

Behaviour of gas-diffusion electrode in various non-aqueous electrolytes for the lithium-air system

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Lithium-air batteries have recently received attention due to their high theoretical specific capacity, which is much higher than that of existing lithium-ion batteries.

This work aims to study the gas-diffusion electrode behavior in various non-aqueous electrolytes, potential candidates for use in lithium-air battery, and also its work in a semi cell against lithium metal electrode.

Gas-diffusion electrode was prepared with two catalysts – pyrolyzed CoTMPP and Active Carbon Co/Ni tested in a standard 2032 button cell. The slow cycling voltammetry (CV) of CoTMPP electrode shows irreversible O₂ reaction instead of Co/Ni electrode where the capacity of oxygen evolution reaction is about 3 times less than of the oxygen reduction reaction. Nevertheless, the obtained reversibility at slow CV, the galvanostatic cycling tests at 1 mA shows irreversibility of the process most probably to the very high polarization at that current.

Keywords: lithium-air battery, non-aqueous aprotic electrolyte, catalysts for oxygen reduction reaction, gas-diffusion electrode, cobalt tetramethoxyphenil porphirine (CoTMPP).

INTRODUCTION

The progress of humanity demands more and more energy resources, which in most cases are limited. The technological revolution led to invention of steam engine, in-exhausting engines, automobiles, fossil-fuel power plant etc., uses fossil materials as source of energy. These materials are both exhaustible and ecological polluters and lead to a global change of climate. Therefore the science community must seek new high effective electrochemical power sources, with bigger energy capacity for saving of the energy obtained by renewable resources as photovoltaic, wind power electricity, hydroelectricity etc.

Such battery could be based on the Lithium-Air electrochemical system, because of its high theoretical specific capacity (13000Wh/kg) [1] close to that of the petrol (13200 Wh/kg). This would allow applying this system in areas demanding high electricity power as electrical vehicles, mobile electronics, UPS etc.

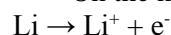
The concept of Li-air battery was introduced by researchers at Lockheed in 70s years of 20th century. They proposed aqueous alkaline solution as electrolyte but the problems relating to low

efficiency and safety problem due to the parasitic chemical reaction of Li with the water generating hydrogen led to the abandonment of this concept in the 1980s [2-5].

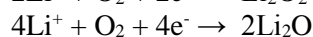
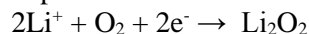
In 1996 Abraham and Jiang [6] devise a prototype of a working reverse system: Li-Air using non-aqueous aprotic electrolyte. The interest of this electrolyte is generated by its successful usage in lithium-ion batteries and will lead to the faster usage of the new system in real products.

The possible electrochemical reactions in the Lithium-Air system with non-aqueous aprotic electrolyte are done on the limit of gas-diffusion electrode (GDE) – electrolyte [3] and are as follow:

On the negative electrode



On the positive electrode



It becomes clear that the electrochemical mechanism of the reactions on the positive electrode is not totally defined and the ultimate results depend a lot from the used catalysts.

To the present moment the problems with the contemporary Lithium-Air batteries are the following:

1. Low practical energy density versus the theoretical

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2. High polarization of the air electrode during the charge-discharge cycles;
3. The oxidation of the electrolyte and the gas-diffusion electrode leads to side products (CO_2)
4. Low power density according to Li-ion
5. Battery capacity depends on the electrolyte quantity that is wetted the electrode. The low solubility and diffusion of the oxide in contemporary electrolytes also has resulted in low outcomes.
6. The metal lithium tends to transformation of dendrites leading to the necessity of using a protective layer between the metal and the electrolyte
7. Keeping of the reaction products (Li_2O , Li_2O_2);

These problems are mainly a result of the inefficiency of gas-diffusion electrode including the difficult transportation of O_2 through the pores and the more important depositing of the products of the reaction of oxygen reduction in the active layer of the electrode [7-9].

