

**TARGET COMPLEX PROGRAMME FOR  
RESEARCH OF NAS UKRAINE**

*Development of scientific bases for hydrogen production, storage and use in  
autonomous energy supply systems*

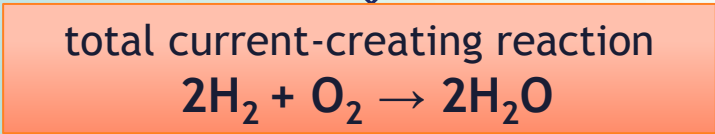
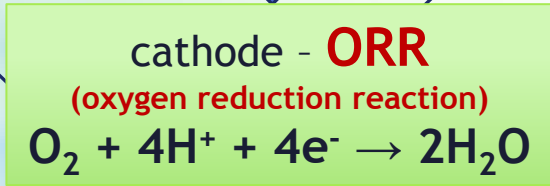
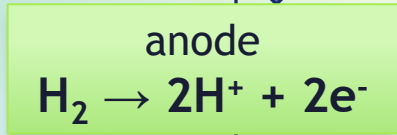
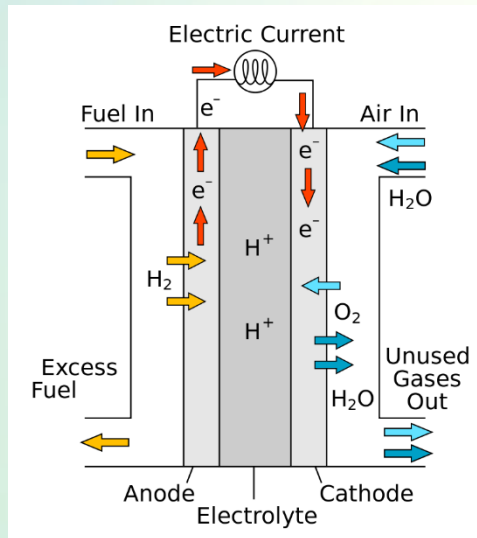
**Development of oxygen reduction hybrid electrocatalysts based on  
carbonized nanostructured organic conjugated polymers for  
hydrogen-oxygen fuel cells**

**Project 19**

**Project leaders: Prof. Vyacheslav Koshechko, Prof. Vitaly Pokhodenko  
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# Oxygen reduction reaction (ORR) - a cathode process, which is implemented in fuel cells



**Pt-electrocatalysts are considered as the most efficient in ORR, but they have disadvantages:**

<b>PtB</b> Platinum Black Catalysts	<b>PtC</b> Platinum on Vulcan / Carbon
<b>Pt Alloy</b> Platinum Alloy Catalysts	

- **high price**
- **limited resources of Pt**
- **poisoning by CO and CH<sub>3</sub>OH**

So, it is attractive to obtain highly active and stable ORR electrocatalysts, which do not contain precious metals

**Pt free Me-N-C catalysts (Me = Co and/or Fe), which are obtained via pyrolysis of various Me,N,C-contained precursors, are considered as one of the most promising alternatives to Pt-based ORR-electrocatalysts**

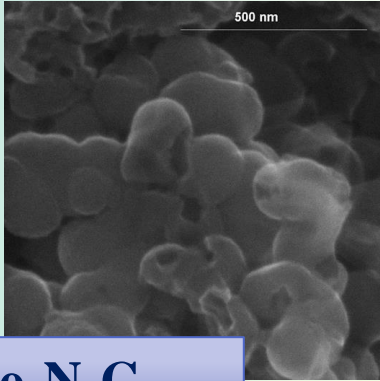
### *Purpose of the project:*

Development of carbonized cobalt- and iron-containing hybrid nanocomposites derived from nitrogen-containing conjugated polymers and of d-metal salts or Co-containing deep eutectic solvents (alone or together with nanosized carbon materials) as effective noble metals free ORR electrocatalysts for low-temperature fuel cells.

### *The main tasks of the project :*

- obtaining of new precious metals free Co(Fe)-N-C hybrid electrocatalysts for ORR, including those with nanoparticles of sulfides or phosphides Co (or Fe) in their composition, by pyrolysis of precursors based on nitrogen-containing conjugated polymers or deep eutectic solvents;
- determination of the composition, structure, basic physicochemical and functional properties of the developed electrocatalysts, as well as the mechanism of oxygen reduction on them in acidic and alkaline electrolytes;
- determination of operational parameters of laboratory model of hydrogen-oxygen fuel cell using developed electrocatalysts.

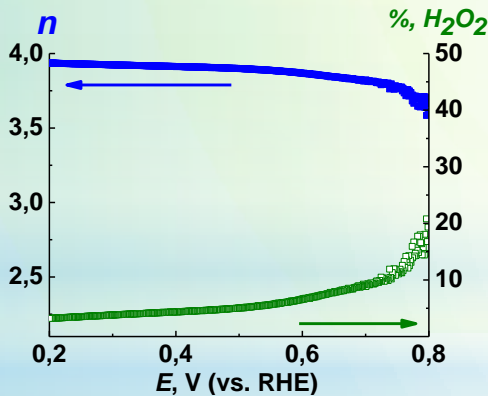
**Co<sub>9</sub>S<sub>8</sub>/Co-N-C<sub>MLG</sub> ORR electrocatalyst obtained by pyrolysis of the system 2,6-diaminopyridine (monomer)/ammonium persulfate (oxidant) (instead of pre-synthesized poly-2,6-diaminopyridine) together with multilayer graphene (MLG) and Co (II) salt**



