Communication

Testing a Lithium-Oxygen (Air) Battery: Catalytic Properties of Positive Electrode Materials

Vera Bogdanovskaya [ORCID] **and Oleg Korchagin** *

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russia
* Correspondence: oleg-kor83@mail.ru

Abstract: Although research in the field of lithium-oxygen (air) batteries (LOB) is rapidly developing, few comprehensive studies on the dependence of the catalytic properties of positive electrode materials on LOB test conditions are present. In this paper, the influence of the current density, the type of oxidizer (pure oxygen or air), and a solvent in the electrolyte (DMSO or tetraglyme) on the electrocatalytic properties of PtM/CNT systems (M = Ru, Co, Cr) used as a positive electrode is investigated. It is shown that at a current density of 500 mA/g, more pronounced catalytic effects are observed during the LOB operation than that at 200 mA/g. The obtained results may be explained by the reduced adverse impact of surface passivation with lithium peroxide in the presence of catalysts compared to a similar effect when using unmodified carbon nanotubes (CNT). It is established that the influence of the current density on the catalytic properties continues upon the transition from oxygen to air as an oxidizer. When studying the effect of electrolytes on the catalytic properties of materials subjected to long-term LOB cycling, it is shown that the catalytic effects are most prominent when charged in a tetraglyme medium. Although using a catalyst has practically no effect on the number of cycles for both electrolytes, LOB having tetraglyme exceeds the cyclability of LOB having DMSO.

Keywords: lithium-oxygen (air) battery; oxygen reduction reaction catalysis; oxygen evolution reaction catalysis; carbon nanotubes; nonaqueous electrolytes

1. Introduction

Lithium-oxygen (air) battery (LOB) comprises a promising lithium power source of high power density that exceeds the characteristics of most known batteries [1]. For the past 10–15 years, the number of studies devoted to various issues of LOB development has been increasing, including the synthesis of positive electrode materials; electrolyte optimization along with the selection of salt and solvent; the improvement of the corrosion resistance of lithium electrode; transition from pure oxygen to air as an oxidizer. Since it is essential to ensure the stable functioning of lithium, primarily electrolytes based on aprotic solvents are used for LOB. Here, optimizing the structure of a positive electrode is of critical importance for establishing a functional LOB, since voltage losses during its operation are mainly associated with oxygen reduction and evolution reactions [2]. When discharging the LOB having an aprotic electrolyte, a two-electron oxygen reduction reaction (ORR) occurs on a positive electrode, which in the simplest case can be described by the following sequence of stages [3]:

$$O_2 + \bar{e} \rightarrow O_2^- \text{ (superoxide anion)} \tag{1}$$

$$O_2^- + Li^+ \rightarrow LiO_2 \text{ (lithium superoxide)} \tag{2}$$

$$2\, LiO_2 \rightarrow Li_2O_2 + O_2 \tag{3}$$

$$LiO_2 + \bar{e} + Li^+ \rightarrow Li_2O_2 \tag{4}$$

When charged, the reverse process takes place, namely the oxygen evolution reaction (OER):

$$Li_2O_2 \rightarrow 2Li^+ + O_2 + 2\bar{e} \tag{5}$$

Upon discharging the LOB, the potential as well as voltage drop of the positive electrode occurs, due to a number of interrelated factors: high overvoltage of electrochemical stages (1, 4); the reduction in the active surface due to the deposition of insoluble lithium peroxide (Li_2O_2), having extremely low electrical conductivity [4]; diffusion limitations related to both the properties of the used electrolyte and partially blocked surface due to the deposition of Li_2O_2. The first two factors cause an increase in the charge transfer resistance across the electrode/electrolyte and Li_2O_2/catalyst interfaces. The effect of diffusion limitations is most pronounced at a high coverage of the positive electrode surface with lithium peroxide. This leads to a sharper decrease in voltage than in the initial region of the discharge, where the losses associated with the overvoltage of electrochemical reactions predominate. The charging process is associated with a sharp increase in voltage due to the slow solid-state oxidation of Li_2O_2, as well as diffusion limitations on the removal of released oxygen from the reaction zone. With a long stay of the LOB in conditions of high charge voltage, side processes of degradation of the active material of the positive electrode and electrolyte components may occur. This reduces the reversibility of cycling and limits the lifetime of the LOB. Thus, the requirement to ensure minimum discharge and charge overvoltage when designing the LOB positive electrode architecture has at least two goals. First, an increase in the energy efficiency of the functioning of the LOB. Secondly, an increase in the reversibility of the discharge/charge and, as a consequence, the cyclability of the LOB. To achieve these goals, it is necessary first of all to develop an optimal active material for the positive electrode of the LOB. The active material should exhibit optimal pore structure and surface area for the accumulation of lithium peroxide, on the one hand, and catalytic properties in both ORR and OER, on the other hand.