The usage of suitable catalysts could solve the biggest part of the existing problems, to improve the reaction dynamic which will lead to the diminishing of energy loss connected to polarization and also to the perspective of a reverse reaction to be done. The literature data [10, 11] pointed that the usage of bipolar catalysts can improve the oxygen reduction and the fragmentation of the ultimate products. The cobalt containing catalysts Co/Ni (Cobalt/Nickel) and CoTMPP (Co-tetramethoxyphenylporphyrin) we used in metal-air systems with water based electrolytes were checked in Li-air system in order to see the reaction kinetics and the polarization of charge/discharge cycles. Reason for this is given to us by the fact that these catalysts were explored in detail and successfully installed in the Zn-Air and Mg-Air batteries developed in IEES – BAS.

The aim of this research is to study the sustainability of the electrode gas-diffusion layer in several electrolyte solutions as well as the electrochemical behaviour of a couple different catalysts in lithium-air system with aprotic non-aqueous electrolyte.

EXPERIMENTAL

The CoTMPP-700 catalyst was especially immobilized on VS-50 for SEM and EDS investigations. The CoTMPP solution was impregnated on dispersed SiO_2 (VS50) and after drying was heated in Ar atmosphere at $700\text{ }^\circ\text{C}$. Pyrolysed CoTMPP catalyst was produced by impregnation of acetylene black with CoTMPP

solution, drying and subsequent treatment in Ar at $800\text{ }^\circ\text{C}$. During the heat treatment the CoTMPP molecule is decomposed and the pyrolysis residual products are formed in the porous structure of the carbon substrate and are responsible for the observed high electrochemical activity of the catalyst in Zn-Air system [12]. Active Carbon CoNi catalyst was prepared by impregnation of active carbon Norit NK with a solution of both Co- and Ni-acetates, drying and heat treatment in air at $300\text{ }^\circ\text{C}$. The electrodes were prepared via consecutive pressing of gas-diffusion layer and catalyst active layer.

We observe the behavior of a couple carbon materials in non-aqueous non-proton electrolytes and explore the behavior of cobalt containing catalysts Co/Ni and CoTMPP. That's why we did two types of experiments: wetting tests and basic electrochemical examinations.

Gas diffusion (GD) layer was prepared by a special technology described previously [13]. Teflonized acetylene black with PTFE content of 35% (XC-35) or 40% (XC-40) were used for preparing. The PTFE was used as binder and lyophobic agent. After the teflonizing, the material was palletized by pressing at 200 kg cm^{-2} . Thus prepared gas-diffusion layer mainly contains mesopores with sizes 20nm and 50nm and it is successfully used in our Zn-Air and Mg-Air batteries [14]. The pores size significantly influences the electrode behavior in the Li-air system and the optimal size mentioned in the literature [15-17] is also between 20 to 60nm.

We check pellets of teflonized acetylene black, carbon paper TP 0,120mm thick and also polymeric material Nafion[®] of the company Alfa Aesar 0,180mm thick for wetting in Propylene carbonate (PC)/Ethylene carbonate (EC), Dimethoxyethane (DME) and PC/Dimethyl carbonate (DMC) solvents.

A simple weight method was used for checking the porosity of the GD layer. The pellets with previously checked weight and volume were wetted in acetone for few hours. After drying of the surface the weight of the pellets was checked again. The porosity was calculated on the collected data. Mercury porosimetry method was not used due to the flexibility of the pellet which will be smashed by the pressure.

The gas diffusion electrode (GDE) was prepared by adding the mixture of catalyst and teflonized acetylene black on the one side of the pellet and a nickel grid on the other as a current collector and

for mechanic stability. The components again were pressed with 300 kg cm^{-2} .

For the electrochemical tests of gas-diffusing electrode we did a semi-cell against metal lithium electrode. The cell assembling was done in an argon glove box with less than 50 ppm moisture. A standard button cell type 2032 with five 0,2 mm holes on the can was used for this purpose. The used electrolyte was LiClO_4 solved in a solution of PC:EC – 1:1. The used separators were AGM type, the thickness of the lithium foils was 0,3mm. A layer of Parafilm® was putted on the holes of the assembled cell before taking out from the box and the cell was closed with the device for button cell 2032. Before the electrochemical research start the Parafilm® layer was removed and the open circuit voltage (OCV) was measured. Cycling voltammetry (CV) analysis was done on EcoChemie® Autolab® device and the charge-discharge cycling was carried out on a homemade galvanostatic cycling device in the voltage limits between 1,8 to 4,6 V at a constant current of 0,5 and 1 mA.

