Lowering the cost of catalysts for electrochemical energy conversion devices

Diogo Santos, Biljana Šljukić, Luís Amaral, César Sequeira

Center of Physics and Engineering of Advanced Materials (CeFEMA),

Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

**diogosantos@tecnico.ulisboa.pt*

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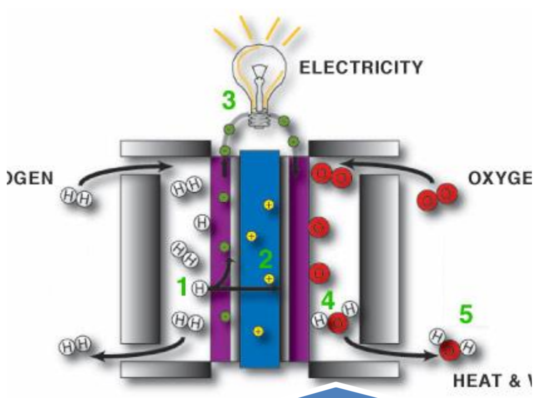
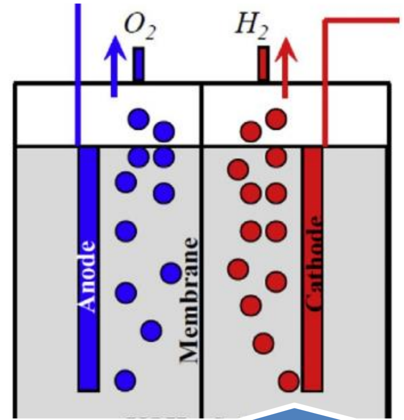
Electrochemical energy conversion devices

Batteries



Fuel cells



Electrolysers

What are fuel cells?

Typical FCs use H_2/O_2

- **safety issues**
- **high cost for gas storage**

Why not using liquid fuels?

Direct borohydride fuel cell

- $NaBH_4$
- O_2



- high energy density
- room temperature operation

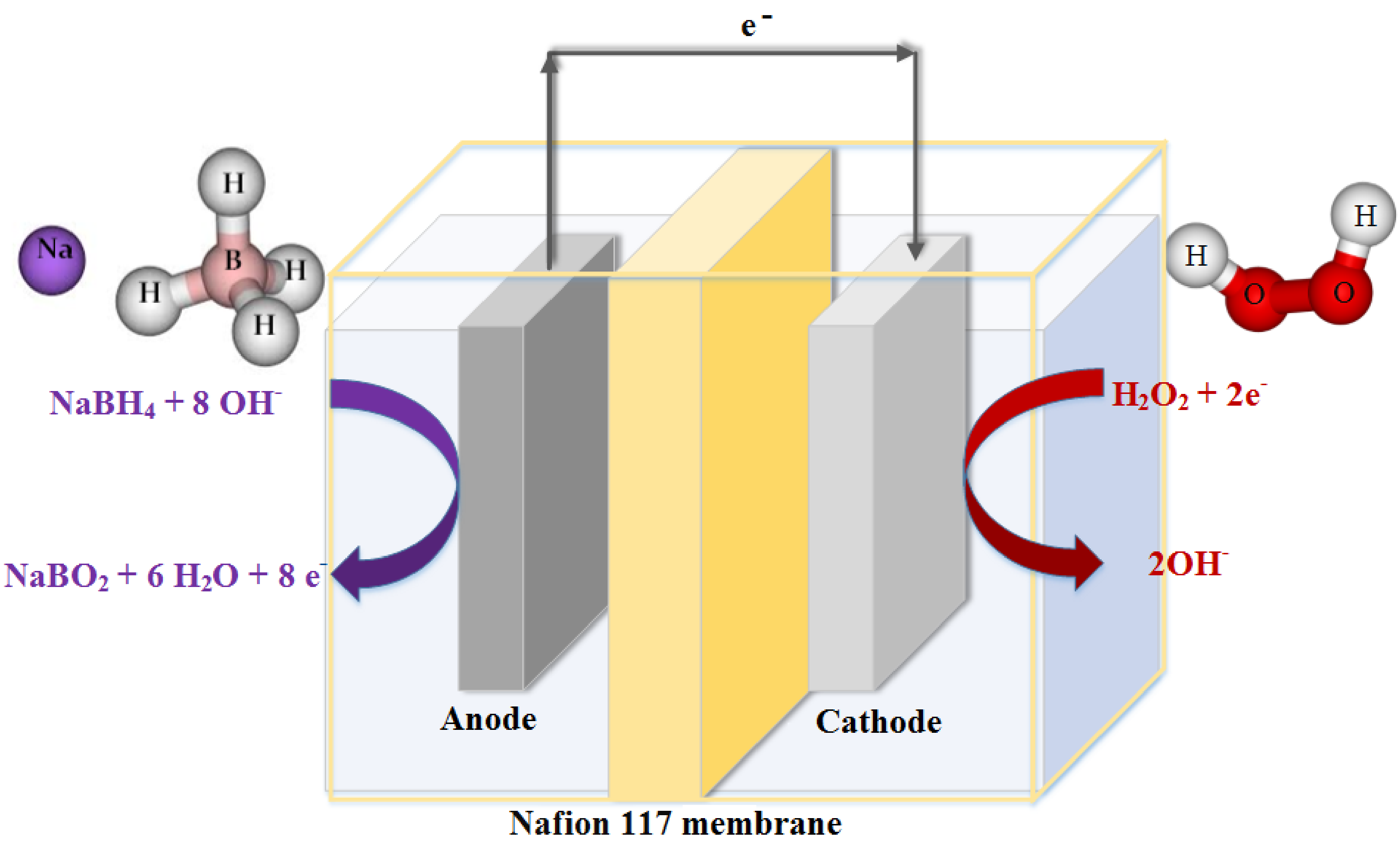
→ promising for portable applications (e.g., cell phones, laptops)

Direct borohydride/ peroxide fuel cell

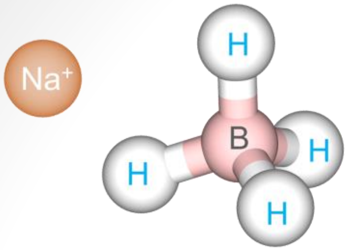
- $NaBH_4$
- H_2O_2

← Can we feed the fuel cell with both liquid fuel and liquid oxidant?

Direct borohydride/peroxide fuel cell



- simplified storage, thermal management and internal processing
- **promising solution for <u>space, underwater</u>, and specific terrestrial applications where O_2 is not available**

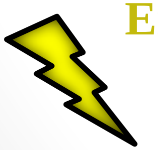


$NaBH_4$

- specialty reducing agent in the manufacture of pharmaceuticals
- bleaching agent in the manufacture of paper
- **hydrogen/energy carrier** (last decade)

Hydrogen carrier → Borohydride hydrolysis reaction

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2$$



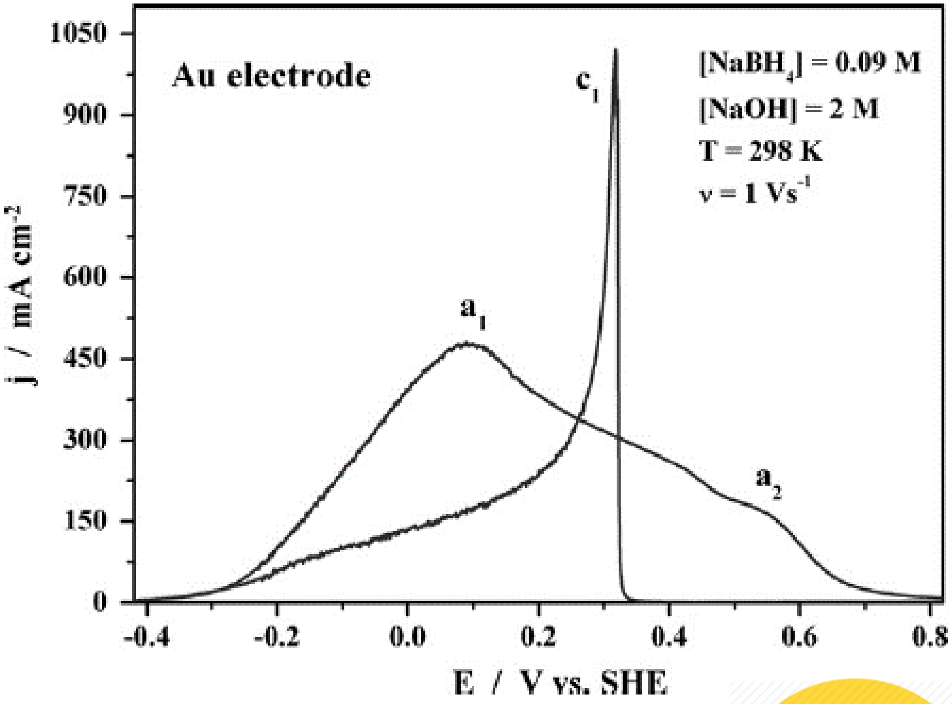
Energy carrier → Borohydride oxidation reaction

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad (E^0 = -1.24 \text{ V vs. SHE})$$

ELECTROCATALYSTS for BH_4^- OXIDATION

Fundamentals of the BH_4^- oxidation reaction (BOR) in alkaline media

- Au selected for being non-catalytic for BH_4^- hydrolysis
- calculation of kinetic and diffusional parameters that characterise BH_4^- oxidation



However, Au has high price and low BOR kinetics (compared to Pt)

D.M.F. Santos, C.A.C. Sequeira, J. Electrochem. Soc., 156, F67-F74, 2009
D.M.F. Santos, C.A.C. Sequeira, J. Electrochem. Soc., 157, F16-F21, 2010
D.M.F. Santos, C.A.C. Sequeira, Electrochim. Acta,, 55, 6775-6781, 2010

ELECTROCATALYSTS for BH_4^- OXIDATION

Looking for cheaper anode electrocatalysts…

Zn electrode tested for BOR using CV, CA, and CP

CV indicated number of exchanged electrons = 4

Possible mechanism involves initial oxidation of Zn,
$Zn + 2H_2O \rightarrow ZnO_2^{2-} + 4H^+ + 2e^-$

followed by partial oxidation of BH_4^- to hydroxyborohydride (BH_3OH^-)
$BH_4^- + 2OH^- \rightarrow BH_3OH^- + H_2O + 2e^-$