The characteristics of catalysts for the LOB positive electrode largely depend on the synthesis methods and test conditions, complicating comparisons between catalysts having similar compositions synthesized by different authors. Furthermore, the analysis of the activity of carbon materials and catalysts based on platinum metals (Pt, Pd, Ru) within one work, as a rule, demonstrates the advantage of catalysts, particularly, during LOB charging [5,6]. According to Tripachev et al. [6], binary catalytic systems (PtRu/C, PdRu/C) ensure better reversibility of lithium peroxide formation than that of XC-72 carbon black and monometallic Pd/C and Ru/C. An efficient bifunctional PtAu/C catalyst was proposed by Lu et al. [7], where Au ensures its high activity in ORR along with Pt accelerating the reverse process. In work [8], by means of density functional theory (DFT) calculations, it was shown that using a CoPt/C catalyst for a LOB positive electrode can reduce the overvoltage of ORR and OER. The first effect is attributed to an increase in the binding energy of lithium to adsorbed LiO_2 during discharge (Reaction (4)), while the low overvoltage of OER is driven by reduced adsorption energy of LiO_2 on the CoPt/C surface. The results of these calculations were subsequently confirmed by experimental data [9,10], which showed the efficiency of PtCo/C catalysts having various compositions during LOB discharge and charge.

The characteristics of the LOB (discharge capacity, cyclability, and discharge and charge voltages) depend on its operation conditions. Although the electrochemical testing conditions (values of current density and discharge and charge cutoff voltages), oxidizer (oxygen or air), and the electrolyte composition play an essential role, the dependence of the catalytic properties of positive electrode materials on the LOB test conditions within one work is still lacking in the literature. The works [11–13] can be noted as an exception. However, F.S. Gittleson et al. [11] considered only the effect of the nature of the solvent (DMSO or tetraglyme) on the characteristics of Pt/C, Pd/C, and Au/C monometallic catalysts at a fixed LCA discharge/charge current (50 μA). Studies of the electrochemical characteristics of PdCu/Ketjen Black carbon (KB) (EC600D) [12] and Pt/carbon nanofibers [13] catalytic systems included measurements of single charge-discharge curves at various current densities (100, 200, 500, 1000 mA/g). At the same time, similar experiments were not carried out

for the corresponding carbon carriers. To the best of our knowledge, there are no works in the literature that would compare the catalytic effects observed during the operation of a LOB in pure oxygen and air atmospheres.

In this work, the efficiency of binary PtM/C (M = Ru, Co, Cr) catalysts in comparison with that of carbon support (carbon nanotubes (CNT)) under various LOB discharge/charge current density, the use of pure oxygen and air, as well as electrolytes based on DMSO and tetraglyme (TEGDME), were investigated, in order to determine the directions for more detailed research on the optimization of positive electrode materials and LOB operation conditions.

2. Results and Discussion

In this paper, the influence of a number of factors (the current density of LOB discharge/charge, the type of an oxidizer (pure oxygen or air), the solvent in the electrolyte (DMSO or TEGDME) on the electrocatalytic properties of PtM/CNT systems is investigated.

Figure 1 shows the discharge-charge curves of LOB based on PtRu/CNT, PtCr/CNT catalysts, and CNT support, obtained in an atmosphere of pure oxygen at current densities of 200 and 500 mA/g using 1M $LiClO_4$/TEGDME as an electrolyte. As can be seen, the nature of the catalytic effects, evidenced by a decrease in the charge voltage or an increase in the discharge capacity, depends on the current density. At 200 mA/g, the discharge capacity of the LOB having CNT exceeds the characteristics of the LOB having catalysts, while, during charging, minor advantage of catalysts over CNT is observed. At 500 mA/g, the capacity increases upon the transition from CNT to catalysts. The decrease in charge voltage is more pronounced at 500 mA/g than at 200 mA/g when using catalysts, rather than CNT.

The obtained data shows that at a low current density, the critical factor limiting the LOB capacity lies in a decrease in the volume and/or diameter of the pores as a result of structural changes of the CNT during the formation of a catalyst. With an increase in current density from 200 mA/g to 500 mA/g, the LOB discharge capacity (and, accordingly, the amount of formed Li_2O_2) decreases by 1.5 times for catalysts and over 3 times for CNT. On the one hand, this can be explained by an increase in the resistance of the electrolyte and transport limitations on oxygen delivery; on the other hand, by the deposition of a more compact Li_2O_2 precipitate having a smaller crystallite size at a higher current density as shown in the work [14]. The latter effect facilitates the passivation of a positive electrode during discharge at 500 mA/g in comparison with the discharge at 200 mA/g. Using mathematical modeling, Albertus et al. showed [4] that the influence of the passivation of a positive electrode surface by oxygen reduction products on the nature of the LOB discharge curve exceeds that of oxygen transport limitations. On the basis of these data, an increase in the LOB discharge capacity observed in this work at a current of 500 mA/g in the presence of catalysts can be explained by a decrease in the surface passivation compared to non-modified CNT. This assumption is indirectly confirmed in the work [15], where a dense lithium peroxide precipitate is formed on the PtRu/Super P catalyst having better adhesion to the surface of the active material than that of a looser precipitate formed on Super P carbon black. Such a variation in the Li_2O_2 structure in the presence of a catalyst, in the authors' opinion, leads to a decrease in contact resistance at the Li_2O_2/positive electrode boundary, resulting in reduced voltage losses during the LOB operation.

