

## Polycrystalline Platinum Rotating Disc Electrode Study of the Liquid System 0.2 M LiClO<sub>4</sub> -H<sub>2</sub>O-DMSO in Nitrogen and Oxygen Atmosphere

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The electrochemical reactions in the system dimethylsulphoxide (DMSO)-water with 0.2 M LiClO<sub>4</sub> added as the supporting electrolyte, saturated either by nitrogen or by oxygen, were investigated by voltammetry on polycrystalline platinum rotating disc electrode. In the water-rich composition region, the reduction of decomposition voltage was observed, which was attributed to the suppression of inhibiting effect of platinum oxide on oxygen evolution reaction. By comparing experimentally determined limiting current density of oxygen reduction reaction to the one calculated by means of Levich equation, it was confirmed that the 4e<sup>-</sup> path holds in the DMSO mole fraction region between 0 and 70 mol.%, while in the DMSO-rich region, combined effect of both the depression of reaction path toward to 1e<sup>-</sup> one, and the electrode passivation by lithium compounds, became effective.

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**Keywords:** Oxygen reduction reaction, polycrystalline Pt electrode, rotating disc, mixed solvent DMSO-H<sub>2</sub>O, voltammetry

### 1. INTRODUCTION

During several last decades, the kinetics of oxygen reduction reaction (ORR) in aqueous solutions presents a subject of extensive investigations, connected to the development of fuel cells. On platinum surface, the reduction takes place under consumption of four electrons per O<sub>2</sub> molecule, i.e. via so called 4e<sup>-</sup> pathway, yielding either water or hydroxyl ion [1,2], depending on pH of the electrolyte solution.

In aprotic electrolyte solutions, the mechanism of ORR differs from that observed in aqueous solutions [3-11]. By comparative investigations on Pt, Au and Hg electrodes in 0.1 M (Et)<sub>4</sub>NClO<sub>4</sub> in

dimethylsulphoxide (DMSO) Roberts et al. [7,8] found that the reduction of  $O_2$  molecule proceeded through two one-electron steps, yielding superoxide ( $O_2^-$ ) anion in the first step at -0.75 V vs. SCE, and peroxide ion ( $O_2^{2-}$ ) in the second one. The second charge transfer step appeared at considerably lower potential of -2.02 V vs. SCE, and it was non-feasible on Pt electrode. The kinetic parameters for the first step of reduction did not depend on the type of electrode materials. The authors determined also the diffusion coefficients of both molecular oxygen and superoxide anions in DMSO, to amount to  $D_{O_2} = 3.25 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $D_{O_2^-} = 1.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , respectively. Vasudevan et al. [9] investigated ORR in dimethylformamide (DMF), DMSO and acetonitrile (AN) on glassy carbon (GC), graphite and Pt electrode by means of the rotating disc voltammetry technique. In each of the solutions they found diffusion controlled first reduction step yielding superoxide, with the starting potential being dependent on the nature of solvent and on the nature of electrode material. Further reduction step to the peroxide anion manifested themselves as an irreversible peak at the potential more negative for even 1V. In the presence of moisture or other protic compounds, superoxide ion lost the stability, and thus ORR proceeded directly to peroxide anion under consumption of two electrons per  $O_2$  molecule [5,8, 9,11]. Wieckowski et al. [12] studied water adsorption from DMSO solution on platinum using direct tritium radioelectrochemical method, finding that adsorption occurs in the second ad-layer of the Pt-DMSO interface.

Laoire et al. [13] investigated the influence of the nature of supporting electrolyte on ORR in various solvents: DMSO, AN, dimethoxyethane (DME) and tetraethylene glycol dimethylether (TEGDME). The authors claimed that in the solutions with tetrabutyl ammonium ions ( $TBA^+$ ) the oxygen reduction reaction occurred as a reversible  $1e^-$  process, yielding superoxide ions, while in the electrolyte solutions based on lithium salts, the reduction reaction proceeded as multistep process yielding the species  $O_2^-$ ,  $O_2^{2-}$  and  $O^{2-}$ .

In a completely miscible binary solvent system, by changing the solvent mole ratio, one can change continuously the physico-chemical characteristic of the solution. For liquid binary system  $H_2O$ -DMSO many characteristics were published, for instance, heat of mixing [14], viscosity [14-18], density [14,18], phase diagram [19], sound velocity [20] and spectrochemical characteristics [21,22]. The investigations indicated a strong intermolecular interaction leading to a stable hydrate of the composition  $DMSO \cdot 3H_2O$  [6].