Carbon-supported $Pt_{0.75}M_{0.25}$ (with M = Ni or Co) electrocatalysts

- charge transfer coefficients, number of electrons exchanged, standard heterogeneous rate constants and activation energies for BH_4^- oxidation
- $Pt_{0.75}Ni_{0.25}$/C electrocatalyst was found to be more active for BOR than $Pt_{0.75}Co_{0.25}$/C, with both of them showing superior activity than Pt/C

D.M.F. Santos, C.A.C. Sequeira, J. Electrochem. Soc., 157, B13-B19, 2010
B. Šljukić, J. Milikić, D.M.F. Santos, C.A.C. Sequeira, Electrochim. Acta, 107, 577-580, 2013

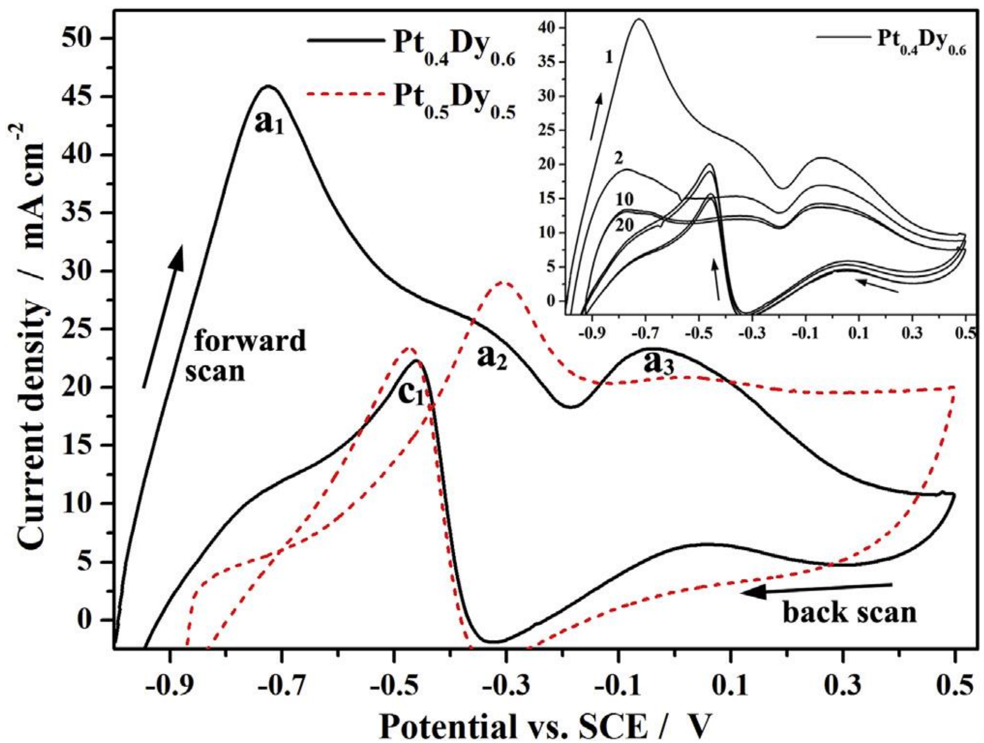
ELECTROCATALYSTS for BH_4^- OXIDATION

Did you say rare earths…?

Pt-RE alloys show <u>improved electrocatalytic activity</u> for several types of electrochemical reactions

Pt-RE (RE = Ce, Ho, Sm, Dy) electrodes were used to study BOR

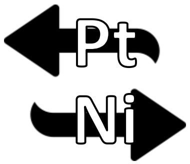
average value of n = 2



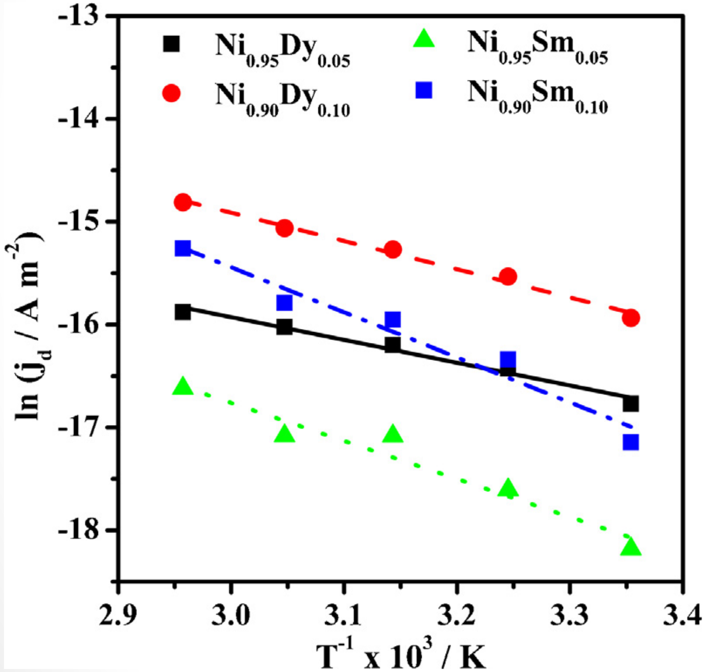
D.M.F. Santos, P.G. Saturnino, D. Macciò, A. Saccone, C.A.C. Sequeira, Catal. Today 170, 134-140, 2011
B. Šljukić, J. Milikić, D.M.F. Santos, C.A.C. Sequeira, D. Macciò, A. Saccone, J. Power Sources, 272, 335-343, 2014

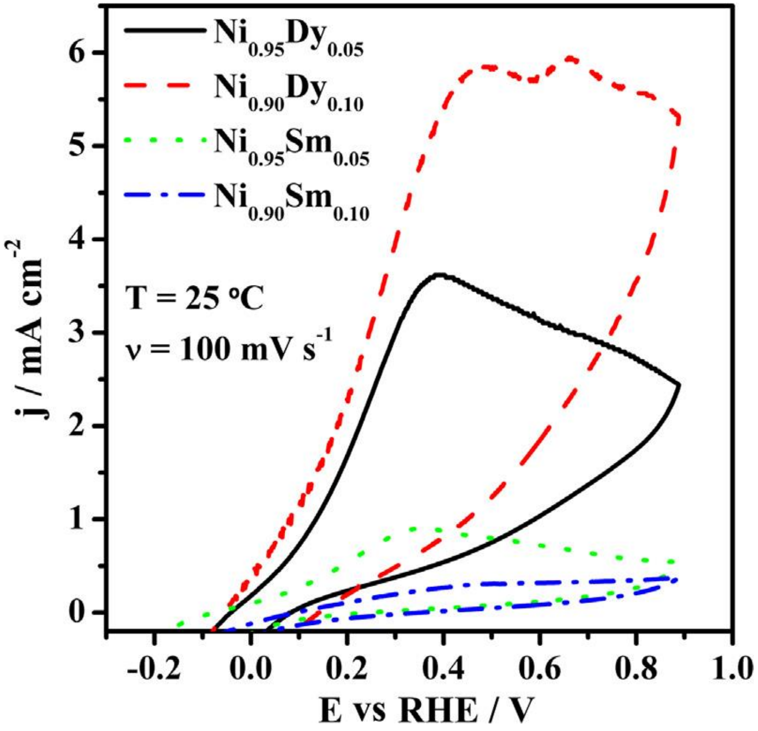
ELECTROCATALYSTS for BH_4^- OXIDATION

Can we further decrease the cost of the anode electrocatalyst?



Ni-RE (RE = Ce, Sm, Dy) electrodes were prepared and used to study BOR





Activation energies of 18 and 23 kJ mol^{-1} for BOR at $Ni_{0.95}Dy_{0.05}$ and $Ni_{0.90}Dy_{0.10}$, respectively

- good activity, low overpotentials, at lower cost

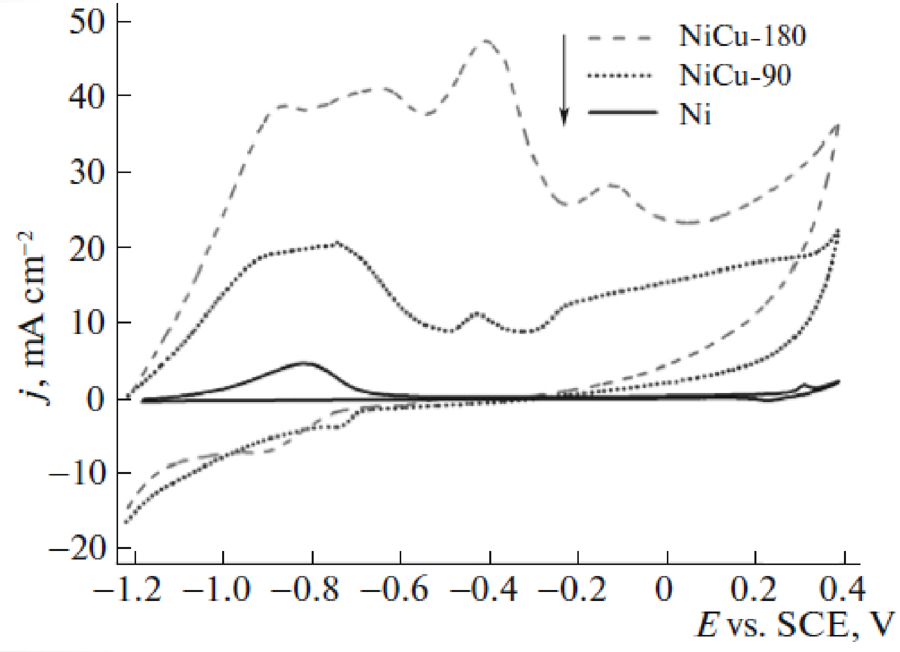
D.M.F. Santos, B. Šljukić, L. Amaral, J. Milikić, C.A.C. Sequeira, D. Macciò, A. Saccone, Electrochim. Acta, 190, 1050-1056, 2016