In Figure 2, the values of the discharge capacity of the LOB having CNT and PtCr/CNT obtained in air and oxygen atmospheres at 200 and 500 mA/g are compared. It should be noted that the nature of the differences between the properties of the catalyst and support retains when using air as an oxidizer. At 200 mA/g, a high LOB discharge capacity is achieved for CNT, while, at 500 mA/g, an advantage of the catalyst is observed. Here, the transition from oxygen to air leads to a decrease in the discharge capacity by almost 7 times at a current density of 200 mA/g. At a current density of 500 mA/g, a similar transition is accompanied only by a 2-fold decrease in capacitance. These results agree with the conclusion that oxygen transport limitation has less effect on the LOB discharge process than that of lithium peroxide passivation of the electrode, which is most pronounced at

500 mA/g. This effect largely depends on the mechanism of lithium peroxide formation. At a current density of 500 mA/g, lithium peroxide is formed on the surface of the electrode, hence a denser insulating film, while, at a current density of 200 mA/g, the process allegedly occurs in solution.
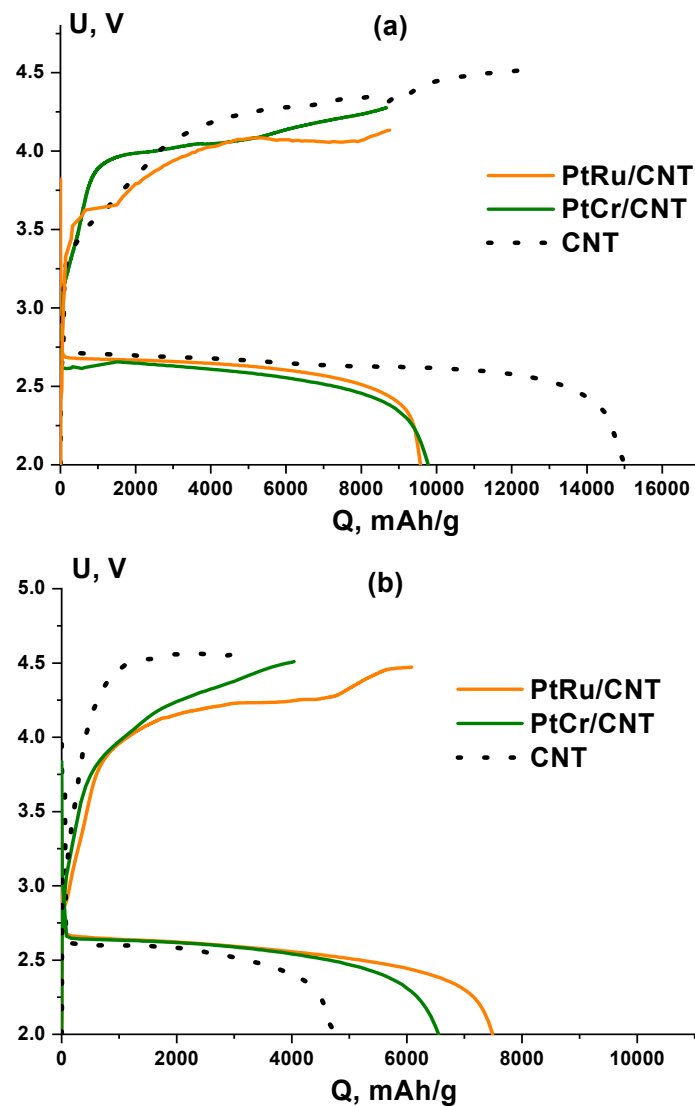

Figure 1. Discharge-charge curves of LOB obtained in an atmosphere of pure oxygen at current densities of 200 mA/g (**a**) and 500 mA/g (**b**) using various materials in the positive electrode. 1M LiClO$_4$/TEGDME.
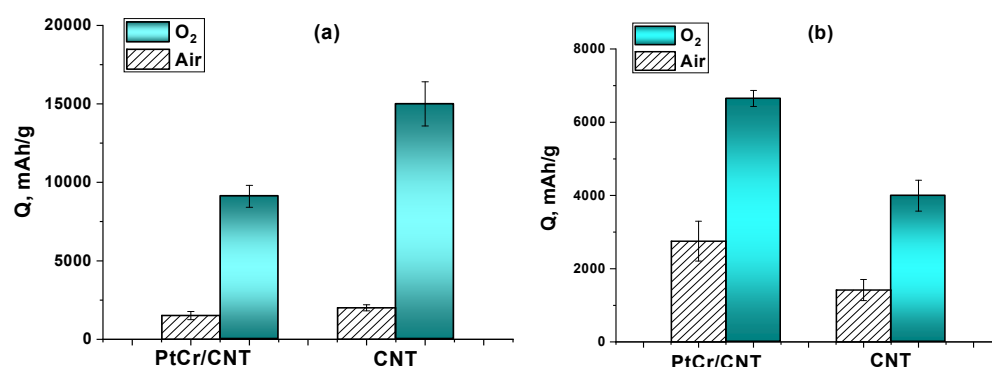
Figure 2. The discharge capacity of LOB based on PtCr/CNT and CNT measured at 200 mA/g (**a**) and 500 mA/g (**b**) in atmospheres of pure oxygen and air. The capacity values are presented with mean square deviation (according to the data of three experiments). 1M $LiClO_4$/TEGDME.

