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Kinetics of oxygen reaction and discharge/charging overvoltages of Li-O_2 battery with aprotic electrolytes

Oleg V. Korchagin, Vera A. Bogdanovskaya*, Oleg V. Tripachev, Viktor V. Emets

Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation

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ABSTRACT

The measurement method is suggested and kinetic curves of the oxygen reaction are obtained for the first time on highly dispersed XC-72 and 20Pt/XC-72 active materials in lithium-containing aprotic electrolytes based on DMSO and TEGDME. The relationship between the kinetic overvoltage of the oxygen reaction and discharge/charging overvoltage are studied in a Li-O_2 battery. It is found that the catalyst does not affect either the oxygen reduction kinetics or the Li-O_2 battery discharge overvoltage. At the same time, the charging overvoltage of a Li-O_2 battery with the catalyst is found to be lower than that of a Li-O_2 battery with the carbon material. It is shown that the latter effect is maybe more related to the structural changes of the cathode reaction product than to electrocatalysis of the oxygen evolution reaction.

1. Introduction

In the recent years, the intensive interest to study of oxygen reduction/evolution reactions (oxygen reaction)[1] in nonaqueous (aprotic) electrolytes is observed. This fact is primarily associated with active development of alkali metal-oxygen batteries, for which these reactions are critical. The Li-O_2 system [1,2] has the highest theoretical capacity. In the course of discharge of the lithium-oxygen battery (LOB), the oxygen reduction reaction (ORR, the cathode reaction) takes place on the positive electrode with formation of insoluble lithium peroxide:

$$O_2 + Li^+ + e^- \rightarrow LiO_2 \quad (1)$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2 \quad (2)$$

$$LiO_2 + e^- + Li^+ \rightarrow Li_2O_2 \quad (3)$$

The charging of LOB is accompanied by the oxygen evolution reaction (OER, the anodic reaction):

$$Li_2O_2 \rightarrow O_2 + 2Li^+ + 2e^- \quad (4)$$

The thermodynamic equilibrium potential for the reaction of $2Li + O_2 \leftrightarrow Li_2O_2$ is 2.96 V [3].

Occurrence of the two reactions at the same electrode makes it necessary to develop bifunctional electrocatalysts to ensure acceleration of ORR and the reverse process. Development of such materials requires studying the kinetics and elucidation of the mechanism of oxygen reaction [4]. The objective estimation of the role of catalytic properties of the material requires separating the kinetic component of overvoltage and eliminating the contribution of ohmic and transportation losses. The solution of this problem is complicated by the blocking of the electrode by lithium peroxide with high ohmic resistance. At present, kinetic polarization curves of oxygen reaction in the aprotic media were obtained correctly enough only on a model electrode of smooth carbon [5].

The aim of this work was to plot kinetic curves characterizing the electrochemical overvoltage of the oxygen reaction on the electrode free of Li_2O_2 and to compare them with the discharge–charging curves of LOB measured after reaching the full electrode surface coverage by Li_2O_2. The active materials of the positive electrode were commercial materials used extensively in power sources, namely, the XC-72 carbon black and 20Pt/XC-72 (*E*-TEK) (20 wt% Pt loading) catalyst [2,6]. The electrolytes for LOB [7,8] were prepared on the basis of DMSO and tetraglyme (TEGDME) solvents and the $LiClO_4$ salt (with the concentration of 1M).

2. Experimental

The experiments were performed in a “Swagelok”-type cell simulating the operating conditions of LOB. The preparation of electrolyte, cell assembly and electrochemical measurements were performed in an airproof dry box deaerated by argon (high purity). Lithium foil was used as an anode. Water was further removed from the solvents using 3 Å molecular sieves. The particulars of the design and cell assembly

* Corresponding author.
E-mail address: bogd@elchem.ac.ru (V.A. Bogdanovskaya).

[1] In the paper, the term of “oxygen reaction” is used to denote the oxygen reduction/evolution reactions localized at the same electrode.

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were described in more detail in [9].

Thin-layer positive electrodes (100 $\mu g_{carbon}\ cm^{-2}_{geom}$ [2]) were developed to perform electrochemical studies on an equally accessible electrode surface. The electrodes were formed by application of the suspension of the active material and polyvinylidene fluoride (PVDF) as the binding substance in 1-methyl-2-pyrrolidone onto a polypropylene separator. The ratio of PVDF/carbon material was 1:4. The separator with the active layer (the positive electrode) was dried in air and conditioned under vacuum at the temperature of 100 °C for at least 12 h.

The assembled "Swagelok"-type LOB cell with the studied electrode was purged by high purity oxygen for at least 30 min. After the open circuit voltage value became constant, the series of galvanostatic discharge/charging cycling curves in a broad current density range (23–600 $\mu A\ cm^{-2}_{geom}$) was measured. Three discharge curves corresponding to the surface coverage of 3, 6 and 11% of a Li_2O_2 monolayer[3] were measured for each current density. It was found that in the case of the maximal coverage of the positive electrode by lithium peroxide, which corresponded to the battery voltage drop to 2.0 V, the system loses more than 30% of discharge capacity as early as in the second cycle of discharge/charging. At the low electrode surface coverage by Li_2O_2 the reversibility of the system increases significantly. This allows assuming that the electrode surface becomes completely free from the cathodic reaction product in the course of the charging. Besides, at the low electrode surface coverage by Li_2O_2 the influence of the deposit morphology on the overpotential of the both oxygen reaction components is minimal. This allows ignoring the contribution of the change in the morphology of Li_2O_2 to the overvoltage of the process when the current density and composition of electrolyte are varied.

All the curves were corrected for the high-frequency ohmic resistance of system mainly related to the resistance of electrolyte. The latter was evaluated using the standard electrochemical impedance spectroscopy technique [11].