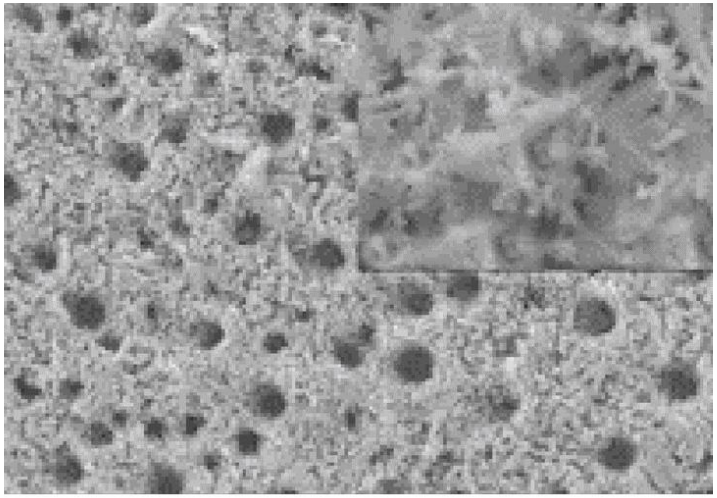
D.M.F. Santos, B. Šljukić, L. Amaral, D. Macciò, A. Saccone, C.A.C. Sequeira, J. Electrochem. Soc. 161, 5, F594-F599, 2014

ELECTROCATALYSTS for BH_4^- OXIDATION

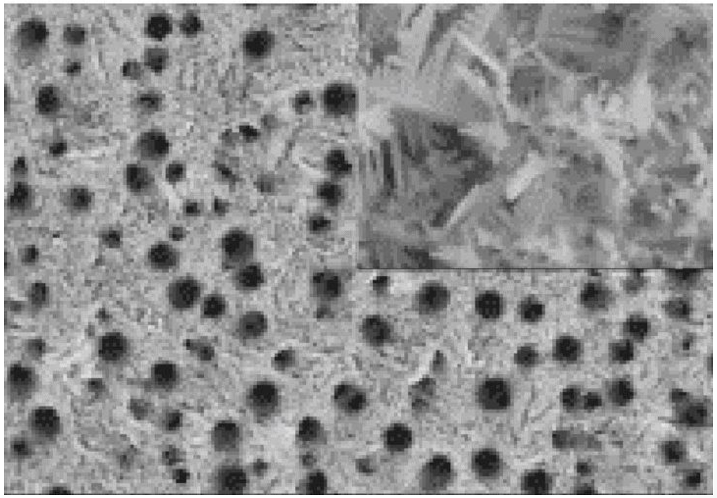
Three-dimensional nanostructured **Ni-Cu foams** for borohydride oxidation

62 wt.% Ni and 32 wt.% Cu





Ni–Cu foams deposited at 1.5 A cm^{-2} for 90 s

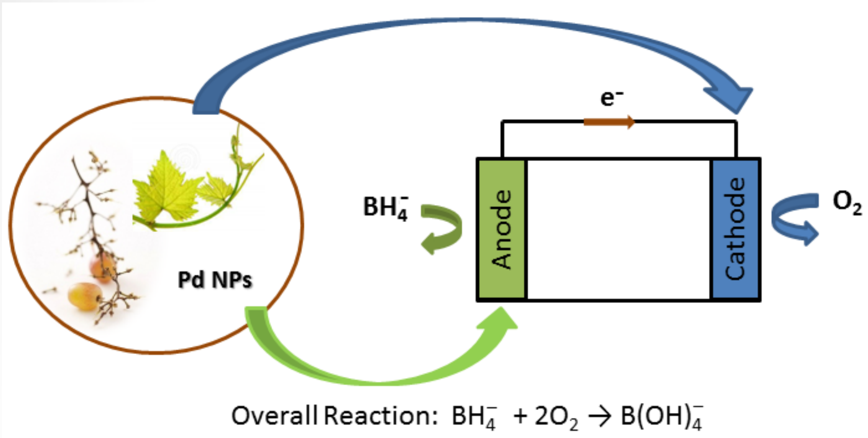


Ni–Cu foams deposited at 1.5 A cm^{-2} for 180 s

n values for BOR higher than other Ni-based alloys

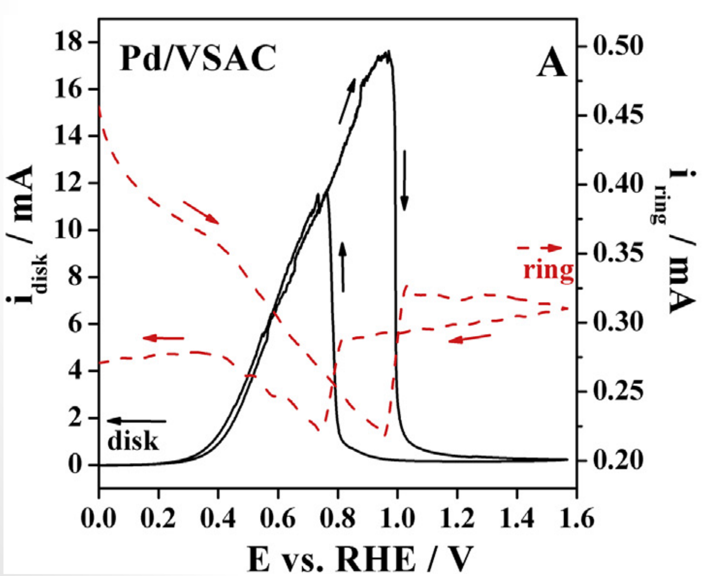
D.M.F. Santos, S. Eugénio, D.S.P. Cardoso, B. Šljukić, M.F. Montemor, Russ. J. Phys. Chem. A, 89, 2449-2454, 2015

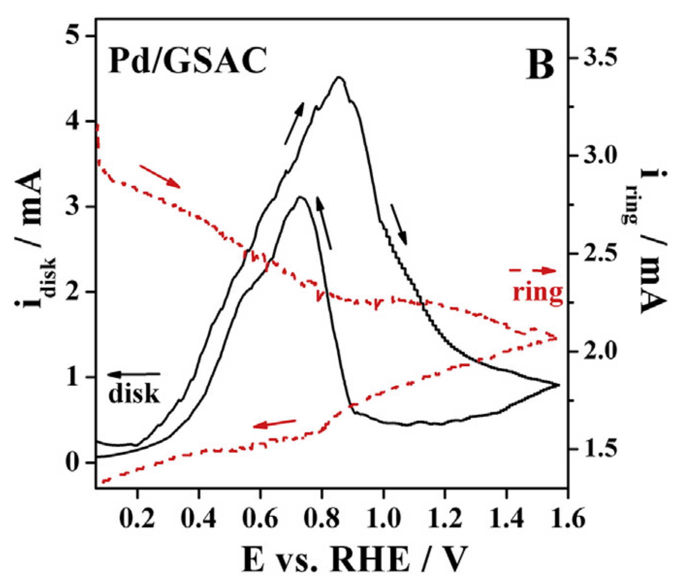
ELECTROCATALYSTS for BH_4^- OXIDATION



Biobased carbon–supported palladium electrocatalysts for borohydride fuel cells

Activated carbons prepared from grape stalk (GS) and vine shoots (VS) used as catalysts support



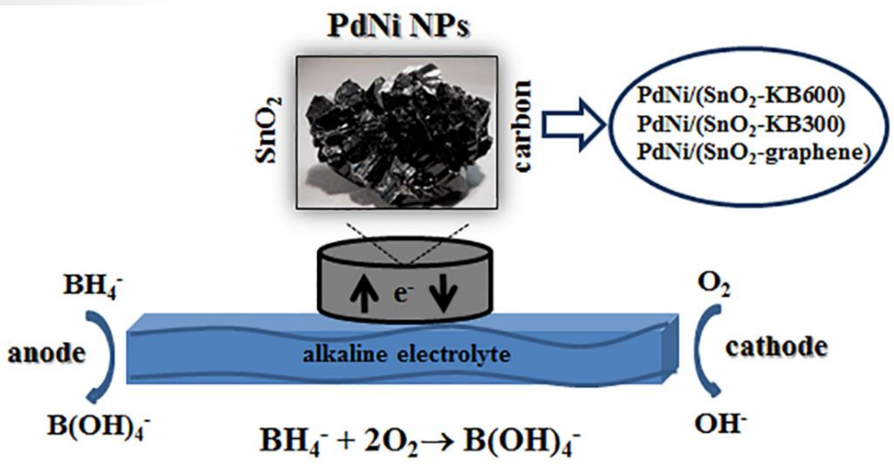


n for BOR:

VSAC: 2.0
GSAC: 5.6

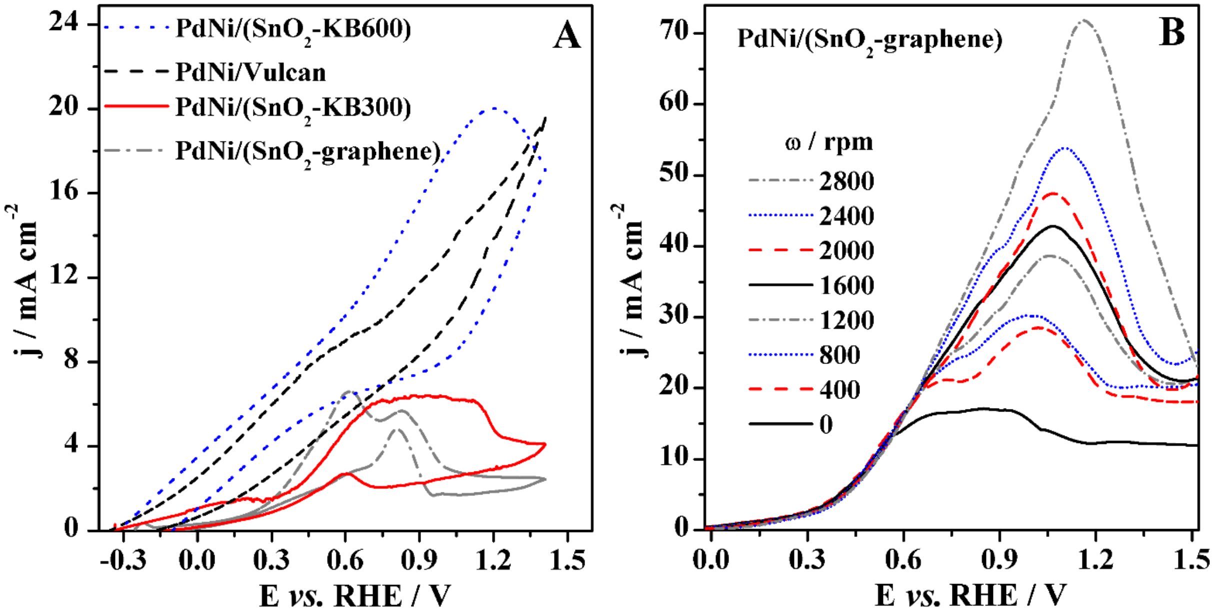
M. Martins, B. Šljukić, C.A.C. Sequeira, O. Metin, M. Erdem, T. Sener, D.M.F. Santos, Int. J. Hydrogen Energy, 41, 25, 10914-10922, 2016

ELECTROCATALYSTS for BH_4^- OXIDATION



SnO_2-C supported **PdNi nanoparticles** for borohydride fuel cells

BOR RDE studies revealed n values ranging from 1.9 for PdNi/(SnO_2-graphene) to 3.4 for PdNi/(SnO_2-KB300).