The environment in which the electrochemical reaction proceeds has a significant influence on the characteristics of the active materials. In an aprotic solvent having a low donor number (for example, TEGDME, DN = 16.6 [16]), ORR is accompanied by the formation of adsorbed lithium superoxide (Reaction (2)), which can further disproportionate (Reaction (3)) or be electrochemically reduced (Reaction (4)) to peroxide. As a result, a dense Li_2O_2 precipitate is formed, which quickly blocks the active surface of the electrode. Unlike in solvents having a high donor number (for example, DMSO, DN = 29.8 [17]), the superoxide ion is stabilized in the solution phase by Reaction (1) (the mechanism of homogeneous catalysis [16]). In this case, Li_2O_2 forms a bulk (toroidal) porous precipitate. Usually, this allows a higher amount of Li_2O_2 during LOB discharge to be accumulated and, accordingly, a capacity higher in solvents having high DN than that in solvents having low DN to be obtained [18].

As shown in Figure 3, during the transition from TEGDME to DMSO, the LOB discharge capacity increases for all studied materials.

In addition, in the case of using a catalyst, the increase rate of capacity is higher than that for the CNT (50 and 10%, respectively). As discussed above, when charging LOB in TEGDME, lower overvoltage of the process is achieved by using the catalyst than that using CNT (Figures 1 and 3a). The external surface area of active materials (In a DMSO medium, the LOB charge voltages align for the CNT and catalyst. Following the obtained results and available literature data [16], it can be assumed that for the homogeneous ORR in a DMSO medium (in solution), the dependence of the process kinetics on the external surface area (S_{ext}) value decreases, resulting in the near capacity values for the LOB based on the CNT and catalyst. S_{ext} comprises an important characteristic that determines their capacity to accumulate lithium peroxide during the LOB discharge [19]. The S_{ext} value is defined by the total BET surface area, excluding the surface area of micropores (pores having a diameter of ≤ 2 nm). Since a loose precipitate Li_2O_2 is formed in a medium having high DN, the influence of the catalyst on the kinetics of its dissolution is weakened, which causes the alignment of the LOB charge curves for CNT and PtCo/CNT at 200 mA/g (Figure 3b). In the TEGDME medium, the ORR proceeds through the formation of the adsorbed LiO_2 form followed by the formation of a dense peroxide precipitate, which leads to a decrease in the discharge capacity of the LOB based on a catalyst having a lower S_{ext} than that of CNT. On the other hand, such a Li_2O_2 structure promotes the catalytic properties of the positive electrode material during the LOB charging, which is expressed in a decrease in the charge voltage during the transition from CNT to PtCo/CNT (Figure 3a). When moving from a current density of 200 mA/g to 500 mA/g in a DMSO medium, the advantage of CNT over PtCo/CNT somewhat decreases (Figure 3c). At the same time, the catalyst provides a lower voltage than CNT, at least in the initial charge region at a current density of 500 mA/g. These data may indicate an increase in the fraction of ORR that occurs with the formation of a dense precipitate of lithium peroxide in DMSO with an increase in current

density, which causes an increase in the effect of the catalyst on the process. On the other hand, as follows from a comparison of Figures 1b and 3c, at 500 mA/g, the catalytic effects in TEGDME are more pronounced than in DMSO.
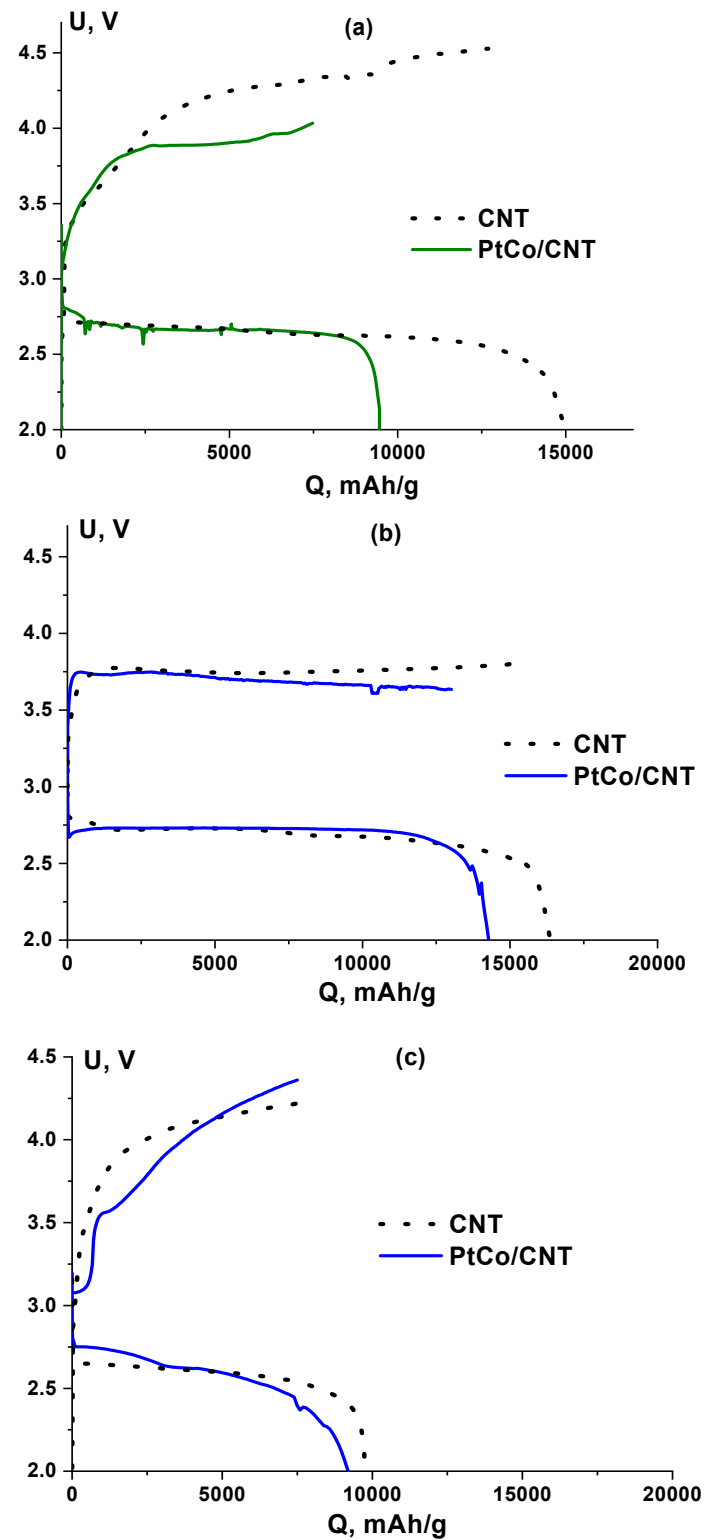