RESULTS AND DISCUSSION

The SEM images of Co/Ni catalyst incorporated on Norit NK substrate are shown on Fig. 1 where the places of EDS analysis are numbered. The Co/Ni catalyst mainly covers the surface of Norit NK particles. The results of EDS analysis are illustrated in Fig. 2. Except the presence of carbon due to the Norit NK it is evident the catalyst of Co and Ni oxides (non-stoichiometric ones). The traces of magnesium registered by EDS (Fig. 2a, b) most probably are due to some impurities in Norit NK.

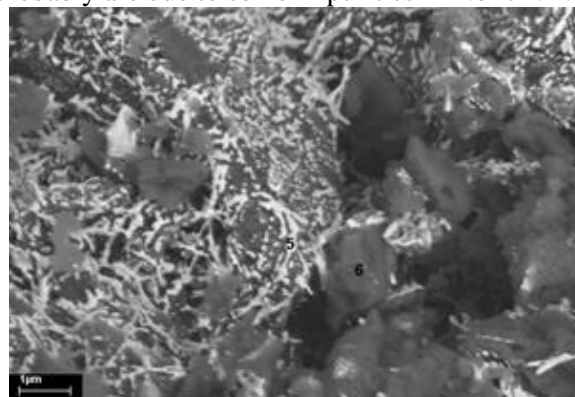
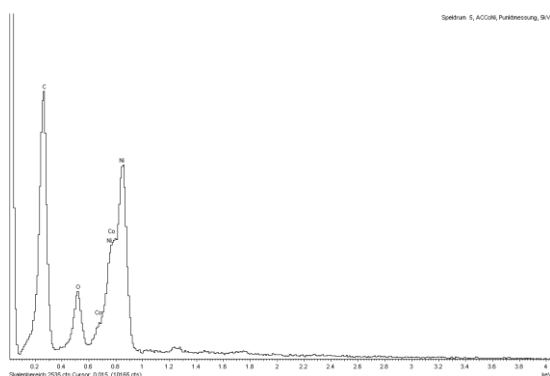
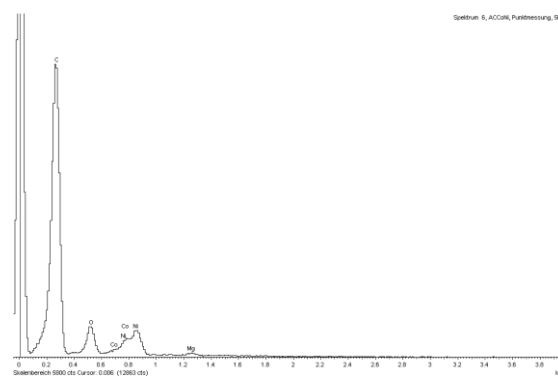


Fig. 1. SEM image of Norit NK immobilized with Co/Ni catalyst



(a)



(b)

Figure 2. EDS analysis results from points 5 (a) and 6 (b) on SEM picture (**Fig. 1**).