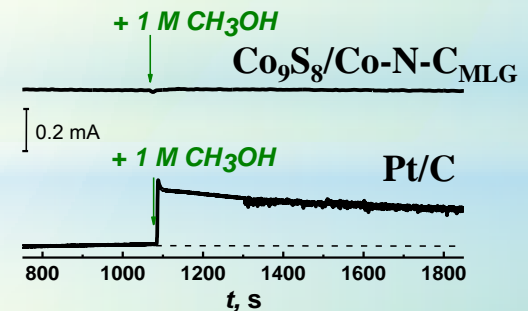
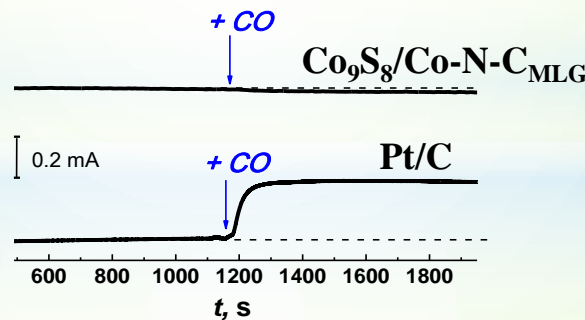
Co-N-C<sub>MLG</sub>

It was found that Co<sub>9</sub>S<sub>8</sub>/Co-N-C<sub>MLG</sub> is characterized by higher ORR activity in comparison with analogue obtained on the basis of acetylene black (Co<sub>9</sub>S<sub>8</sub>/Co-N-C), which may be due to the dominance in the composition of such catalysts of different active sites (CoN<sub>x</sub>, C/N<sub>x</sub>, Co<sub>9</sub>S<sub>8</sub>), where adsorption, activation and catalytic transformations of O<sub>2</sub> take place.

Catalyst	$E_{onset}$ mV, vs. RHE	$E_{1/2}$ mV, vs. RHE	Tafel slope, mV/dec	%H <sub>2</sub> O <sub>2</sub> %	$n$	4e%, %
0.5 M H <sub>2</sub> SO <sub>4</sub>						
Co <sub>9</sub> S <sub>8</sub> /Co-N-C <sub>MLG</sub>	775	680	71	6	3.9	94
Co <sub>9</sub> S <sub>8</sub> /Co-N-C	720	500	158	16	3.7	84

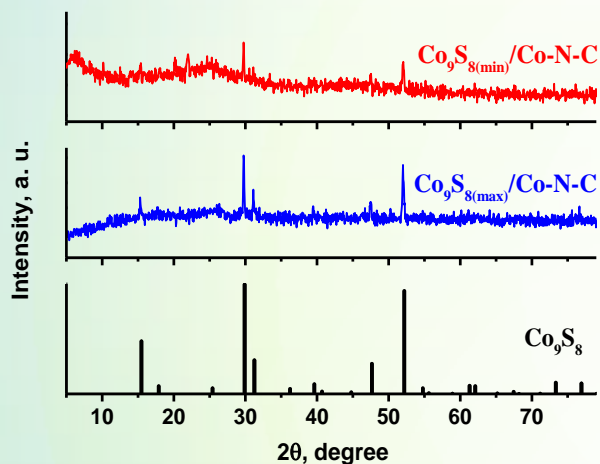


Co<sub>9</sub>S<sub>8</sub>/Co-N-C<sub>MLG</sub> is provide preferred 4e<sup>-</sup> reduction oxygen to water in 0.5 M H<sub>2</sub>SO<sub>4</sub> which was evidenced by the number of electrons ( $n$ ) and the yield of hydrogen peroxide (% H<sub>2</sub>O<sub>2</sub>).



Unlike Pt/C catalyst, Co<sub>9</sub>S<sub>8</sub>/Co-N-C<sub>MLG</sub> had is high tolerance to CO or methanol

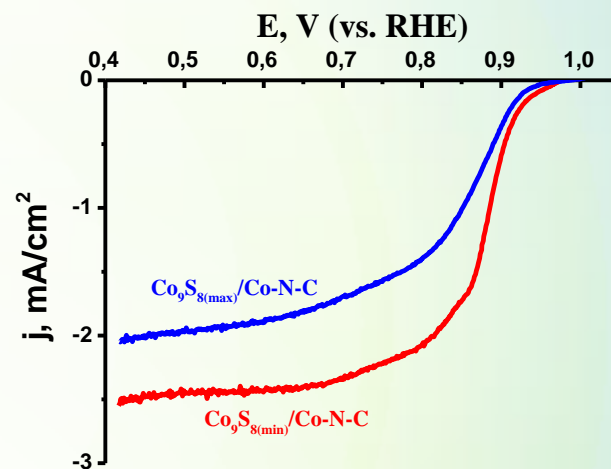
## ORR performance of $\text{Co}_9\text{S}_8/\text{Co-N-C}$ electrocatalysts with higher and lower $\text{Co}_9\text{S}_8$ content - $\text{Co}_9\text{S}_{8(\text{max})}/\text{Co-N-C}$ and $\text{Co}_9\text{S}_{8(\text{min})}/\text{Co-N-C}$



XRD-patterns of  $\text{Co}_9\text{S}_{8(\text{max})}/\text{Co-N-C}$ ,  $\text{Co}_9\text{S}_{8(\text{min})}/\text{Co-N-C}$ , and  $\text{Co}_9\text{S}_8$

Catalyst	$E_{1/2}$ , V	n	$\text{H}_2\text{O}_2\%$
$\text{Co}_9\text{S}_{8(\text{min})}/\text{Co-N-C}$	0,88	3,75	12,5
$\text{Co}_9\text{S}_{8(\text{max})}/\text{Co-N-C}$	0,87	3,50	24,7

It was found that the reduction of  $\text{Co}_9\text{S}_8$  content in the  $\text{Co}_9\text{S}_8/\text{Co-N-C}$  catalysts obtained using poly-5-aminoindole, slightly affects the values of  $E_{\text{onset}}$  and  $E_{1/2}$  in the alkaline electrolyte, but provides a higher limiting current density and lower  $\text{H}_2\text{O}_2$  yield, which may be due to either a decrease in the degree of agglomeration of sulfide particles in the composite, or greater availability of  $\text{CoN}_x$  sites, which are likely to be more active in ORR compared to  $\text{Co}_9\text{S}_8$ .