Figure 3. Discharge-charge curves of LOB obtained in an atmosphere of pure oxygen in 1M LiClO$_4$/TEGDME at 200 mA/g (**a**) and in 1M LiClO$_4$/DMSO at 200 mA/g (**b**) and 500 mA/g (**c**).

The results of cycling under limited discharge capacity of the LOB based on CNT and PtCo/CNT in DMSO and TEGDME media are shown in Figure 4. The duration of the charge in each cycle corresponded to that of the discharge. Similar to single cycles (Figure 3), during prolonged cycling, the influence of catalytic effects is most noticeable during charging in the TEGDME medium. At the same time, the use of a limited capacity contributes to more pronounced catalytic effects on the charge compared to similar effects observed when the LSC is charged after a full discharge to 2 V (Figure 1a). On the other hand, the positive effect of the catalyst is limited mainly to the first 50–60 cycles. It should be noted that the catalyst has no influence on cyclability; in addition, the similarity of the discharge and charge voltages for LOBs based on CNT and PtCo/CNT is mainly observed, which suggests the similarity of the mechanisms of degradation of the objects of study.
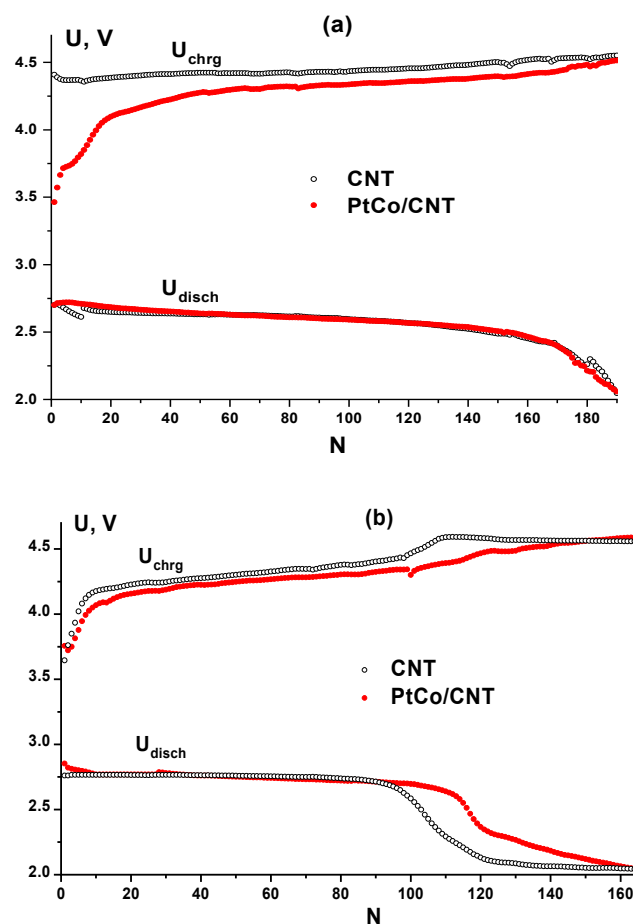

Figure 4. The dependences of discharge (U_{disch}) and charge (U_{chrg}) cutoff voltages of LOB on the cycle number. (**a**) 1M $LiClO_4$/TEGDME; (**b**) 1M $LiClO_4$/DMSO. O_2 atmosphere, discharge/charging capacity is 200 mAh/g, current density is 1C.