The kinetics of ORR in the studies published thus far was modified exclusively by use of heterogeneous, primarily platinum based, catalysts and temperature [1,2]. The use of two miscible solvents was limited to a high prevalence of one of them, i.e. to the presence of the other one at impurity level [5-11]. The one of the rare papers considering the ORR in mixed solvent electrolyte under wide variation of solvent mole ratios is that by Fujinaga et al. [23]. They investigated ORR in 0.1 M  $Et_4NClO_4$  in  $H_2O$ -DMSO saturated by air, by means of voltammetry on dropping mercury electrode. The other similar study we found in the literature relates to the acetonitrile-water mixtures [24]

In this work we reexamined the Fujinaga's work [23] about ORR in mixed  $H_2O$ -DMSO solvent with 0.2M  $LiClO_4$  supporting electrolyte, using platinum instead of mercury as electrode material, and rotating disc technique instead of polarography. The reason to use platinum as electrode material is its contemporary importance in ORR catalysis. Enlarged solubility of oxygen in aprotic solvents [23] and

in aprotic solvent/water systems [24], as a potential benefit for the rate of ORR, present an additionally encouragement of such investigations. The solvent system H<sub>2</sub>O-DMSO is suitable because it was widely investigated from the aspects of the characteristics necessary for the use of Levich equation, such as densities and viscosities [14,18], oxygen solubility and diffusion coefficients [23]. First series of measurements emphasized the voltammetry in inert atmosphere, in order to examine the voltage window of electrochemical stability of electrolyte solutions, and the second series of measurements related to the voltammetry in oxygen saturated solutions, in order to investigate the ORR in this mixed solvent electrolyte.

## 2. EXPERIMENTAL

Commercially wet stock samples of DMSO (Carlo Erba, p.a.) and LiClO<sub>4</sub> (Merck, p.a.) were used as purchased. The content of moisture was determined by Karl Fischer method, and accounted for during solutions preparation. In normal bottles of 50 ml the amount of LiClO<sub>4</sub> needed to obtain 0.2 M solution, and water and DMSO in required mole ratios were added. The initial wetness of chemicals limited the highest content of DMSO to amount to 93 mol.%. The other solution contained 78, 56, 27, 6 and 0 mol.% of DMSO.

For electrochemical investigations, a three-electrode cell connected to the PAR Model 273 potentiostat/galvanostat was used. Polycrystalline platinum rotating disc electrode driven by a PINE rotator as working electrode, wide Pt foil as counter electrode, and saturated calomel electrode (SCE) as reference one, were used. Working temperature was kept at 25 °C. A series of voltammograms was performed under nitrogen atmosphere (99.9995 vol.% N<sub>2</sub>) and the other one was performed under conditions of oxygen saturation (99.9995 vol.% O<sub>2</sub>).

## 3. RESULTS AND DISCUSSION

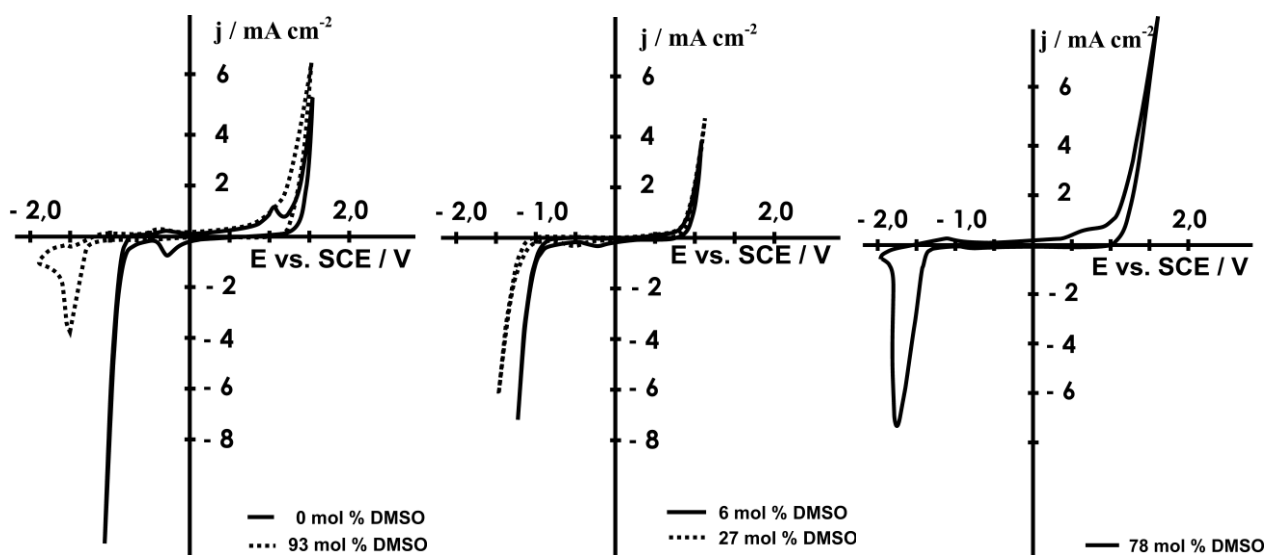
### 3.1. Voltammograms in inert atmosphere