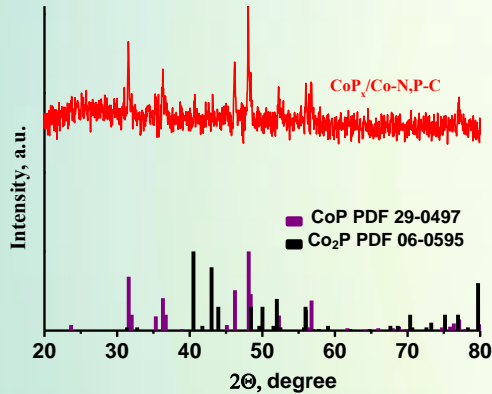
RDE polarization curves for  $\text{Co}_9\text{S}_{8(\text{max})}/\text{Co-N-C}$  and  $\text{Co}_9\text{S}_{8(\text{min})}/\text{Co-N-C}$  in an  $\text{O}_2$ -saturated 1 M NaOH; rotation rate – 1200 rpm, scanning rate –  $5 \text{ mV s}^{-1}$ .

## **New approaches to the preparation of polyaniline (PAni) derived Co-N-C electrocatalysts is proposed**

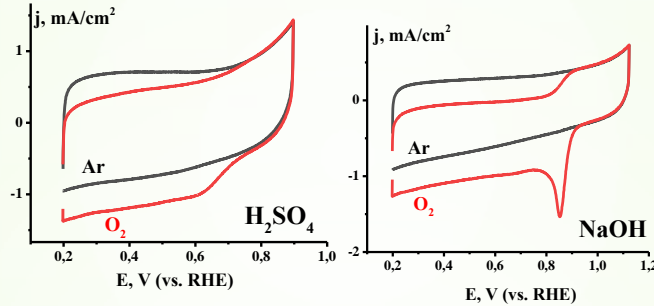
- **The aniline,  $H_2O_2$ , Co (II) salt and a catalytic amount of Fe (II) salt are using for the formation of a polymeric precursor composite which is subjected to the further carbonization. Such approach, on the one hand, excludes the stage of pre-obtaining of PAni, and on the other hand – avoids the formation of  $Co_9S_8$  nanoparticles in the composition of Co-N-C electrocatalysts during carbonization process**
- **The possibility of effective replacement of traditional PAni by poly-*o*-aminobenzoic acid in the creation of pyrolyzed Co-N-C electrocatalysts ORR is shown. Such possibility allows not to disturb the type of polymeric nitrogen source (because poly-*o*-aminobenzoic acid undergoes decarboxylation with the formation of PAni already at  $\sim 200^\circ C$ ), and also provides a more developed, porous catalyst structure due to  $CO_2$  gassing in poly-*o*-aminobenzoic acid decarboxylation process**
- **It is established that the use in the formation of Co-N-C catalyst of PAni, nanostructured using a "soft" template –  $\beta$ -cyclodextrin, allows to increase the available for the electrolyte solution surface area of the catalyst, which determines its functional advantages over the composite, which is obtained on the basis of unstructured PAni**

# Co<sub>2</sub>P,CoP/Co-N,P-C ORR electrocatalyst obtained by pyrolysis of phosphoric acid doped polyaniline and Co (II) salt

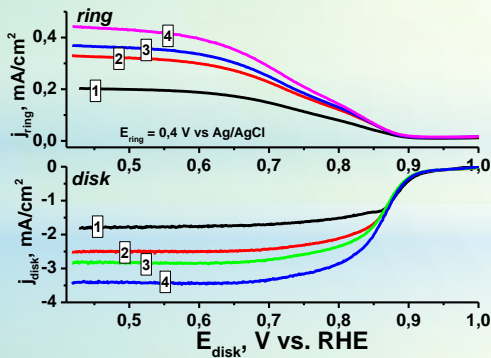
It was shown, that carbonization of the phosphoric acid doped PANi together with the salt of Co (II) yielded carbon nanocomposites co-doped with cobalt, nitrogen and phosphorus with CoP (preferably) and Co<sub>2</sub>P particles – CoP<sub>x</sub>/Co-N,P-C, which are able to possess high ORR activity in acidic and alkaline electrolytes