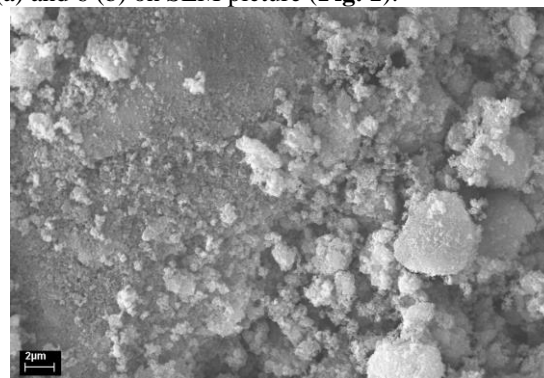
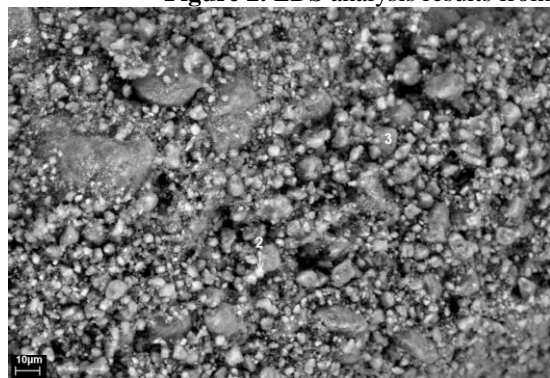


Figure 3. SEM image of CoTMPP-700 catalyst incorporated on VS-50.

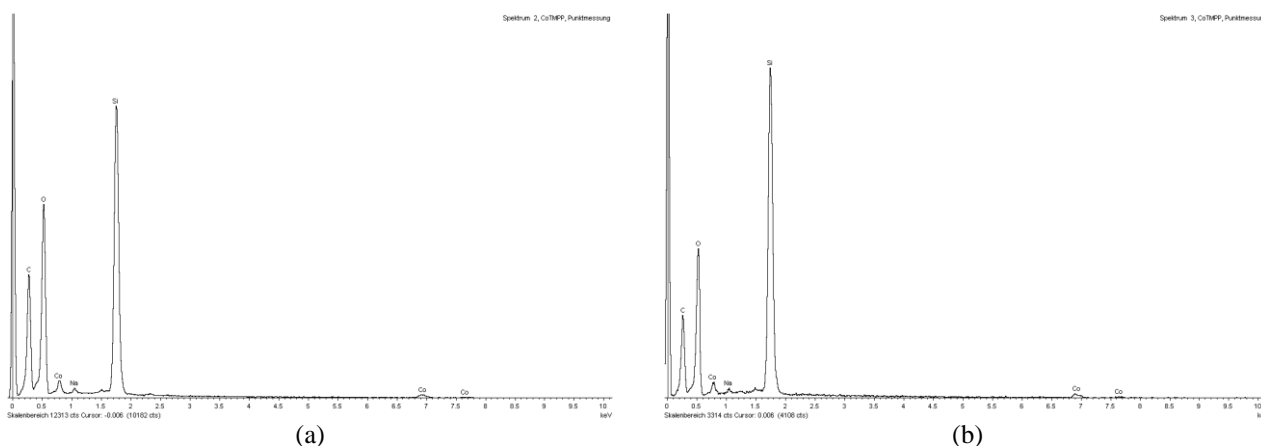


Figure 4. Results from EDS carried out in p. 2 and p. 3. (Fig.3a).

The same investigations were carried out for the other catalyst. SEM picture of CoTMPP-700 catalyst incorporated on VS-50 are shown on Fig.3. Different size of particles were obtained after the pyrolysis process which is probably due to the generation of carbon particles from CoTMPP pyrolysis and SiO₂ particles agglomeration initiated by the same process (Fig. 3a and Fig.3b).

Energy dispersion spectroscopy was applied in points 2 and 3 mentioned in Fig. 3a. The results are illustrated in Fig.4. VS-50 explained the presence of silicon while the carbon in the spectra is due to the CoTMPP pyrolysis. The choice of VS as a substrate allows us to demonstrate the carbon generation during the CoTMPP decomposition.

The registered small amount of Sodium most probably is due to the production of VS-50 which is dispersed SiO₂.

The next stage of work was to explore the wetting ability of the carbon materials XC-35, XC-40, teflonized carbon paper and Nafion® in a solution of PC/EC, a mixture of PC/DMC and pure DME. The results are listed in Table1.

The results show that all carbon materials were wetted in PC/DMC and partially wetted in PC/EC after 40 days staying. DME solvent covers only the surface of the pellets and there is not wetting in the pellet volume. Based on these results for the initial electrochemical studies we worked with EC/PC solvent because it is a widely used solvent in the Li-Ion batteries. The Nafion® membrane was swelling after a prolonged contact with the tested solvents. Probably its usage as a protect layer for the metal lithium won't be proper.