The cyclability of LOB having TEGDME exceeds that of having DMSO. The latter result agrees with the data described in the work [20], according to which higher reversibility of LOB cycling in a solvent having low DN (TEGDME) than that in high-DN (DMSO) is observed. This may be attributed to the formation of amorphous lithium peroxide in TEGDME, oxidized with a higher yield compared to that of the oxidation of toroidal Li_2O_2 particles formed in DMSO. In addition, lithium peroxide, as well as superoxide can react with DMSO under long-term experimental conditions [21]. LiOH comprising one of the products in these reactions remains unoxidized upon LOB charging and accumulates on the positive electrode. The described effects may reduce the cyclability of the LOB having a DMSO-based electrolyte.

3. Materials and Methods

3.1. Synthesis and Structural Characteristics of Materials

Carbon nanotubes (CNT) used as catalyst support were examined as reference material. Prior to the synthesis of catalysts, CNT were pretreated in order to functionalize their surface with oxygen-containing groups essential for dispersion of metal particles and hydrophilization. The pretreatment of CNT was carried out in a 1M NaOH solution at 100 °C for 1 h under continuous stirring. Following processing, a sample was washed using deionized water until neutral pH and dried in a vacuum oven.

Synthesis methods and structural characteristics of PtM/CNT catalysts (M = Ru, Co, Cr) were partially described elsewhere [9,22]. In all cases, H_2PtCl_6 was used as a platinum-containing precursor. The calculated platinum content in each catalyst amounted to 20 wt% at a molar ratio of Pt/M = 1/1. $Ru(OH)Cl_3$, 5,10,15,20-Tetrakis(4-methoxy-phenyl)porfirin cobalt (II) (Aldrich) (CoTMPP), and chromium phthalocyanine (CrPC) (Aldrich) were used as precursors of modifying elements (Ru, Co, Cr), respectively. The PtRu/CNT catalyst was synthesized using the low-temperature borohydride method [9]. The thermochemical synthesis of PtCo/CNT and PtCr/CNT catalysts was carried out at 600–700 °C [22].

As noted in the work [9], these synthesis methods and precursors usually lead to the formation of bimetallic alloys (solid solutions of metals). Here, according to the XPS data, platinum metal, platinum oxides, and modifying elements in the form of oxides, as well as traces of metals, are present on the surface of catalysts. Figure 5 shows the XPS data for the PtCo/CNT catalytic system. Platinum is present in metal form (binding energy of 71.2 eV) and oxides (74.2 and 75.6 eV for PtO and PtO_2, respectively). Cobalt is present mainly in the form of oxide CoO (780.4 eV).
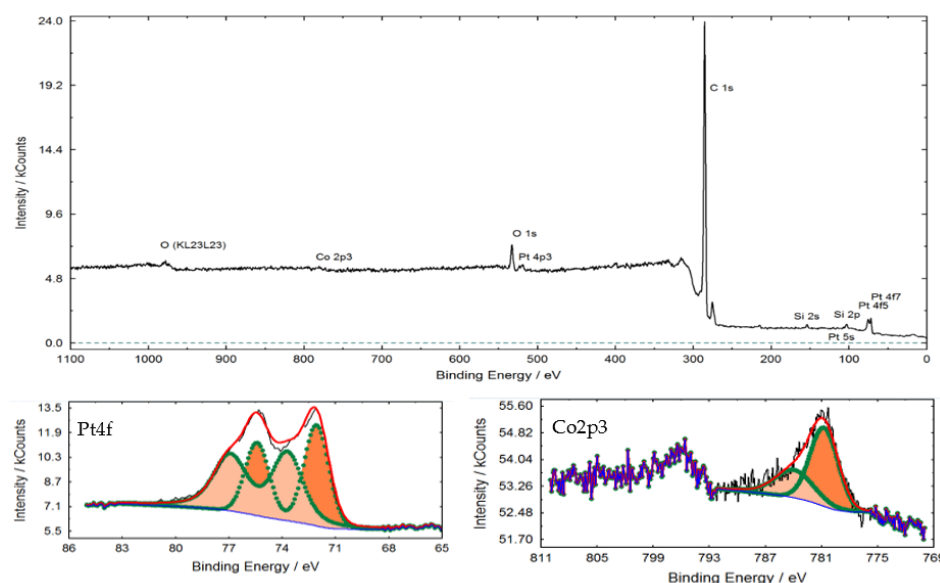

Figure 5. Overview XPS spectrum for PtCo/CNT catalyst and spectra for individual Co and Pt.

CNT following alkaline treatment are characterized by the value of S_{ext} = 293 m^2/g. The formation of the studied binary catalysts leads to a decrease in S_{ext} by 20% per mass of the carbon support [22].