XRD-patterns of CoP<sub>x</sub>/Co-N,P-C, CoP and Co<sub>2</sub>P



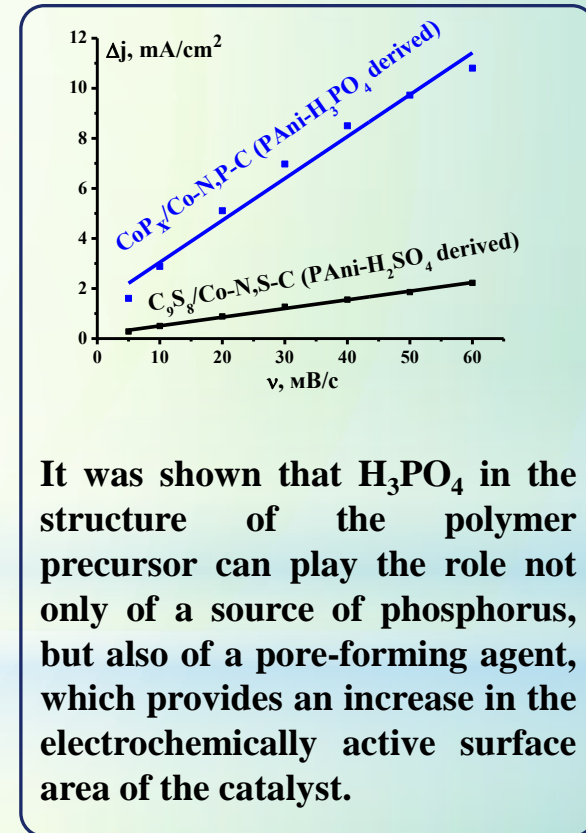
Cyclic voltammograms of CoP<sub>x</sub>/Co-N,P-C in deaerated and saturated with oxygen 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M NaOH



RRDE polarization curves for CoP<sub>x</sub>/Co-N,P-C in an O<sub>2</sub>-saturated 1 M NaOH at a rotation rates of 600 (1), 1200 (2), 1800 (3), and 2400 (4) rpm.

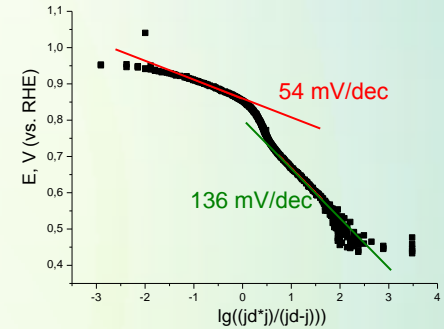
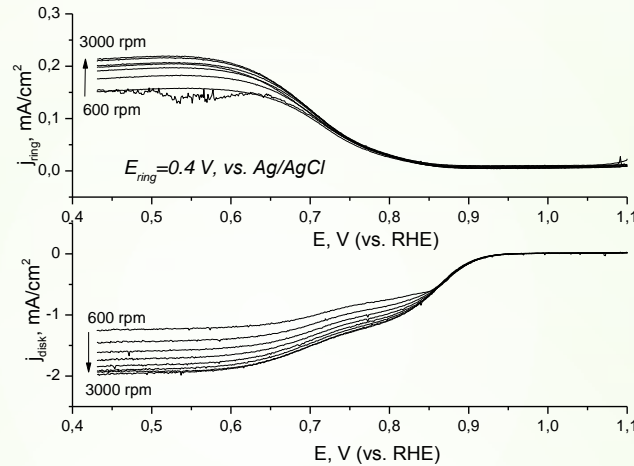
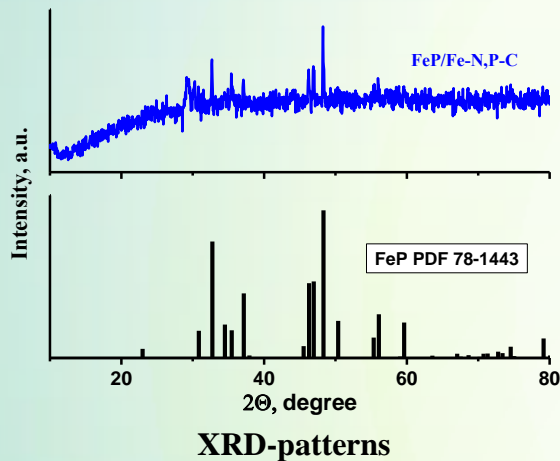
ORR performance of catalysts in 1.0 M NaOH (calculated at 1800 rpm)

E <sub>onset</sub> , V	E <sub>1/2</sub> , V	n	H <sub>2</sub> O <sub>2</sub> %
0,96	0,86	3,6	19,9

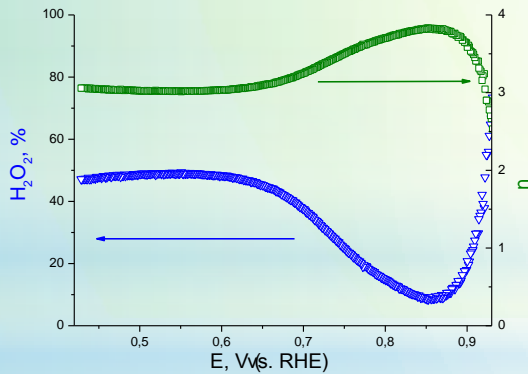


It was shown that H<sub>3</sub>PO<sub>4</sub> in the structure of the polymer precursor can play the role not only of a source of phosphorus, but also of a pore-forming agent, which provides an increase in the electrochemically active surface area of the catalyst.

# FeP/Fe-N,P-C ORR electrocatalyst obtained by pyrolysis of phosphoric acid doped polyaniline and Fe (III) salt



Two waves are observed for polarization curves. It can be assumed that there are two kinds of ORR active sites on catalyst due to which oxygen reduction occurs at two different potential ranges



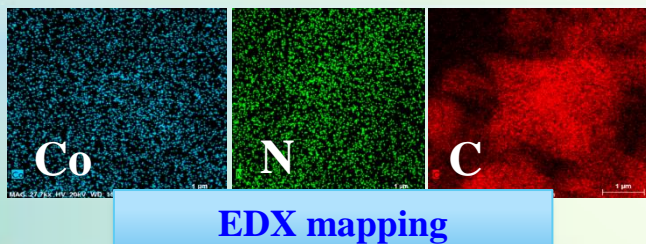
ORR performance of catalysts in 1.0 M NaOH (calculated at 1500 rpm)

	$E_{1/2}$ , V	b, mV/dec	n	H <sub>2</sub> O <sub>2</sub> , %
More positive potential range	0.89	52	3.7	15
Less positive potential range	0.78	136	3.1	46