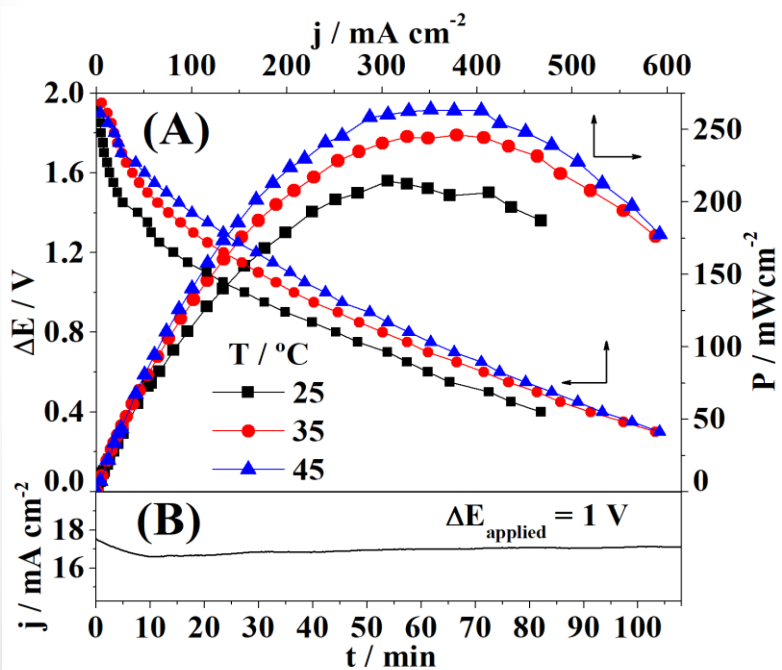


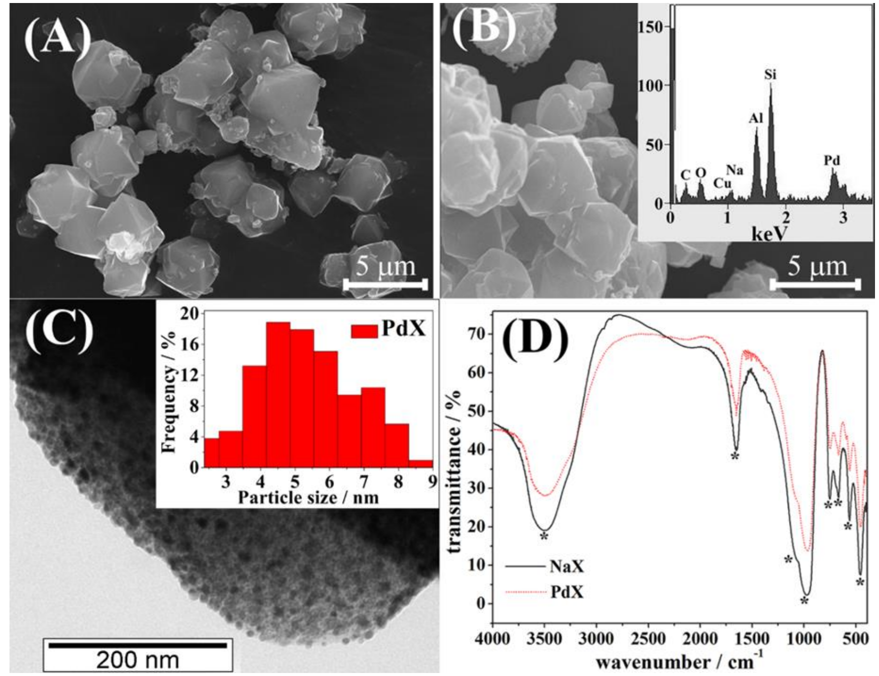
M. Martins, B. Šljukić, C.A.C. Sequeira, O. Metin, M. Erdem, T. Sener, D.M.F. Santos, Int. J. Hydrogen Energy, 41, 25, 10914-10922, 2016

ELECTROCATALYSTS for BH_4^- OXIDATION

PdX zeolite

prepared by Pd ion exchange with Na ion within zeolite X





<u>BOR is a 1st order reaction at PdX</u>

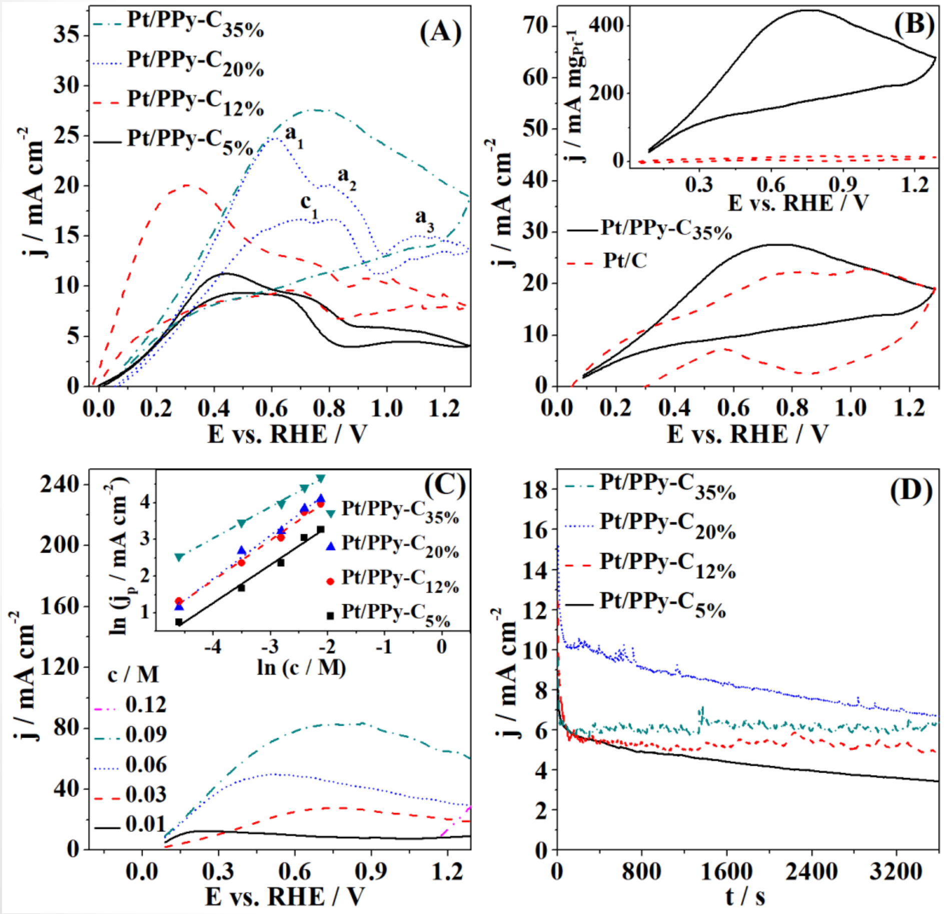
3.4 < n < 5.1, depending on $NaBH_4$ conc.

A DBPFC using PdX anode generates power densities as high as ***263 mW cm^{-2} at 45 °C***

R.C.P. Oliveira, M. Vasić, D.M.F. Santos, B. Babić, R. Hercigonja, C.A.C. Sequeira, B. Šljukić, Electrochim. Acta 269 (2018) 517–525

ELECTROCATALYSTS for BH_4^- OXIDATION

Four Pt/PPy-C electrocatalysts with different amounts of carbon



Pt/PPy-C$_{35\%}$* - *highest activity for BOR with an almost complete oxidation of BH_4^- and negligible activity for the undesirable BH_4^- hydrolysis concurrent reaction.

Electrocatalyst	n	E_a / kJ mol^{-1}	α	β
Pt/PPy-C$_{5\%}$	6.5	18	0.42	1.03
Pt/PPy-C$_{12\%}$	6.0	13	0.75	1.09
Pt/PPy-C$_{20\%}$	7.2	15	0.83	1.17
Pt/PPy-C$_{35\%}$	7.6	10	0.94	0.85

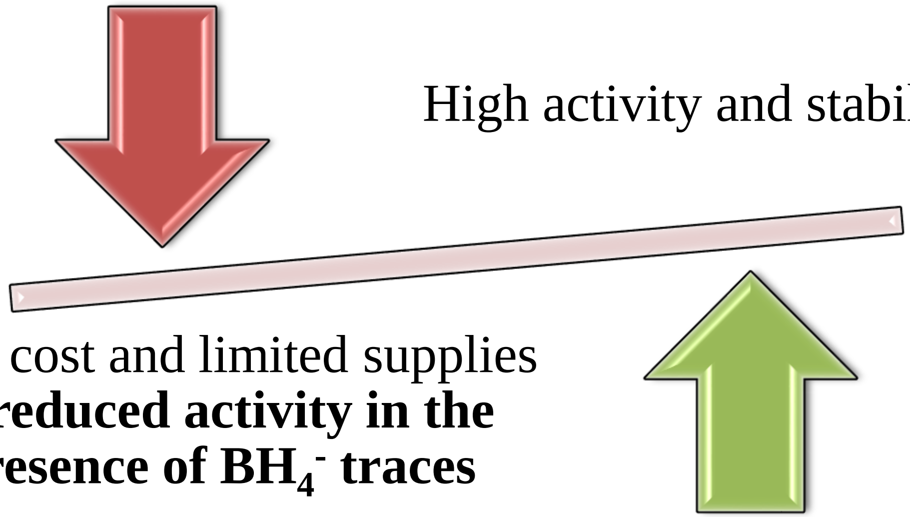
R.C.P. Oliveira, J. Milikić, E. Daş, A.B. Yurtcan, D.M.F. Santos, B. Šljukić, Appl. Catal. B, 2018 (in press)

