygen electrode surface and stabilized in the electrolyte, as demonstrated by EQCM measurements. Once the solution saturates some discrete nuclei are formed and grow as more superoxide is generated. These nuclei, however, are discrete (a significant part of the electrode remains uncovered) and the resistance associated with the discharge products remains almost constant. This relates to a flat plateau in the potential vs. time (or capacity) plot. As discharge continues (Fig. 8b) more nuclei are generated, resistance is increased, and oxygen reduction is hindered leading to a fall in the potential. Consequently, the ORR gradually turns from a solution-process to a surface-process. By the end of the discharge (Fig. 8c) the oxygen electrode becomes saturated with discharge products and the impedance quickly increases, reaching a maximum. At this point the ORR almost completely stops being a solution mediated process and very small nuclei (or a thin film) form on the electrode surface. Finally, the electrode is not able to adsorb and reduce more oxygen and the cell potential falls. In addition, during all this period the discharge product nuclei are slowly transformed into passivating species.

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**Fig. 8**. Schemes of the model proposed for the discharge product accumulation and removal. Orange boxes in the galvanostatic cycle indicate the part to which each scheme corresponds.

At the onset of the charge process the smallest nuclei are oxidized and resistance is significantly decreased (Fig. 8d). The OER resumes a solution-mediated route and although there is a flat charge plateau resistance does not decrease further as the electrode/electrolyte interface is not fully recovered; there are still nuclei being slowly re-dissolved and then oxidized (Fig. 8e). At the same time, the passivating electrode/products and impedance is increased.

In order to further validate the discharge product growth and removal model Na-O2 cells were discharged to approximately 75, 44, 22 and 7.5 % of their depth of discharge (DoD) and then charged to 3.0 V (galvanostatic cycles are displayed in Fig. S9a). Meanwhile, impedance was measured every 30 minutes. Based on the model proposed in Fig. 8 the discharge deposits by the end of the discharge should be less isolated as the DoD is increased and, therefore, the resistance decrease in the first stages of the charge should be more noticeable, as the ORR becomes predominantly a surface-process as the DoD increases. Resistance evolution of the different cells is presented in Fig. S9b, highlighting the end of each discharge by a vertical line. As previously shown, resistance after a full discharge (100 %) was decreased after the first fraction of the charge. Nevertheless, when the cell was discharged to the 75 % of the DoD resistance remained almost constant after the first charge step, evidencing the lack of product saturation on the oxygen electrode before the charge. For the rest of the measurements the resistance after charging was higher than before charge. It can be concluded that for “early cutoffs” there is not a significant removal of discharge products from the electrode surface to affect the cell impedance; products are removed from the solution. When turning to “late cutoffs”, however, the electrode surface is covered by discharge products that are partly removed until the OER can be carried out via a solution based mechanism.

**4. Conclusions**

In the present work a discharge product accumulation, elimination and passivation model for Na-O2 batteries was developed based on different electrochemical techniques. The combination of electrochemical impedance spectroscopy (EIS) with galvanostatic measurements provided a unique approach for analyzing Na-O2 cells. Anode and cathode processes were distinguished and the accumulation of discharge products in the oxygen electrode was monitored. In addition, the cathode processes have been analyzed for the first time with a 3-electrode set up, monitoring the changes in the impedance of the oxygen electrode without the contribution of the sodium anode. Discharge product deposition and removal was demonstrated to be a solution-process for the NaO2 nuclei formed in the initial stages of the discharge. As the ORR continues, however, the oxygen electrode becomes covered by smaller nuclei (NaO2 thin film) that lead both the ORR and the OER to become surface-processes. Evidence of formation of passivating products were also found using EIS, cycling voltammetry and Electrochemical Quartz Crystal Microbalance (EQCM), which has been used for the first time in Na-O2 batteries. Furthermore, a solution mediated ORR was also evidenced by means of EQCM. Overall, these electrochemical techniques are valuable in aiding the in-situ analysis of the cathode processes of Na-O2 cells.

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**Figure captions**

**Figure 1.** (a) First galvanostatic cycle of a Na-O2 cell using a 2-electrode set up between 1.5 and 3.0 V at 0.1 mA cm-2. Impedance scans are numbered; measurements during discharge and charge are highlighted by blue and red circles, respectively. Plots of the imaginary impedance component vs. the logarithm of the frequency (Bode plot) as recorded (b) during discharge and (c) during charge are shown. Comparison of the Bode plots obtained using the 2-electrode set up, and the anode and the cathode contribution using a reference sodium electrode after (d) full discharge and (e) full charge are also shown.

**Figure 2.** Analysis of the evolution of the resistances with the galvanostatic cycle.

**Figure 3.** (a) Galvanostatic cycles carried out with the 2-electrode (purple line) and 3-electrode set up (black line).

**Figure 4.** Bode plots of the oxygen electrode recorded during (a) discharge and (b) charge.

**Figure 5.** Analysis of the evolution of the resistances measured with the 3-electrode set up during the galvanostatic cycle.

**Figure 6**. (a) Plot of the cyclic voltammogram (CVs) and variation of frequency as measured by the EQCM cell. (b) Mass gain in the electrode calculated using Sauerbrey’s equation using the experimental variations in frequency. Mass change based on the ideal formation of NaO2 (red) and Na2O2 (blue), as calculated from the CV curves.

**Figure 7**. Cyclic voltammetry carried out at 10 mV s-1 limiting the anodic sweep to 4.2 (black line), 3.8 (red line) and 3.5 V (blue line). The first 3 cycles are shown in all cases.

**Figure 8**. Schemes of the model proposed for the discharge product accumulation and removal. Orange boxes in the galvanostatic cycle indicate the part to which each scheme corresponds.

**Figure S1**. (a) Picture of the quartz crystal microbalance measurement system. (b) Picture of the electrochemical cell of the quartz crystal microbalance. (c) Back and (d) front faces of the quartz crystal used as oxygen electrode. (e) Picture of the digital frequency controller used in the measurements.

**Figure S2.** Equivalent circuits selected for fitting: (a) the first step of the discharge, (b) points 2 – 9 in the discharge process, (c) final stage of the discharge (points 10 and 11), (d) charge process, (e) anode contribution in 3-electrode configuration and (f) cathode contribution in 3-electrode configuration

**Figure S3.** Experimental and fitted Nyquist plots and Bode diagrams with the 2 electrode set up recorded (a) at half discharge and (b) full discharge. Inset in each figure shows the equivalent circuit used for the fitting.

**Figure S4**. Resistance values obtained by the 2- and 3- electrode set up after (a) full discharge and (b) full charge.

**Figure S5**. Comparison of the Nyquist plots obtained using the 2-electrode set up in the 8th and 11th measurements of the discharge and those obtained for the anode and the cathode using the 3-electrode set up.

**Figure S6**. SEM images of a fully discharged oxygen electrode.

**Figure S7.** Equivalent circuits selected for the fitting of the (a) points 1 – 7 in the discharge process and charge process, and (b) points 8 – 14 in the discharge process.

**Figure S8.** Experimental and fitted Nyquist plots and Bode diagrams obtained with the 3-electrode set up and applied equivalent circuits (a) at 1st discharge step and (b) after 8 discharge steps.

**Figure S9**. (a) Galvanostatic cycles carried out to the 7.5 (olive line), 22 (green line), 44 (blue line) 75 (red line) and 100% (black line) of the depth of discharge. (b) Resistance evolution of the cathode with the galvanostatic cycle. Vertical lines correspond to the measurement between the last discharge and the first charge periods.