In order to examine the voltage window of electrochemical inertness of the electrolyte solutions on platinum electrode, first a series of voltammograms in inert atmosphere was recorded, by blowing the nitrogen stream through the electrolyte cell. In Fig. 1 the corresponding voltammograms are shown. In water containing solutions, the decomposition voltage is determined by the appearance of the currents of hydrogen and oxygen evolution. The decomposition voltages presented in in Table I are determined by the extrapolation of the linear parts of currents densities, from the region of high currents to the intersection with potential axis, and thus contain the sum of equilibrium decomposition voltage and both cathodic and anodic kinetic overvoltages. Having in mind that kinetic overvoltage of hydrogen evolution on platinum is much lower than the one for oxygen evolution, one may consider the data in Table 1 as the potentials of oxygen evolution expressed versus the equilibrium potential of hydrogen electrode in the same solution.

**Table 1.** The decomposition voltage (V) of DMSO - H<sub>2</sub>O mixtures with 0.2 M LiClO<sub>4</sub> supporting electrolyte on polycrystalline Pt electrode for different mole fractions (mol %) of DMSO.

Mol. % DMSO	V
0	2.25
6	1.93
27	2.11
56	2.35
78	2.57
93	2.57

In the DMSO-free solution, within the decomposition voltage window, one may perceive anodic and cathodic current peaks, which, as well known, correspond to the formation and reduction of platinum surface oxides (Fig. 1, left). In DMSO containing solutions these peaks are almost completely absent. To explain the absence of oxide formation, one may recall an old paper by Krtić et al. [25], where the authors evidenced by IR spectroscopy examinations a strong adsorption of DMSO molecules from DMSO-water solutions on Pt surface.

**Figure 1.** The voltammograms of 0.2 M LiClO<sub>4</sub> in DMSO + H<sub>2</sub>O mixtures on polycrystalline Pt disc electrode in inert atmosphere at rotation rate 10 revolutions per second (rps) and scan rate 50 mVs<sup>-1</sup> at 25 °C. The insets designate the mole fraction of DMSO in solution mixtures

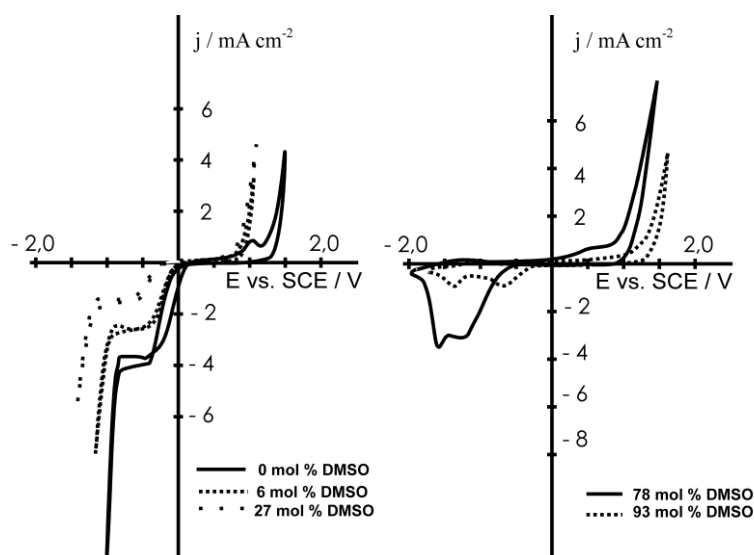
We may conclude that DMSO adsorption prevents the anodic passivation of platinum arising from oxide formation. In recent studies by Srejić et al. [26] and Smiljanić et al. [27], similar inhibition of Pt oxide formation was evidenced in water solutions containing acetonitrile. Since Pt oxide inhibits oxygen evolution, one may expect that the prevention of its formation, might reduce the overvoltage of oxygen evolution under condition that DMSO acts as a weaker inhibitor of oxygen evolution in comparison to platinum oxide. It appears that the experiments support such assumptions, since,