ELECTROCATALYSTS for O_2 REDUCTION

ORR

- **$4e^-$**
  - $O_2 + 2H_2O + 4e^- \rightarrow 4\,OH^-$
    $E^0 = 0.40$ V vs. SHE
- **$2e^-$**
  - $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$
    $E^0 = -0.08$ V vs. SHE
  - $HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$
    $E^0 = 0.88$ V vs. SHE

ELECTROCATALYSTS for O_2 REDUCTION

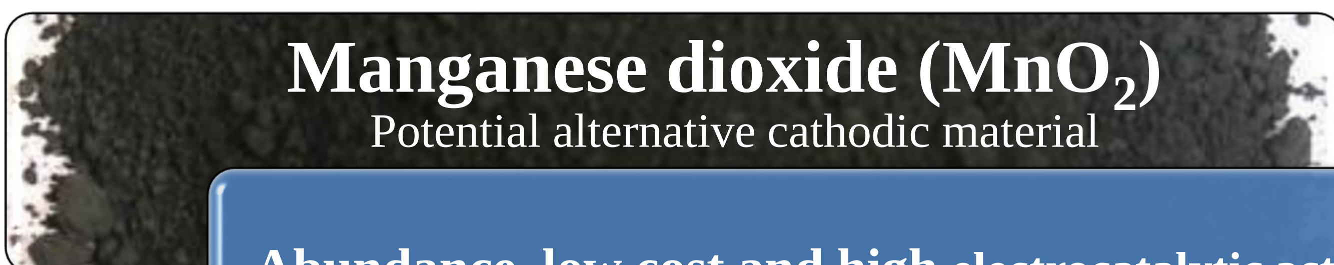


High activity and stability

Pt

The most commonly used electrocatalyst in fuel cells

High cost and limited supplies & **reduced activity in the presence of BH_4^- traces**



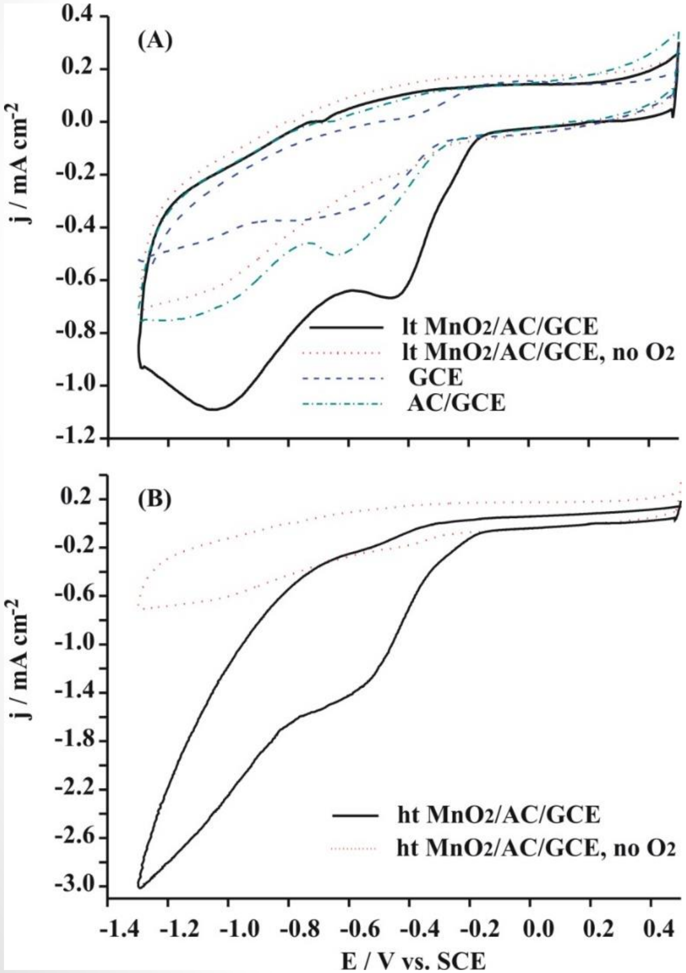
Manganese dioxide (MnO_2)

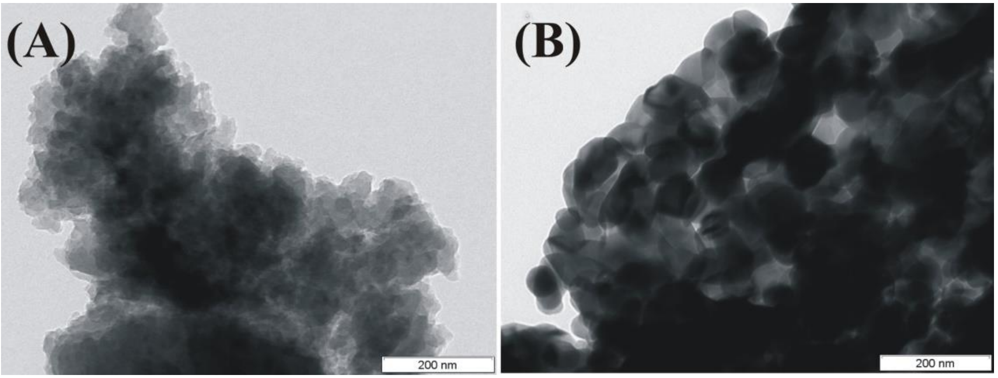
Potential alternative cathodic material

Abundance, low cost and high electrocatalytic activity for ORR even in the presence of BH_4^- traces

ELECTROCATALYSTS for O_2 REDUCTION

***lt*MnO$_2$/AC and *ht*MnO$_2$/AC**



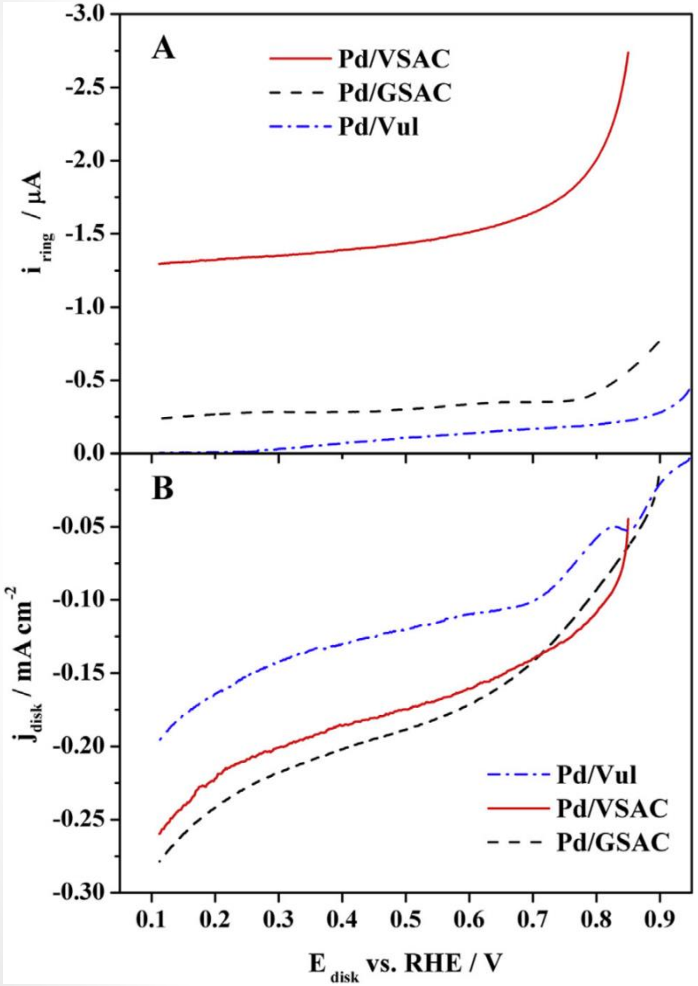


$$\frac{1}{j} = \frac{1}{j_d} + \frac{1}{j_k} = \frac{1}{0.62nFD^{2/3}\nu^{-1/6}C_{bulk}\omega^{1/2}} + \frac{1}{j_k}$$

	***ht*MnO$_2$/AC**	***lt*MnO$_2$/AC**
n	**4**	2
$j_{k,}$ mA cm^{-2}	**5.1**	1.7
b mVdec^{-1}	**64**	140

B. Šljukić, D.M.F. Santos, C.A.C. Sequeira, J. Electroanal. Chem.,2013, 694, 77-83

ELECTROCATALYSTS for O_2 REDUCTION



Biobased carbon–supported Pd electrocatalysts for ORR

RRDE studies of Pd/VSAC and Pd/GSAC electrocatalysts in O_2–saturated 1 M NaOH solution recorded at 10 mV s^{-1} and 2000 rpm