The measured porosity of the teflonized carbon pellets (35% Teflon) by the method described above is in the range 76 – 79 %.

The second part of the work was the study of the electrochemical behaviour of the GDE with both catalysts. The assembled button cells 2032 were connected to the EcoChemie Autolab® device by a button cell holder (Fig.5) for a slow voltammetry cycling. The electrodes were tested in the potential range 1,8 – 4,8V with scan rate of 50 – 70 μV/s. The tests were started from the OCV potentials: OCV_{CoNi} = 3,067V and OCV_{CoTMPP} = 3,26V.

Table1. Wetting of teflonized carbons and Nafion® membrane in different aprotic electrolyte

Material	Solvent		
	EC/PC	PC/DMC	DME
XC35* 0,7 mm	Wetted	Wetted	Wetted surface
XC40* 0,7 mm	Wetted	Wetted	Wetted surface
NAFION* 0,18 mm	Material swelling and solvent color change	Solvent color change	Material swelling and solvent color change
Carbon Paper 0,12 mm	No wetting	No wetting	No wetting



Fig. 5. Li-Air button cell 2032 and holder

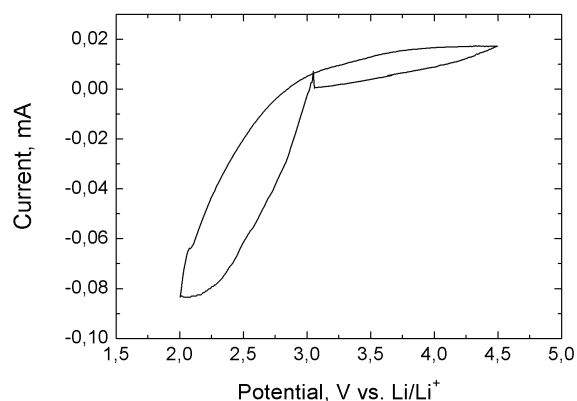


Fig. 6. Charge-discharge voltage curve for Co/Ni catalyst at 0,6mA current.

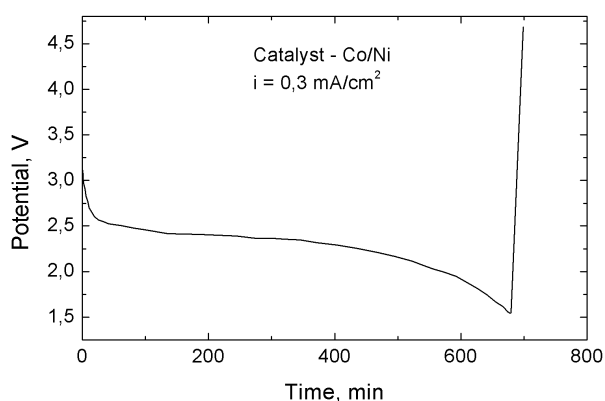


Fig. 7. Slow cycling voltage test of Co/Ni catalyst.

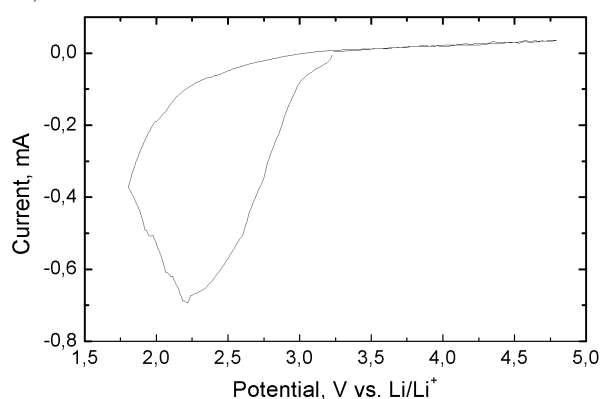


Fig. 8. Charge-discharge voltage curve for CoTMPP catalyst at 1mA current.