obviously, the decomposition voltage experiences a rapid decrease upon addition of DMSO to the fractions 6 and 27 mol %. Further increase in DMSO content above 27 % causes the increase in decomposition voltage, which may be simply a thermodynamic consequence of decreasing activity of water with the decrease of its mole fraction.

In the solution with 93 mol.% DMSO, the electrochemical processes follow those described in ref. [28] for DMSO with LiCl as supporting electrolyte. Namely while dry solution of 1M LiCl in DMSO displayed high inertness on Pt electrode, enabling cathodic deposition of metallic Li at -3.3 V vs. SCE, the presence of water, even at a trace level, caused almost complete passivation of the cathodic processes. The passivation was visible as a passivation peak at approx. -1.3 V vs. SCE, and such behavior retained with the increase of H<sub>2</sub>O mole fraction up to 30 %. After Aurbach et al. [29,30] cathodic passivation originated from the deposition of lithium oxide as an slight soluble compound, arising through the reaction of Li ions with the cathodic products of H<sub>2</sub>O, O<sub>2</sub> and CO<sub>2</sub>.

On the DMSO-rich side of the H<sub>2</sub>O-DMSO solution system, Krtil et al. evidenced the evolution of sulfone during the progress of anodic polarization [25]. Simultaneous sulfone production and oxygen evolution may be responsible for anodic current limiting anodic polarization in DMSO-rich region of solvent compositions, passing progressively into pure oxygen evolution in water-rich solutions.

### 3.2. Voltammograms in oxygen saturated solutions



**Figure 2.** The voltammograms of polycrystalline Pt rotating disc electrode in oxygen saturated 0.2M LiClO<sub>4</sub> in DMSO- H<sub>2</sub>O mixtures at 25 °C.; rotation rate 10 rps, scan rate 50 mV s<sup>-1</sup>. The insets designate the mole fraction of DMSO in solution mixtures.

If oxygen was blown through the solution 0.2 M LiClO<sub>4</sub> in DMSO-H<sub>2</sub>O mixtures, to the voltammograms shown in Fig. 1, the currents of oxygen reduction were superposed, as shown in Fig. 2. Since the rotation rate was kept constant, 10 rps, the height of current waves depended on other factors, such as oxygen solubility, diffusion coefficients and kinematic viscosity. Fig. 2 demonstrates

the decrease of cathodic current plateau with the increase of mole fraction of DMSO. For pure water solution, the current plateau belongs doubtless to the limiting diffusion current of oxygen reduction, and its magnitude corresponds to the already published literature values [2]. Up to the mole ratio of DMSO of 27 mol.%, hydrogen evolution limited the cathodic polarization. However, at higher mole fractions of DMSO, passivation processes became visible, enabling the extension of cathodic polarization beyond the limits stated by hydrogen evolution.

In order to examine to which mole fraction of DMSO the experimentally determined limiting currents, readable in Fig. 2, present the limiting diffusion currents of ORR, the calculation of diffusion currents was performed according to the Levich equation:

$$j_l = 0.62 n F A D^{2/3} \omega^{1/2} \nu^{-1/6} C \quad (1)$$

where is  $n$  – number of electrons per one  $O_2$  molecule,  $F$  – Faraday constant,  $A$  – electrode surface area,  $D$  – diffusion coefficient of molecular oxygen,  $\omega$  – angular electrode rate,  $\nu$  – kinematic viscosity of the solution, and  $C$  – the concentration of dissolved oxygen in saturated solution.

The values required for this calculation were sampled from the literature reports and presented in Table 2. The densities and viscosities of DMSO- $H_2O$  solutions were obtained by interpolation of the data published in the reference [18], (which are practically identical to the ones reported in ref [14]). The solubility and diffusion coefficients of oxygen, observed in 0.1M  $Et_4ClO_4$  in DMSO- $H_2O$  mixtures, were obtained by interpolation of the data by Fujinaga et al. [23]. Solubility of oxygen in water and aqueous electrolyte solutions was published in several references [31,32], and 1.24 mM in pure water and 1.19 mM in 0.1 M electrolyte solutions present the closest mean values.