It was found that at low overvoltage FeP/Fe-N,P-C is characterized in ORR  $b \sim 52$  mV/dec,  $E_{1/2} \sim 0.89$  V, and oxygen reduction on it occurs mainly by 4e mechanism, indicating a sufficiently high efficiency of the obtained catalyst in ORR under these operating conditions



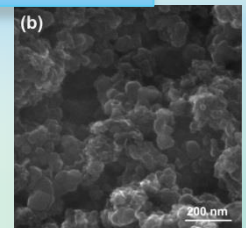
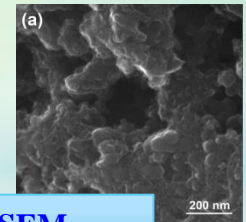
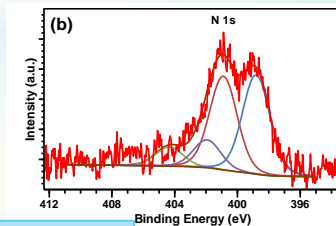
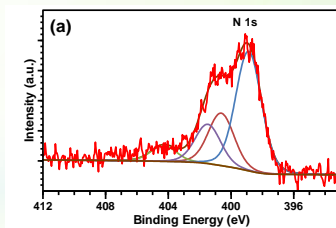
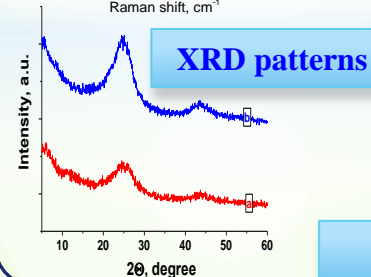
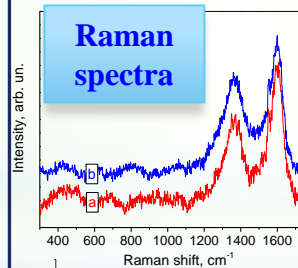
# Co-N-C electrocatalysts for ORR derived from deep eutectic solvents (DES)



For the first time, it was shown the possibility of using a Deep Eutectic Solvent (DES) based on 1-butyl-3-methylimidazolium chloride and hydrated Co (II) nitrate – [Bmim]Cl·xCo(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O – as a source of nitrogen and cobalt to create highly efficient carbonized Co-N-C electrocatalysts toward ORR.

Effect of mass ratio DES: Vulcan XC72 in precursor on composition and physicochemical properties **Co-N-C\_1 (a)** and **Co-N-C\_2 (b)** electrocatalysts

Catalyst	Mass ratio DES : Vulcan XC72 in precursor	Co, at%	N, at%	C, at%	O, at%
Co-N-C_1	9.6:1	0.06	4.82	89.62	5.50
Co-N-C_2	6.1:1	0.03	3.88	93.04	3.05

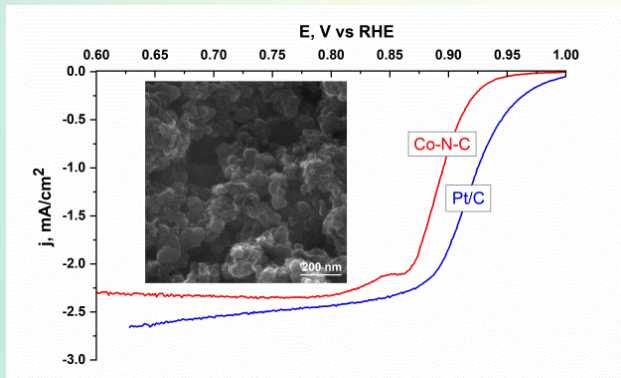


# ORR performance of DES derived Co-N-C electrocatalysts in alkaline electrolyte

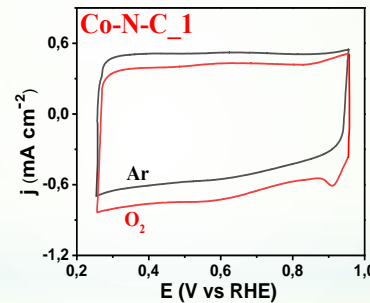
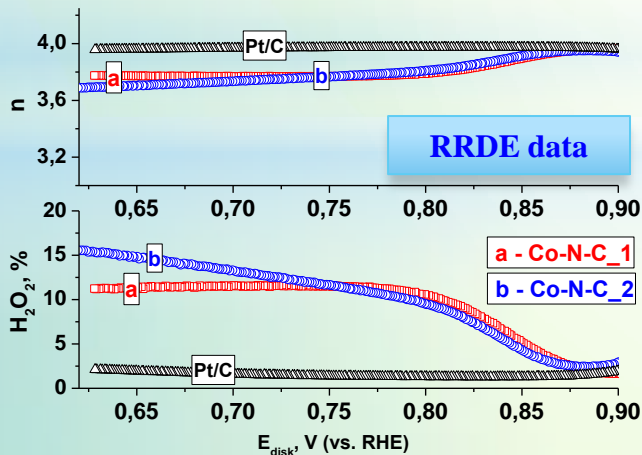
Obtained catalysts are characterized in alkaline electrolyte by  $E_{1/2} \sim 0.89$  V (vs RHE), that is almost not inferior to that for Pt/C catalyst, as well as high electrochemical stability during long-term operation. It was found that ORR on obtained electrocatalysts passes mainly by a 4-electron mechanism, and the yield of  $H_2O_2$ , which is an undesirable intermediate in hydrogen FCs, does not exceed 15%. One of the reasons for the high performance of electrocatalysts may be the efficient formation of active  $CoN_x$  sites in them, which is facilitated by the fact that cobalt, forming a strong bond with the ligand, is uniformly distributed in DES.