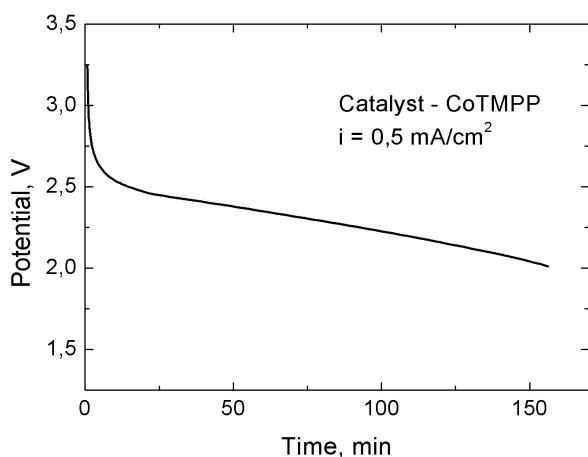


Fig. 9. Slow cycling voltage test of Co/Ni catalyst.

The obtained results from the slow CV of the electrodes with Co/Ni catalyst are shown on Fig.6. A sloping sharp voltage peak of the oxygen reduction reaction is evident. The average voltage value lies between 2.0 – 2.5 V. The obtained electrochemical capacity is 1.64 C. On the opposite side – oxygen evaluation reaction, a small broad peak between 3.1 – 3.6 V is evident. It can be concluded that this catalyst is not enough effective

for this reaction. This conclusion was confirmed from the galvanostatic tests.

The charge-discharge curve of cell with Co/Ni GDE is illustrated on Fig. 7. The electrode possesses specific capacity of 6 mAh at 0.6 mA current. A reverse reaction is not evident at this current rate.

The slow CV of the CoTMPP electrode is given on Fig. 8. A very large voltage peak was obtained for the oxygen reduction reaction with the average voltage value at 2.4 V. This means that the CoTMPP catalyst is very effective for this reaction but unfortunately this catalyst is not effective at all for the opposite oxygen evolution reaction. This is the reason to carry out only discharge galvanostatic test of the cell with CoTMPP GDE. The result is pointed out on Fig. 9. The obtained specific capacity from the electrode is 3 mAh at 1 mA current.

CONCLUSIONS

The obtained discharge capacity is respectively 3 mAh for CoTMPP and 6 mAh for Co/Ni, but this value is obtained at twice less power charge (0,5 mA) from the case of CoTMPP electrode. These

results show that the two catalysts can be used as primary Li/O₂ batteries with non-aqueous electrolyte. The cell with catalyst Co/Ni shows reversibility at the slow cycling voltammetry test, but at a charge of 1mA it is very quickly polarized to the charge voltage limit.

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ПОВЕДЕНИЕ НА ГАЗОДИФУЗИОНЕН ЕЛЕКТРОД В НЕВОДНИ ЕЛЕКТРОЛИТИ ЗА СИСТЕМАТА ЛИТИЙ-ВЪЗДУХ

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(Резюме)

Батериите литий-въздух са многообещаващи поради високият си теоретичен специфичен капацитет, който е много по-висок от съществуващите литиево-йонни батерии.

Целта на настоящата работа е да изследва поведението на газодифузионен електрод в неводни електролити за използване в системата литий-въздух, както и неговата работа в полуклетка срещу метален литиев електрод.

Газодифузионният електрод е приготвен с два вида катализатори: пиролизиран CoTMPP и активен въглен с Co/Ni и е изследван в стандартна клетка тип 2032. Цикличната волтаперометрия (CV) на електрода с катализатор CoTMPP показва необратима O₂ реакция, докато на електрода с Co/Ni катализатор беше установена обратимост на реакция – кислородна еволюция с капацитет 3 пъти по-малък от тази на кислородната редукция. Независимо от получената обратимост при бавна циклична волтаперометрия, на галваностатичните циклични тестове при 1 mA показват необратимост на процеса, който се дължи на много високата поляризация на обратната реакция в газодифузионния електрод при приложения тестов ток.