**Table 2.** Densities ( $\rho$ ), viscosities ( $\eta$ ) and kinematic viscosities ( $\nu$ ) of DMSO- $H_2O$  solutions, diffusion coefficients ( $D_{O_2}$ ) and solubilities ( $S_{O_2}$ ) of molecular oxygen, and limiting currents of ORR, either determined experimentally ( $j_{l, exp}$ ) or calculated by means of Levich equation for  $n = 4$  ( $J_{l, calc}$ ). In the parentheses the calculated value for  $n = 1$  is presented.

DMSO /mol %	$\rho^*$ /kg m <sup>-3</sup> [18]	$\eta^*$ /Pa s [18]	$\nu \times 10^{-6}$ /m <sup>2</sup> /s	$D_{O_2} \times 10^{-9}$ /m <sup>2</sup> s <sup>-1</sup> [23]	$S_{O_2}^{**}$ /mol m <sup>-3</sup> [23]	$j_{l, exp}$ /mA cm <sup>-2</sup>	$J_{l, calc}$ /mA cm <sup>-2</sup>
0	997.1	0.00089	1.173	1,9	1.19	-3.68	-3.52
6	1024	0.00095	1.074	1,5	0.976	-2,87	-2.77
27	1083	0.00169	0.640	1,0	0.848	-1,59	-1.87
56	1098	0.0032	0.343	1,5	1.433	-2.39	-2.33
78	1098	0.00335	0.328	2,0	1.952	-3.18	-3.56
93	1096	0.0023	0.476	2,4	2.1	-0,96	-5.59
100	1095.6	0.00195	0.560	2.7	2.1		-7.01 (-1.75)

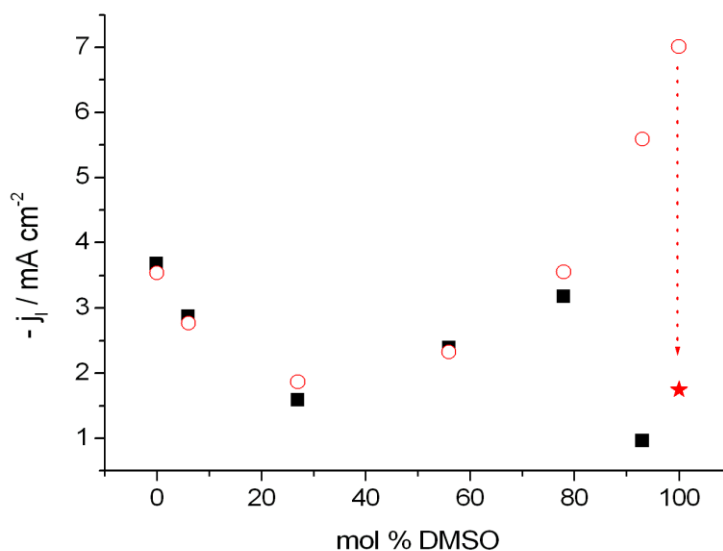
\*determined by interpolation from the literature data

\*\* calculated from the solubility determined by equilibration with air [23].

The data about the solubility of oxygen in pure DMSO are also available [8,33,34], based on coulometry in 0.1 M tetraethyl ammonium perchlorate (TEAM) solution [8], volumetric determination [33] and gas chromatography [34], and a mean value of 2.1 mM may be accepted for oxygen saturated solution. However, for solvent system DMSO-H<sub>2</sub>O, only data from the ref. [23] are available. Since density changes quite slowly, viscosity, O<sub>2</sub> solubility and diffusion coefficient influence significantly the measured current values. The viscosity has the maximum at nearly 30 % H<sub>2</sub>O [14,18], and the O<sub>2</sub> solubility has minimum at nearly 40 mol. % of H<sub>2</sub>O [23]. The change of viscosity directs a significant change of kinematic viscosity [Table 2]. Diffusion coefficient of O<sub>2</sub> in solutions with 0.1 M Et<sub>4</sub>ClO<sub>4</sub> [23] shows the minimum at 40 mol. % of H<sub>2</sub>O. The diffusion coefficient is determined assuming the number of electrons  $n = 2$  for the first step of reduction, characteristic for mercury electrode, and its change to  $n = 1$  in the mole fraction interval 30 - 0 mol.% H<sub>2</sub>O [23]. It is reasonable to assume that the literature values found for DMSO-H<sub>2</sub>O mixtures without [14,18] and with 0.1M Et<sub>4</sub>ClO<sub>4</sub> [23], thanks to high dilution, may be applied without significant error to the 0.2 LiClO<sub>4</sub> solutions studied here.