## ORR performance of Co-N-C and Pt/C catalysts in 1.0 M NaOH

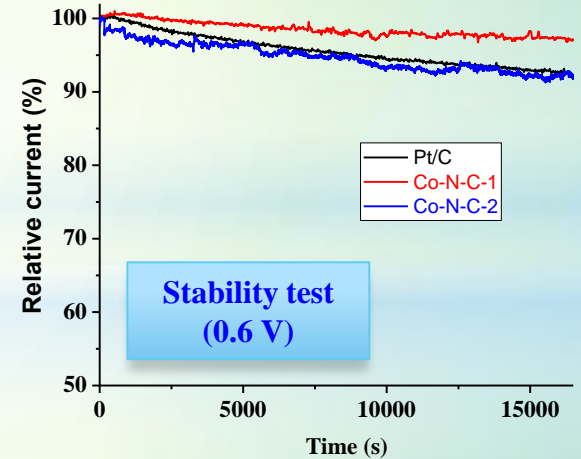
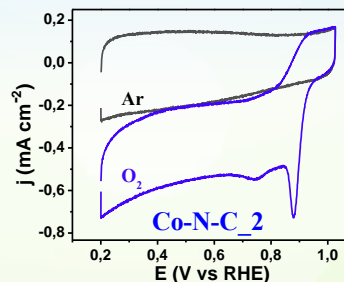
Catalyst	$E_{onset}$ , V vs. RHE	$E_{1/2}$ , V vs. RHE	Electron number, n	$H_2O_2$ yield, %	b, mV/dec
Co-N-C_1	0.99	0.886	3.80	9.5	37.4
Co-N-C_2	0.97	0.894	3.72	14.0	45.3
Pt/C	1.03	0.906	3.97	1.5	40.8



Electrochemical oxygen reduction on commercial Pt/C catalyst and Co-N-C catalyst prepared using DES

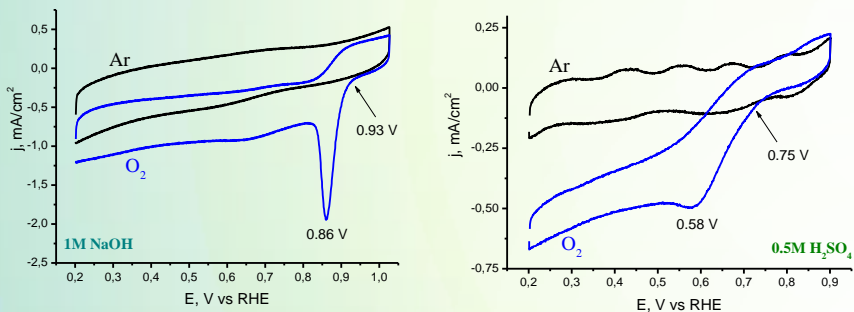


CV data

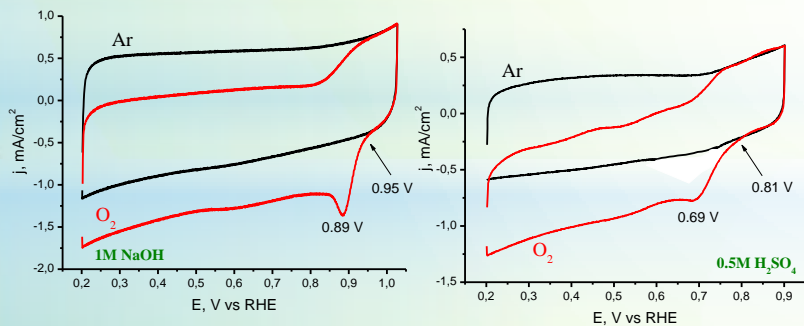


# Co-N-C electrocatalysts for ORR derived from Co-containing DES based on choline chloride

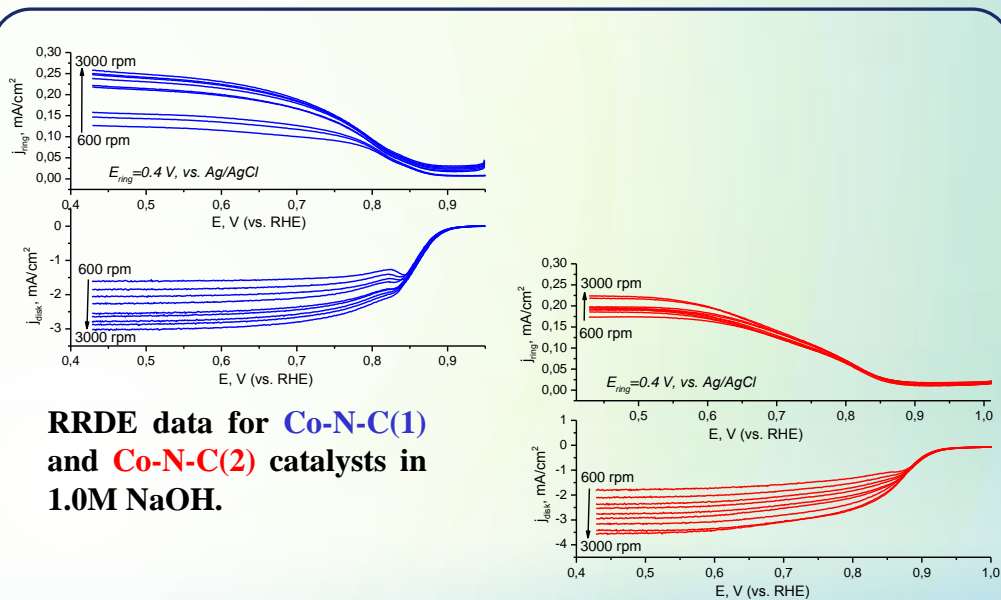
The possibility of using Co-containing DES based on choline chloride –  $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{OH}]\text{Cl}^-$ , which is much cheaper compared to [Bmim]Cl and other alkylimidazolium salts, in the production of Co-N-C catalysts has been shown. Although such catalysts are somewhat inferior in ORR activity ( $E_{\text{onset}} \sim 0.92\text{-}0.95$  and  $\sim 0.75\text{-}0.81$  V, vs RHE in 1.0 M NaOH and 0.5 M  $\text{H}_2\text{SO}_4$ , respectively) by analogues derived from [Bmim]Cl-DES, further optimization of their preparation can, in our opinion, improve their performance.