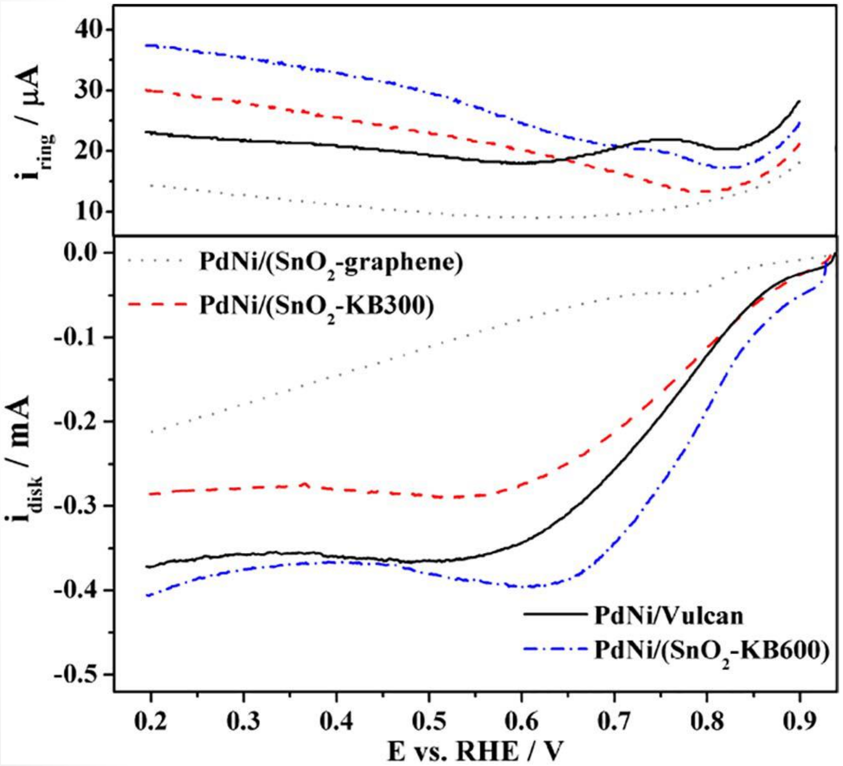
	Pd/GSAC	Pd/VSAC
n	**3.4**	1.7
$j_{k,}$ mA cm^{-2}	0.3	0.3
b mVdec^{-1}	68	75

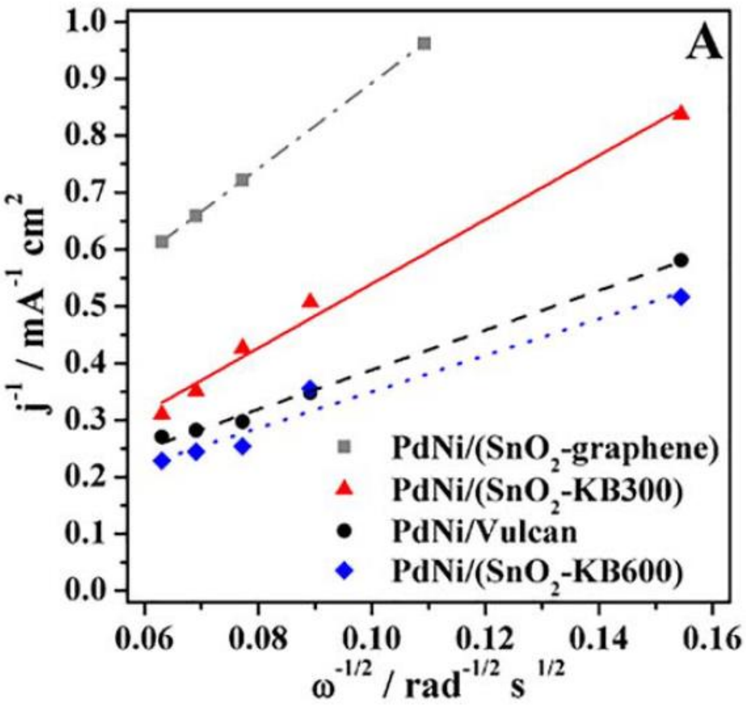
Pd/GSAC shows good electrocatalytic activity for ORR

M. Martins, B. Šljukić, C.A.C. Sequeira, O. Metin, M. Erdem, T. Sener, D.M.F. Santos, Int. J. Hydrogen Energy, 41(25), 10914-10922, 2016

ELECTROCATALYSTS for O_2 REDUCTION

SnO_2-C supported PdNi nanoparticles for ORR

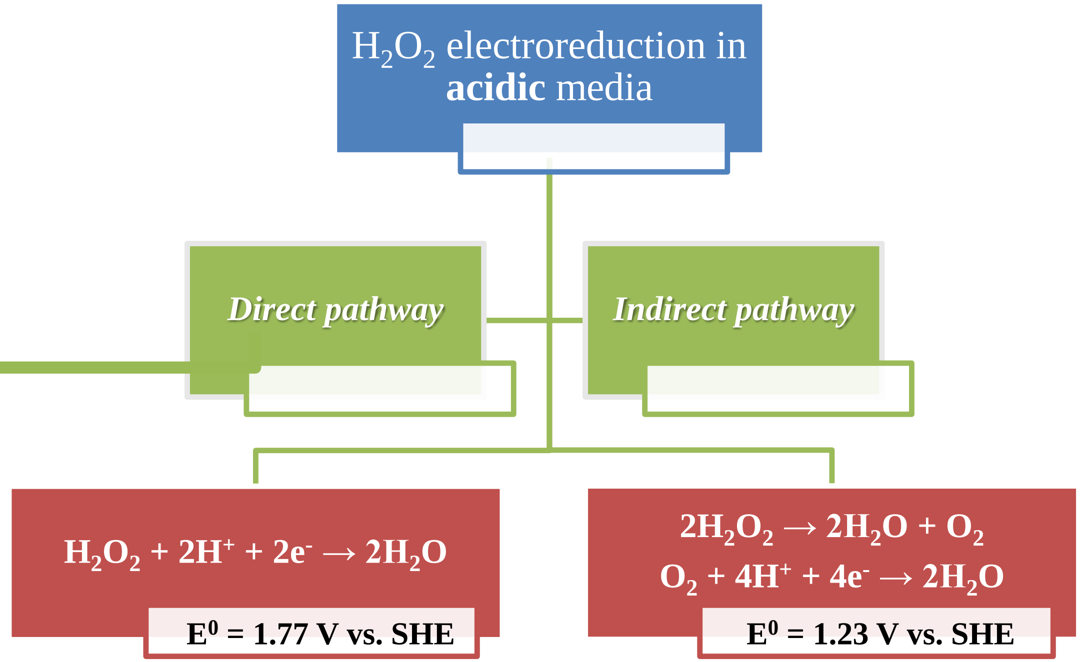




- ***4-electron oxygen reduction at PdNi/(SnO_2-KB600) electrocatalyst***
- *PdNi/(SnO_2-graphene) and PdNi/(SnO_2-KB300) showed n of 2*

B. Šljukić, M. Martins, E. Kayhan, A. Balčiūnaitė, T. Şener, C.A.C. Sequeira, and D.M.F. Santos, J. Electroanal. Chem., 797, 23-30, 2017

ELECTROCATALYSTS for H_2O_2 REDUCTION



(A) “Normal” direct mechanism, commonly at more negative potentials

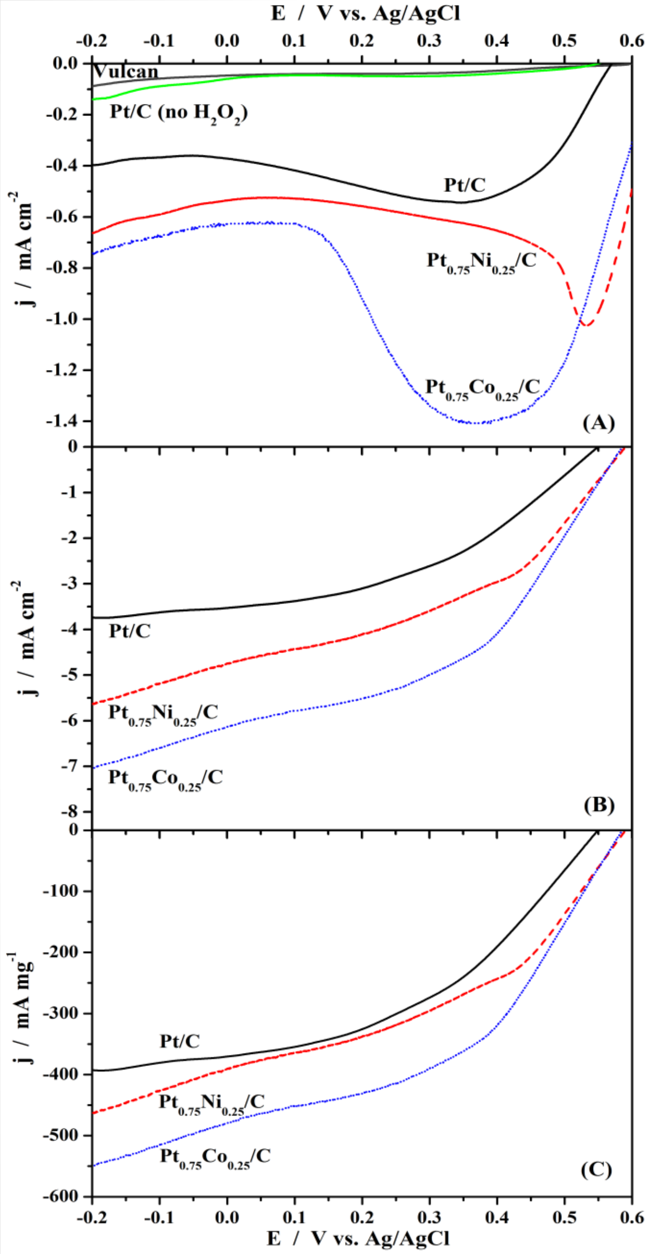
$$H_2O_2 + H^+ + e^- \rightarrow OH_{ads} + H_2O$$

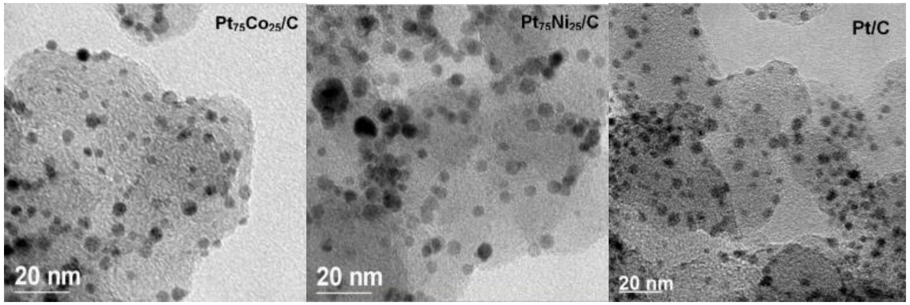
$$OH_{ads} + H^+ + e^- \rightarrow H_2O$$