Fig. 1a shows galvanostatic discharge curves corresponding to the 11% Li_2O_2 monolayer coverage of the positive electrode based on the XC-72 carbon black in 1M $LiClO_4$/DMSO electrolyte.[4] The decrease in the voltage observed at the discharge current is mainly related to electrochemical overvoltage (the curvilinear region of the fast current decrease) and overvoltage associated with precipitation of lithium peroxide in electrode pores and with transport losses (the straight region) [5]. The values of voltage characterizing kinetic losses during oxygen reduction in accordance with [5] were determined by extrapolation of straight curve regions to the zero surface coverage by lithium peroxide (Fig. 1a).

Fig. 1b shows charging curves measured after accumulation of 11% of lithium peroxide at the different current densities. By analogy with the technique of processing discharge curves, the straight regions of the charging curves were extrapolated to their intersection with the voltage axis. Here, the U_{charge} values that corresponded to three coverages of the electrode surface by lithium peroxide were obtained for each current density. The voltage value corrected by the ohmic resistance of the deposit (U_{corr}) was determined by extrapolation of U_{charge} to $Q_{discharge} = 0$ at the given current density (inset to Fig. 1b) [5].

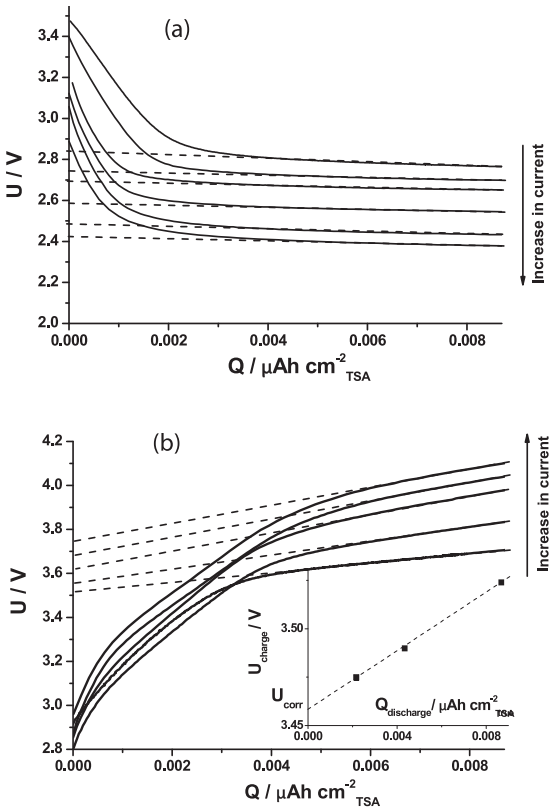

Fig. 1. Galvanostatic discharge curves (a) and charging curves (b) measured on carbon black XC-72 (electrolyte: 1M $LiClO_4$/DMSO) at the current density of 23 to 600 $\mu A\ cm^{-2}_{geom}$. The initial electrode surface coverage by lithium peroxide in the charging curve measurements was 11% of a monolayer. Inset to (b) shows: the dependence of charge voltage ($Q_{discharge}$) at a current density of 75 $\mu A\ cm^{-2}_{geom}$ plotted for determination of U_{corr} by extrapolation.

3. Results and discussion

Kinetic curves of the oxygen reaction on the XC-72 carbon black and 20Pt/XC-72 catalyst in different electrolytes are shown in Fig. 2(a, b). As can be seen, the ORR curves corresponding to the catalyst and carbon support coincide practically in every electrolyte within the measurement accuracy. The curves of the reverse process coincide in DMSO; however, the catalyst in the TEGDME medium is characterized by a smaller overvoltage than that of the carbon support in the low current density region. In TEGDME, as compared to DMSO, the cathode reaction overvoltage increases and the anode reaction overvoltage decreases for each material.

According to numerous works [1,2,5,12], the limiting step of ORR is Reaction (1). Abnormal values of ORR slopes ($> 2.3RT/\alpha F$ or 120 mV at transfer coefficient $\alpha = 0.5$) can be related to the effect of the solvent reorganization energy (solvent-salt-oxygen species interactions), which results in a decrease in the transfer coefficient of ORR [13]. The doubling of the Tafel slope at the voltage of ~2.5 V in each of the electrolytes can be due to the change in the limiting step (process (3) instead of (1)) [12].

The slopes of the OER curves in Tafel coordinates at least at low current density are approximately 120 mV, irrespective of the solvent type. These data agree well with the theoretical and experimental results obtained on a smooth carbon electrode in [5]. According to the theory of formal electrochemical kinetics, the proximity of the curve slopes to the value of 120 mV points to the limitation of the OER rate by transfer of the first electron:

$$Li_2O_2 \rightarrow LiO_2 + Li^+ + e^- \quad (5)$$

[2] Here and further, specific values are referred to the geometrical area or the true surface area (TSA) of the positive electrode. The TSA of the XC-72 carbon black was assumed to be equal to the external surface area (S^C, 155.4 $m^2\ g^{-1}$ [9]) according to the assumption of the authors of [10]. The TSA of the 20Pt/XC-72 according to the BET data approximately corresponds to that of the XC-72 carbon black (as per carbon mass).

[3] The specific charge required for deposition of a single Li_2O_2 monolayer onto the electrode surface was assumed to be 260 $\mu C\ cm^{-2}_{TSA}$ [10].

[4] It was found that the steady–state potential of lithium in 1M $LiClO_4$/TEGDME is approximately 100 mV more positive than the potential of lithium in 1M $LiClO_4$/DMSO. In order to present the obtained data in the same reference electrode scale, the values of voltage obtained in 1M $LiClO_4$/TEGDME were recalculated vs. a lithium electrode in 1M $LiClO_4$/DMSO.