CV data for Co-N-C(1) catalyst derived from DES based on choline chloride and Co(II)



CV data for Co-N-C(2) catalyst derived from DES based on choline chloride, Co(II), and  $\text{ZnCl}_2$



RRDE data for Co-N-C(1) and Co-N-C(2) catalysts in 1.0M NaOH.

ORR performance of Co-N-C catalysts derived from DES based on choline chloride

Catalyst	$E_{\text{onset}}$ , V vs. RHE	$E_{1/2}$ , V vs. RHE	Electron number, n	$\text{H}_2\text{O}_2$ yield, %	b, mV/dec
Co-N-C(1)	0.93	0.856	3.25	37	41
Co-N-C(2)	0.95	0.869	3.38	31	75

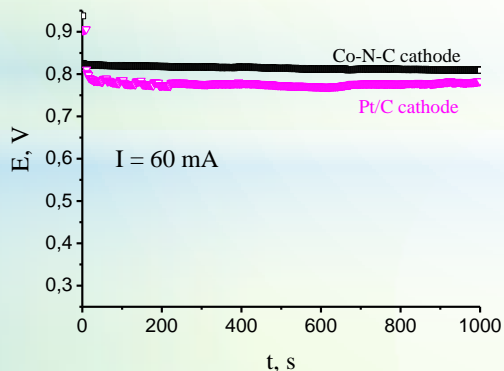
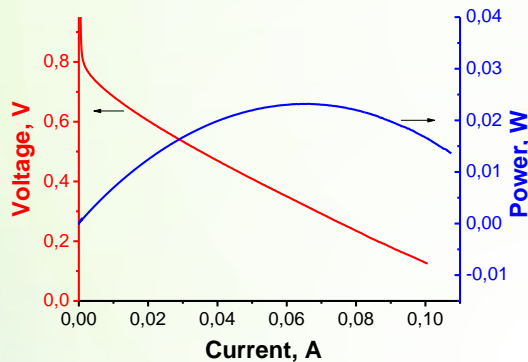
# Testing of Co-N-C electrocatalysts in fuel and zinc-air cell models

## Fuel cell

The ability of DES derived Co-N-C catalysts to stable operation as a part of the membrane-electrode block based on a commercial ion-conducting membrane Nafion in the model of the low-temperature fuel cell is established

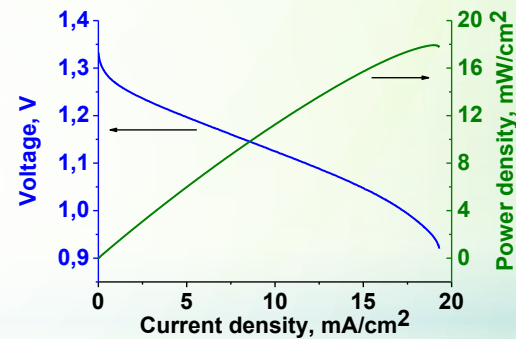
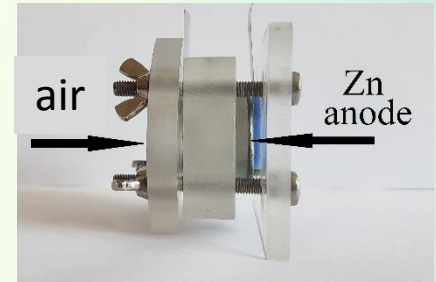


Anode – Pt/C  
Cathode – Co-N-C



## Zinc-air cell

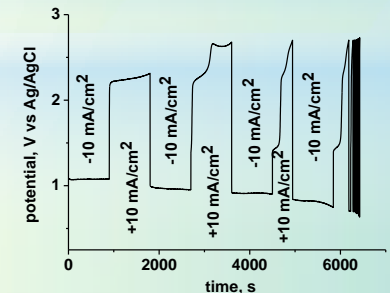
The DES derived Co-N-C composite also is able to stable operation as a electrocatalyst for zinc-air voltaic cell