(B) Autocatalytic direct mechanism

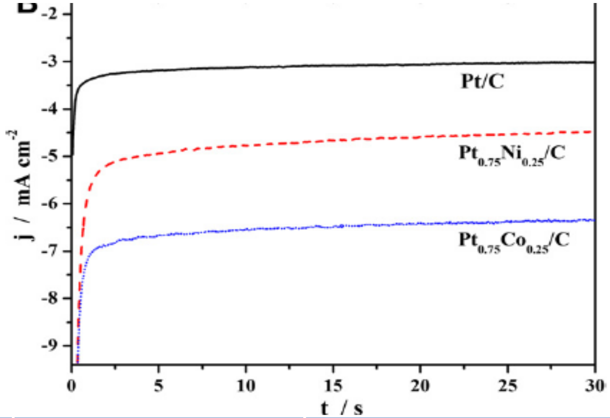
$$H_2O_2 + OH_{ads} + H^+ + e^- \rightarrow 2OH_{ads} + H_2O$$

ELECTROCATALYSTS for H_2O_2 REDUCTION



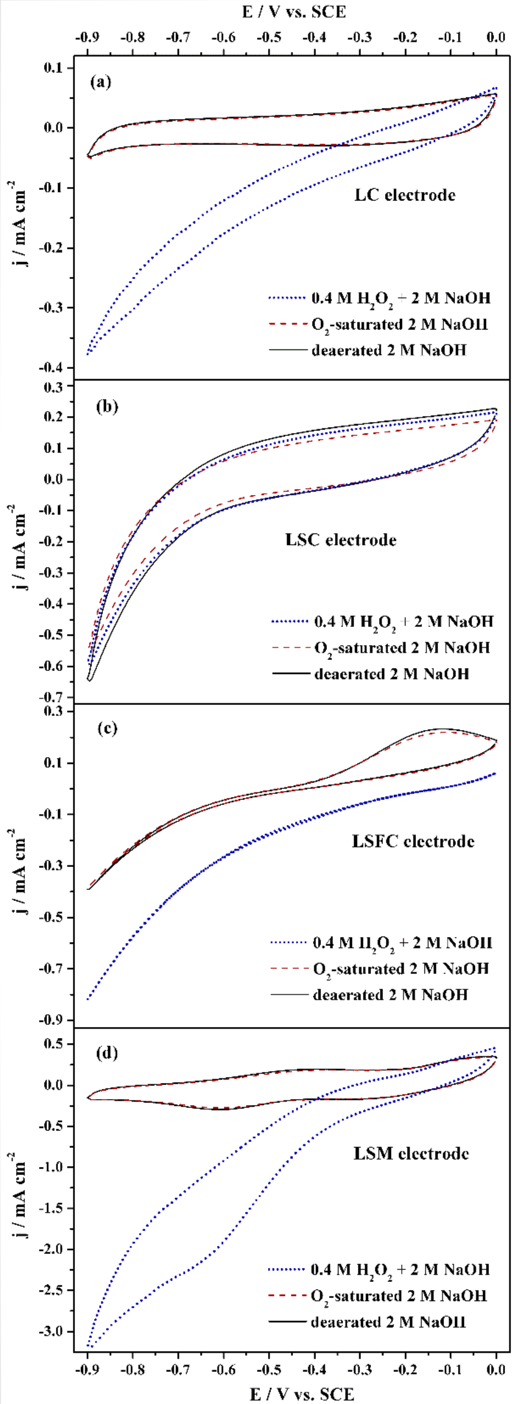


Pt_xM_y/C electrocatalysts



	Pt/C	$Pt_{0.75}Ni_{0.25}/C$	$Pt_{0.75}Co_{0.25}/C$
n	1.0	2.0	1.7
j_k, mA cm^{-2}	8	13	19
k x 10^3 mol^{-1}cm^{3}s^{-1}	7.4	11.2	11.8

A.L. Morais, J.R.C. Salgado, B. Šljukić, D.M.F. Santos, C.A.C. Sequeira, Int. J. Hydrogen Energy, 37, 14143-14151, 2012



ELECTROCATALYSTS for H_2O_2 REDUCTION

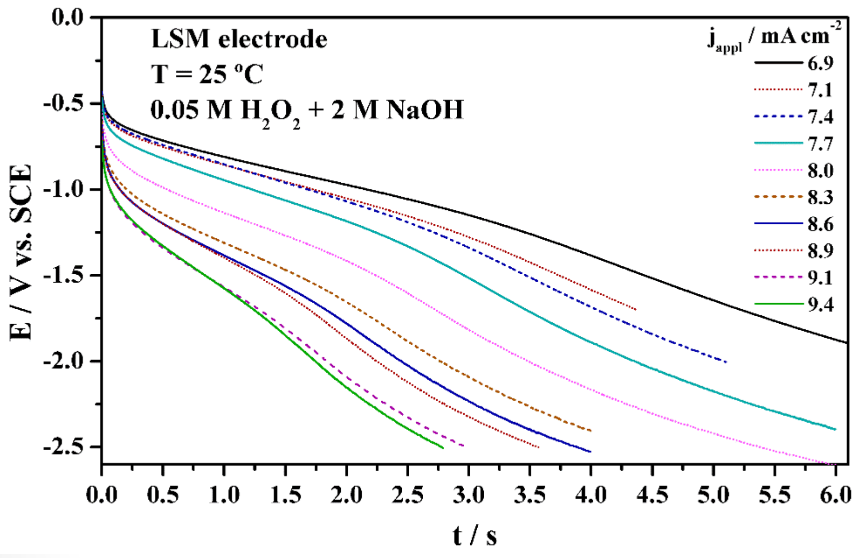
Perovskite oxide electrocatalysts

Studies in alkaline media

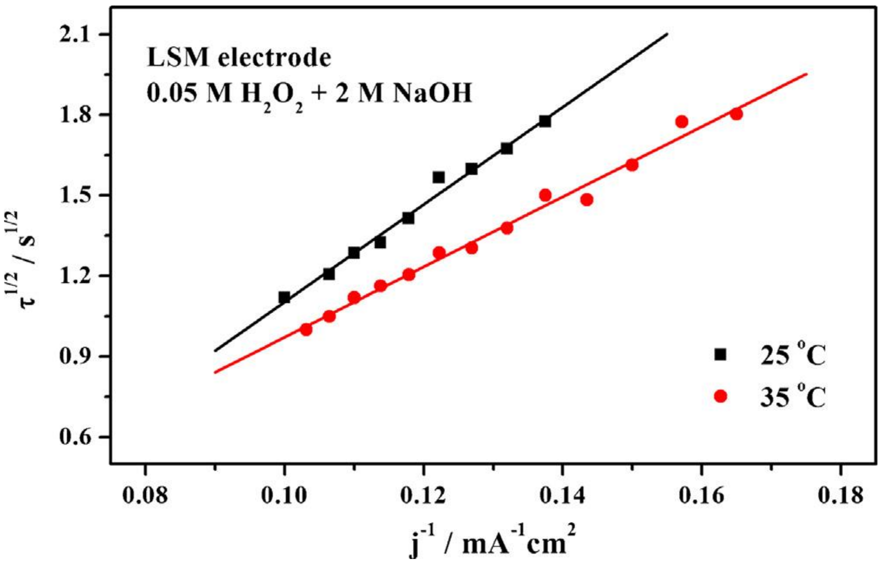
- ✓ $LaCoO_3$ (LC)
- ✓ $La_{0.84}Sr_{0.16}CoO_3$ (LSC)
- ✓ $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_3$ (LSCF)
- ✓ $La_{0.7}Sr_{0.3}MnO_3$ (LSM)

D.M.F. Santos, T.F.B. Gomes, B. Šljukić, N. Sousa, C.A.C. Sequeira, F.M.L. Figueiredo, Electrochim. Acta, 178, 163-170, 2015

ELECTROCATALYSTS for H_2O_2 REDUCTION



CP data for H_2O_2 reduction in LSM electrode at 25 ºC



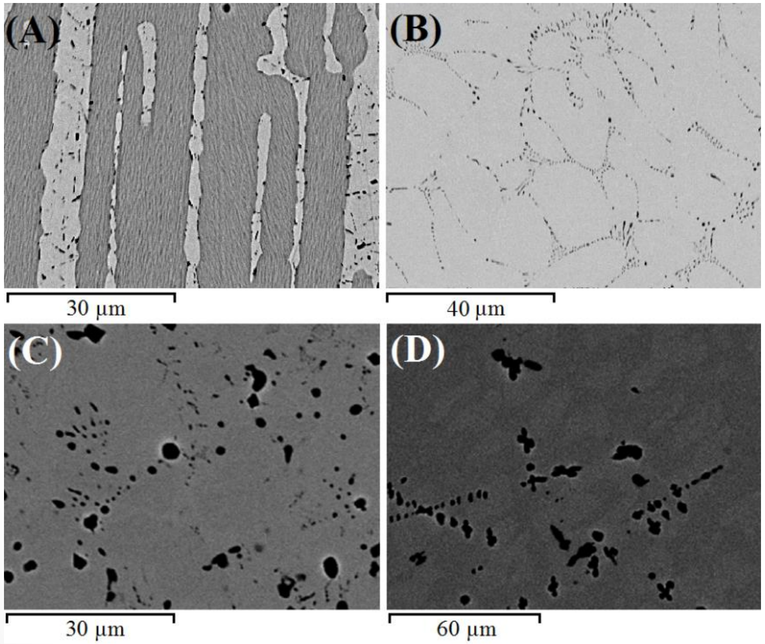
$\tau^{1/2}$ vs. j^{-1} plots for H_2O_2 reduction in LSM electrode