Fig. 3 shows the dependence of limiting current of ORR in function of mole fraction of DMSO in H<sub>2</sub>O-DMSO solutions with 0.2 M LiClO<sub>4</sub> supporting electrolyte, for experimentally determined values (Fig.1) compared to those calculated by means of Levich equation, under assumption of equality  $n = 4$ .

The measured values of limiting current densities, and the ones calculated by use of both the Levich equation and the literature values of diffusion coefficients determined polarographically in [23], agree well mutually up to the DMSO mole fraction of 70 %.



**Figure 3.** The dependence of limiting current of ORR on polycrystalline Pt rotating disc electrode in H<sub>2</sub>O-DMSO solutions with 0.2M LiClO<sub>4</sub> supporting electrolyte, on the mole percent of DMSO; experimental data were recorded at rotation rate 10 rps and scanning rate 50 mV s<sup>-1</sup>. The squares present experimental points, the empty circles the values calculated by means of Levich equation, assuming  $n = 4$  and rotation rate 10 rps. The star denotes calculated value for  $n = 1$ , with other parameters unchanged.

This may be taken as a confirmation that the  $4e^-$  reduction pathway is effective in this composition region. With a further rise of DMSO concentration above 70 mol.%, the experimental values deviate abruptly to lower values in comparison to calculated ones. The decrease of experimentally determined values of limiting current is faster than expected on the basis of the transition  $n = 4$  to  $n = 1$  (the last being characteristic for dry DMSO). For instance, at DMSO concentration of 93 mol.%, experimental value is even more than 6 times lower from the one calculated for  $n = 4$ . Thus one may accept the participation of electrode passivation. Namely, the oxygen reduction reaction produces hydroxyl anions, oxygen peroxide and superoxide, the last one being prevailing with the predominance of DMSO in solvent mixtures. Together with the increase of DMSO concentration, decreases the solubility of lithium oxides and hydroxides, and one may expect its passivating effects to observe at DMSO concentrations above 70 %, the more the higher the concentration [13]. The solutions containing less than 70 % DMSO one should consider as disabling the passivation effects. The passivation not only turns the limiting current below the limit expected for the lowest number of  $n$  ( $n = 1$ ), but also removes its diffusion character at all. Namely, in the solution with 93 mol % DMSO and more, the limiting current of ORR terminated to depend on the rotation rate. Since the suppressing effects to the rate of ORR come to prevalence at DMSO mole ratio 70 % and above, the potentially positive effect of increasing oxygen solubility may not be expressed in this system. This does not mean that these positive effect could not been realized in either other water-organic electrolyte system, or in the same one, by varying the experimental conditions.

#### 4. CONCLUSIONS

The system dimethyl sulphoxide-water with 0.2 M  $\text{LiClO}_4$  supporting electrolyte, saturated either by nitrogen or by oxygen, was investigated by voltammetry on polycrystalline platinum rotating disc electrode. The voltammetry in inert atmosphere evidenced an abrupt decrease of decomposition voltage in the water-rich composition region of the electrolyte solution, amounting to 1.93 V in the solution with 6 mol.% of DMSO, versus 2.25 V in the absence of DMSO. This behavior was explained by inhibition of surface platinum oxide formation on account of DMSO adsorption, which, compared to platinum oxide, should be weaker inhibitor toward oxygen evolution reaction.

Using the literature data obtained by polarography with dropping mercury electrode to analyze the experimental data obtained by voltammetry on polycrystalline platinum rotation disk electrode, it was concluded that on platinum electrode, in the limiting current density region, an unique,  $4e^-$ , pathway of ORR holds in a wide range of DMSO fractions, 0 to 70 mol.%. A decrease of experimental limiting current density of ORR that, in spite of the increase of oxygen solubility, follows the DMSO concentration increase from 70 up to 100 mol. %, is not only due to the transition  $n = 4$  to  $n = 1$ , but also due to the passivation by lithium oxides caused by their limited solubility in DMSO rich solution. Electrode passivation causes that ORR terminates to behave as a diffusion limited reaction.

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