voltaic cell



rechargeable battery



## MAIN CONCLUSIONS

- It was found that  $\text{Co}_9\text{S}_8/\text{Co-N-C}_{\text{MLG}}$  electrocatalyst (obtained by pyrolysis with using of poly-2,6-diaminopyridine and MLG) is characterized by higher ORR activity in comparison with analogue obtained on the basis of carbon black, which may be due to the dominance in the composition of such catalysts of different active sites ( $\text{CoN}_x$ ,  $\text{C/N}_x$ ,  $\text{Co}_9\text{S}_8$ ), where adsorption, activation and catalytic transformations of  $\text{O}_2$  take place. High tolerance of obtained  $\text{Co}_9\text{S}_8/\text{Co-N-C}_{\text{MLG}}$  to CO and methanol, which are able to poison ORR catalysts, in particular Pt-containing, in the service conditions of hydrogen and methanol fuel cells, has been shown.
- New approaches to the formation of polymeric composites-precursor based on polyaniline (PAni) have been proposed, which, upon further carbonization, make it possible to obtain Co-N-C ORR electrocatalysts with a high surface area available for electrolyte (replacement of traditional PAni with poly-o-aminobenzoic acid and nanostructuring PAni using "soft" template -  $\beta$ -cyclodextrin).
- It was shown, that carbonization of the phosphoric acid doped PAni together with the salts of Co (II) or Fe (III) yielded carbon nanocomposites co-doped with cobalt (or iron), nitrogen and phosphorus with phosphide particles of corresponding d-metal –  $\text{CoP}$ ,  $\text{Co}_2\text{P}/\text{Co-N,P-C}$ , and  $\text{FeP}/\text{Fe-N,P-C}$  – which are able to possess high ORR activity in acidic and alkaline electrolytes. It was shown that  $\text{H}_3\text{PO}_4$  in the structure of the polymer precursor can play the role not only of a source of phosphorus, but also of a pore-forming agent, which provides an increase in the electrochemically active surface area of the catalyst.
- For the first time, it was found the possibility of using a deep eutectic solvent (DES) based on 1-butyl-3-methylimidazolium chloride ( $[\text{Bmim}]\text{Cl}$ ) and hydrated Co (II) nitrate as a source of nitrogen and cobalt to create highly efficient carbonized Co-N-C electrocatalysts toward ORR in acid and alkali electrolytes. Such catalysts are characterized in 1.0 M NaOH by high values of onset potential ( $\sim 0.97\text{-}0.99$  V vs. RHE) and half-wave potential ( $\sim 0.89$  V), which are almost not inferior to Pt/C catalyst, as well as long-term electrochemical stability in ORR (reduction of current density 3-8% after 5 h of continuous operation at 600 mV), which is higher or comparable to that for Pt/C. It was shown that ORR on obtained electrocatalysts passes mainly by a 4-electron mechanism ( $n \sim 3.7\text{-}3.8$ ), and the yield of  $\text{H}_2\text{O}_2$ , which is an undesirable intermediate in hydrogen fuel cells, does not exceed 15%.
- The possibility of using Co-containing DES based on choline chloride –  $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{OH}]\text{Cl}^-$ , which is much cheaper compared to  $[\text{Bmim}]\text{Cl}$  and other alkyimidazolium salts, in the production of Co-N-C catalysts has been shown. Although such catalysts are somewhat inferior in ORR activity ( $E_{\text{onset}} \sim 0.92\text{-}0.95$  and  $\sim 0.75\text{-}0.81$  V, vs RHE in 1.0 M NaOH and 0.5 M  $\text{H}_2\text{SO}_4$ , respectively) by analogues derived from  $[\text{Bmim}]\text{Cl}$ -DES, further optimization of their preparation can, in our opinion, improve their performance.
- The ability of the best of the developed catalysts to stable operation in the models of the low-temperature fuel cell and zinc-air cell is established.

## The key publications in the frame of the project

- Y.I. Kurys, O.O. Pariiska, D.O. Mazur, V.G. Koshechko, V.D. Pokhodenko. Electrochemical synthesis of multilayered graphene and its use in Co–N–C electrocatalysts of oxygen reduction and hydrogen evolution. *Russian Journal of Electrochemistry*, 2020, vol.56, pp. 271-284. <https://doi.org/10.1134/S1023193520040072>
- O. Pariiska, D. Mazur, Y. Kurys, R. Socha, V. Koshechko, V. Pokhodenko. Poly-5-aminoindole and graphene-like materials derived bifunctional Co-N-C electrocatalysts for oxygen reduction and hydrogen evolution. *Journal of Solid State Electrochemistry*, 2021, vol.25, pp. 2309-2319. <https://doi.org/10.1007/s10008-021-05009-6>
- O. Pariiska, D. Mazur, K. Cherchenko, Ya. Kurys, V. Koshechko, V. Pokhodenko. Efficient Co-N-C electrocatalysts for oxygen reduction derived from deep eutectic solvents. *Electrochimica Acta*, 2021, submitted.
- Ya. Kurys, O. Pariiska, K. Cherchenko, D. Mazur, V. Koshechko, V. Pokhodenko. Cobalt-nitrogen-carbon electrocatalyst for oxygen reduction, obtained using a deep eutectic solvent. *Ukrainian Patent Application* No a202008235, December 12, 2020.
- O. Pariiska, D. Mazur, Y. Kurys. Co-N-C electrocatalysts of ORR based on conjugated polymers and electrochemically obtained graphene materials. *Book of abstracts of 17<sup>th</sup> European conference on solid state chemistry (17<sup>th</sup> ECSSC)*, Lille, France, September 1-4 2019, p. 86.
- O. Pariiska, K. Cherchenko, D. Mazur, Y. Kurys, V. Koshechko, V. Pokhodenko. Efficient Co-N-C electrocatalysts for oxygen reduction derived from deep eutectic solvents. *Book of abstracts of 6<sup>th</sup> International Symposium on Surface Imaging/Spectroscopy at the Solid/Liquid Interface (ISSIS2021)*, Kraków, Poland, June 6-9, 2021, pp. 157-158.
- O. Pariiska, D. Mazur, Y. Kurys, V. Koshechko, V. Pokhodenko. Co-N-C composites derived from poly-5-aminoindole and different nanosized carbon materials as multifunctional electrocatalysts. *Book of abstracts of 3<sup>rd</sup> International Workshop on Functional Nanostructured Materials (FuNaM-3)*, Kraków, Poland, October 6-8, 2021, p. 102.

Thank you for attention