3.2. Electrochemical Measurements

Electrochemical studies were carried out using Swagelok-type cells having electrodes with a diameter of 12 mm. The electrodes were formed following the procedure described earlier [9]. In brief, ~0.5 mg/cm^2 of suspension of a studied material (per CNT mass) containing a PVDF binder at a ratio of PVDF/CNT = 1/4 was applied to the surface of 39 BB gas diffusion layers (GDL). The electrodes dried for at least 12 h in a vacuum oven

at 90–95 °C were transferred to a sealed glovebox and de-aerated with argon (extra pure grade) to assemble an LOB. Lithium foil was used as a negative electrode. The electrodes were separated by two 25 μm thick Celgard membranes. The aprotic electrolyte was prepared using $LiClO_4$ salt (for batteries, dry, 99.99%) DMSO (anhydrous, ≥99.9%), and TEGDME (99%) (Sigma-Aldrich, St. Louis, MO, USA). The solvent was further dried using 3 Å molecular sieves.

Prior to the tests, the LOB cell was purged with oxygen (extra pure grade) or air drained by a liquid nitrogen trap. To estimate the maximum discharge capacity, a galvanostatic discharge curve was obtained at a current density of 210 mA/g (hereinafter, the values of current density and capacitance are given per CNT mass); the experiment was terminated upon reaching a voltage of 2 V. Cyclic tests were carried out, including the sequential discharge-charge curves recorded at a fixed capacity.

4. Conclusions

The influence of several factors on the catalytic properties of PtM/CNT (M = Ru, Co, Cr) systems in the positive electrode of a lithium-oxygen (air) battery is investigated. It is shown that the value of LOB discharge current density comprises one of the key factors. Thus, at a current density of 200 mA/g, the discharge capacity of the LOB having CNT exceeds that of the LOB having catalysts, while, at 500 mA/g, the catalysts exhibit an advantage over CNT. During charging, the most pronounced catalytic effect is observed at 500 mA/g, as well. The obtained results may be explained by the decrease in the adverse impact of surface passivation with lithium peroxide in the presence of catalysts compared with a similar effect when using unmodified CNT. At the same time, there is no noticeable effect of the nature of the modifying component (Cr, Co or Ru) on the characteristics of the LOB. When the current density changes, the parameters of various catalysts almost change. The nature of the differences between the properties of the catalyst and support retains when using air as an oxidizer. Here, the transition from oxygen to air leads to a decrease in the discharge capacity by almost 7 times at a current density of 200 mA/g. At a current density of 500 mA/g, a similar transition is accompanied by a 2-fold decrease in capacitance. The obtained results may be explained by the lower influence of oxygen transport limitations on the LOB discharge compared to that of the electrode passivation with lithium peroxide. In subsequent work, this assumption will be verified by examining the microstructure of the Li_2O_2 precipitate formed on the catalysts and carbon support at different current densities.

The influence of the electrolyte nature on the catalytic properties of PtCo/CNT system under a single LOB discharge until the maximum capacity and long-term cycling with limited capacity is investigated. For each mode, the influence of catalytic effects is most prominent during charging in a TEGDME medium. The catalyst has no influence on cyclability, while the cyclability of LOB having TEGDME exceeds that of having DMSO. The obtained data shows that investigating the effect of current density on the cycling parameters of LOB having PtM/CNT catalysts and other active materials on a positive electrode in a TEGDME medium is of practical interest.

Author Contributions: Conceptualization, O.K. and V.B.; methodology, O.K. and V.B.; investigation, O.K.; data curation, V.B.; writing—original draft preparation, O.K.; writing—review and editing, O.K. and V.B. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Additional data are available in [9,22] or upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Cao, D.; Bai, Y.; Zhang, J.; Tan, G.; Wu, C. Irreplaceable carbon boosts Li-O$_2$ batteries: From mechanism research to practical application. *Nano Energy* **2021**, *89*, 106464. [CrossRef]
2. Ma, Z.; Yuan, X.; Li, L.; Ma, Z.-F.; Wilkinson, D.P.; Zhang, L.; Zhang, J. A review of cathode materials and structures for rechargeable lithium–air batteries. *Energy Environ. Sci.* **2015**, *8*, 2144–2198. [CrossRef]
3. Laoire, C.O.; Mukerjee, S.; Abraham, K.M.; Plichta, E.J.; Hendrickson, M.A. Elucidating the mechanism of oxygen reduction for lithium-air battery applications. *Phys. Chem. C* **2009**, *113*, 20127–20134. [CrossRef]
4. Albertus, P.; Girishkumar, G.; McCloskey, B.; Sánchez-Carrera, R.S.; Kozinsky, B.; Christensen, J.; Luntz, A.C. Identifying Capacity Limitations in the Li/Oxygen Battery Using Experiments and Modeling. *J. Electrochem. Soc.* **2011**, *158*, A343–A351. [CrossRef]
5. McCloskey, B.D.; Scheffler, R.; Speidel, A.; Bethune, D.S.; Shelby, R.M.; Luntz, A.C. On the Efficacy of Electrocatalysis in Nonaqueous Li–O$_2$ Batteries. *J. Am. Chem. Soc.* **2011**, *133*, 18038–18041. [CrossRef]
6. Tripachev, O.V.; Korchagin, O.V.; Bogdanovskaya, V.A.; Tarasevich, M.R. Specific Features of the Oxygen Reaction on Catalytic Systems in Acetonitrile-Based Electrolytes. *Russ. J. Electrochem.* **2016**, *52*, 456–462. [CrossRef]
7. Lu, Y.-C.; Xu, Z.; Gasteiger, H.A.; Chen, S.; Hamad-Schifferli, K.; Shao-Horn, Y. Platinum–gold nanoparticles: A highly active bifunctional electrocatalyst for rechargeable lithium-air batteries. *J. Am. Chem. Soc.* **2010**, *132*, 12170–12171. [CrossRef]
8. Kim, H.-J.; Jung, S.C.; Han, Y.-K.; Oh, S.H. An atomic-level strategy for the design of a low overpotential catalyst for Li-O$_2$ batteries. *Nano Energy* **2015**, *13*, 679–686. [CrossRef]
9. Bogdanovskaya, V.A.; Korchagin, O.V.; Tarasevich, M.R.; Andreev, V.N.; Nizhnikovskii, E.A.; Radina, M.V.; Tripachev, O.V.; Emets, V.V. Mesoporous nanostructured materials for the positive electrode of a lithium-oxygen battery. *Prot. Met. Phys. Chem. Surf.* **2018**, *54*, 373–388. [CrossRef]
10. Xia, H.; Xie, Q.; Tian, Y.; Chen, Q.; Wen, M.; Zhang, J.; Wang, Y.; Tang, Y.; Zhang, S. High-efficient CoPt/activated functional carbon catalyst for Li-O$_2$ batteries. *Nano Energy* **2021**, *84*, 105877. [CrossRef]
11. Gittleson, F.S.; Sekol, R.C.; Doubek, G.; Linardi, M.; Taylor, A.D. Catalyst and electrolyte synergy in Li–O$_2$ batteries. *Phys. Chem. Chem. Phys.* **2014**, *16*, 3230–3237. [CrossRef] [PubMed]
12. Park, M.; Liang, C.; Lee, T.H.; Agyeman, D.A.; Yang, J.; Lau, V.W.-H.; Choi, S.-I.; Jang, H.W.; Cho, K.; Kang, Y.-M. Regulating the Catalytic Dynamics through a Crystal Structure Modulation of Bimetallic Catalyst. *Adv. Energy Mater.* **2020**, *10*, 1903225. [CrossRef]
13. Bui, H.T.; Kim, D.Y.; Kim, Y.Y.; Kim, D.W.; Suk, J.; Kang, Y. Pt Nanoparticles-Macroporous Carbon Nanofiber Free-Standing Cathode for High-Performance Li-O$_2$ Batteries. *J. Electrochem. Soc.* **2020**, *167*, 020549. [CrossRef]
14. Lau, S.; Archer, L.A. Nucleation and Growth of Lithium Peroxide in the Li–O$_2$ Battery. *Nano Lett.* **2015**, *15*, 5995–6002. [CrossRef]
15. Yang, Y.; Liu, W.; Wang, Y.; Wang, X.; Xiao, L.; Lu, J.; Zhuang, L. A PtRu catalyzed rechargeable oxygen electrode for Li–O$_2$ batteries: Performance improvement through Li$_2$O$_2$ morphology control. *Phys. Chem. Chem. Phys.* **2014**, *16*, 20618–20623. [CrossRef]
16. Abraham, K.M. Electrolyte-Directed Reactions of the Oxygen Electrode in Lithium-Air Batteries. *J. Electrochem. Soc.* **2015**, *162*, A3021–A3031. [CrossRef]
17. Laoire, C.O.; Mukerjee, S.; Abraham, K.M.; Plichta, E.J.; Hendrickson, M.A. Influence of Nonaqueous Solvents on the Electro-chemistry of Oxygen in the Rechargeable Lithium−Air Battery. *Phys. Chem. C* **2010**, *114*, 9178–9186. [CrossRef]
18. Geaney, H.; O'Dwyer, C. Examining the Role of Electrolyte and Binders in Determining Discharge Product Morphology and Cycling Performance of Carbon Cathodes in Li-O$_2$ Batteries. *J. Electrochem. Soc.* **2016**, *163*, A43–A49. [CrossRef]
19. Meini, S.; Piana, M.; Beyer, H.; Schwammlein, J.; Gasteiger, H.A. Effect of carbon surface area on first discharge capacity of Li–O$_2$ cathodes and cycle-life behavior in ether-based electrolytes. *J. Electrochem. Soc.* **2012**, *159*, A2135–A2142. [CrossRef]
20. Augustin, M.; Vullum, P.E.; Vullum-Bruer, F.; Svensson, A.M. Inside the electrode: Looking at cycling products in Li/O$_2$ batteries. *J. Power Sources* **2019**, *414*, 130–140. [CrossRef]
21. Lee, Y.J.; Kwak, W.-J.; Sun, Y.-K.; Lee, Y.J. Clarification of Solvent Effects on Discharge Products in Li–O$_2$ Batteries through a Titration Method. *ACS Appl. Mater. Interfaces* **2018**, *10*, 526–533. [CrossRef] [PubMed]
22. Bogdanovskaya, V.A.; Panchenko, N.V.; Radina, M.V.; Korchagin, O.V.; Novikov, V.T. Catalysts based on carbon nanotubes modified by N, Pt, or PtCo for oxygen reaction catalysis in nonaqueous electrolyte containing lithium ions. *Mat. Chem. Phys.* **2021**, *258*, 123856. [CrossRef]