Sand equation $\tau^{1/2} = n F C (\pi D)^{1/2} / 2j$

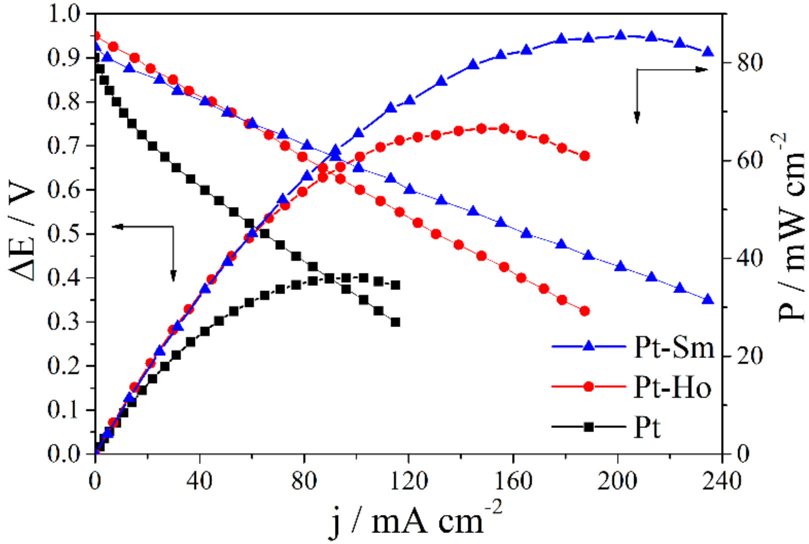
n = 0.8 at 25 °C

ELECTROCATALYSTS for H_2O_2 REDUCTION

Pt-RE electrocatalysts



SEM images of $Pt_{0.5}Sm_{0.5}$ (A), $Pt_{0.5}Ho_{0.5}$ (B), $Pt_{0.5}Dy_{0.5}$ (C) and $Pt_{0.5}Dy_{0.6}$ (D)



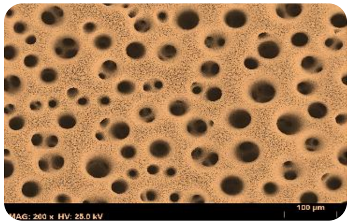
	n	P / mW cm^{-2}	E_{act} / kJ mol^{-1}
Pt	0.79	36	22
$Pt_{0.5}Ho_{0.5}$	1.22	67	19
$Pt_{0.5}Sm_{0.5}$	1.86	85	14

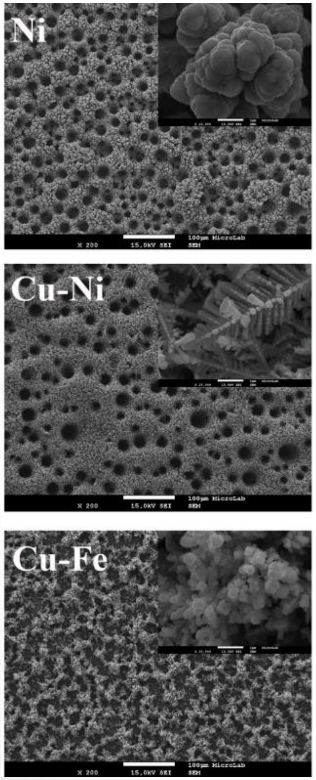
Pt-Dy showed no activity for HPRR

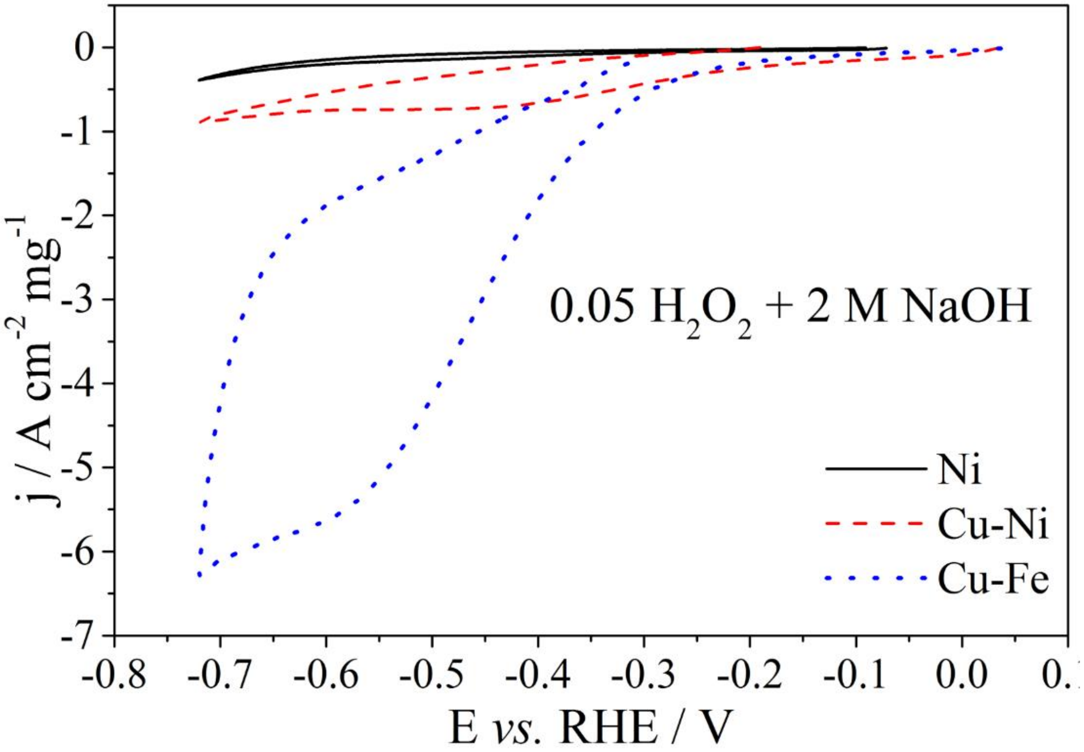
D.S.P. Cardoso, D.M.F. Santos, B. Šljukić, D.M.F. Santos, C.A.C. Sequeira, D. Macciò, A. Saccone, J. Power Sources, 307, 251-258, 2016

ELECTROCATALYSTS for H_2O_2 REDUCTION

Nanostructured 3D Cu-M (M = Fe, Ni) foams





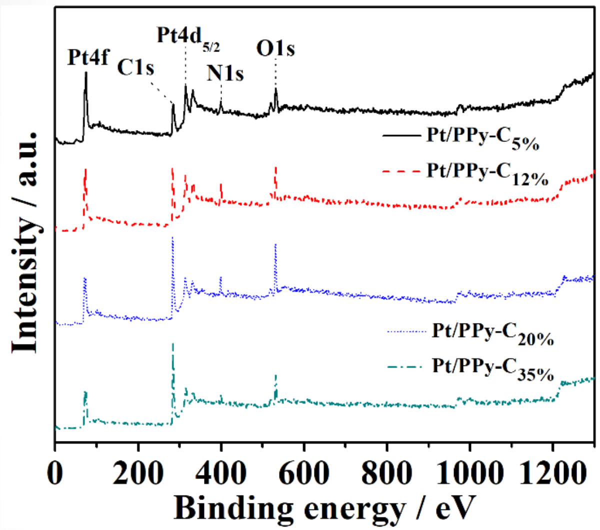


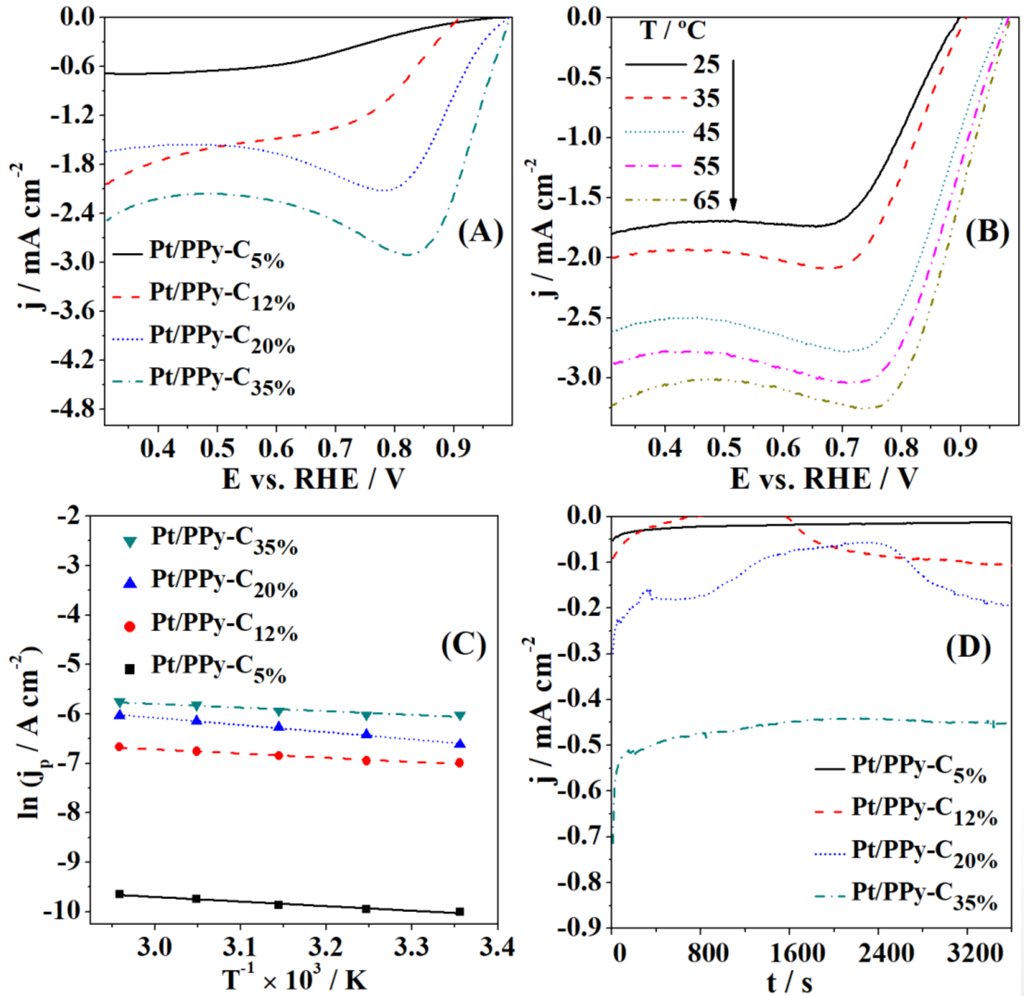
	n
Cu-Ni	0.96
Cu-Fe	1.12

S. Eugénio, D.S.P. Cardoso, D.M.F. Santos, B. Šljukić, M.F. Montemor, Int. J. Hydrogen Energy 41(32), 14370-14376, 2016

ELECTROCATALYSTS for H_2O_2 REDUCTION

Four **Pt/PPy-C electrocatalysts** with different amounts of carbon



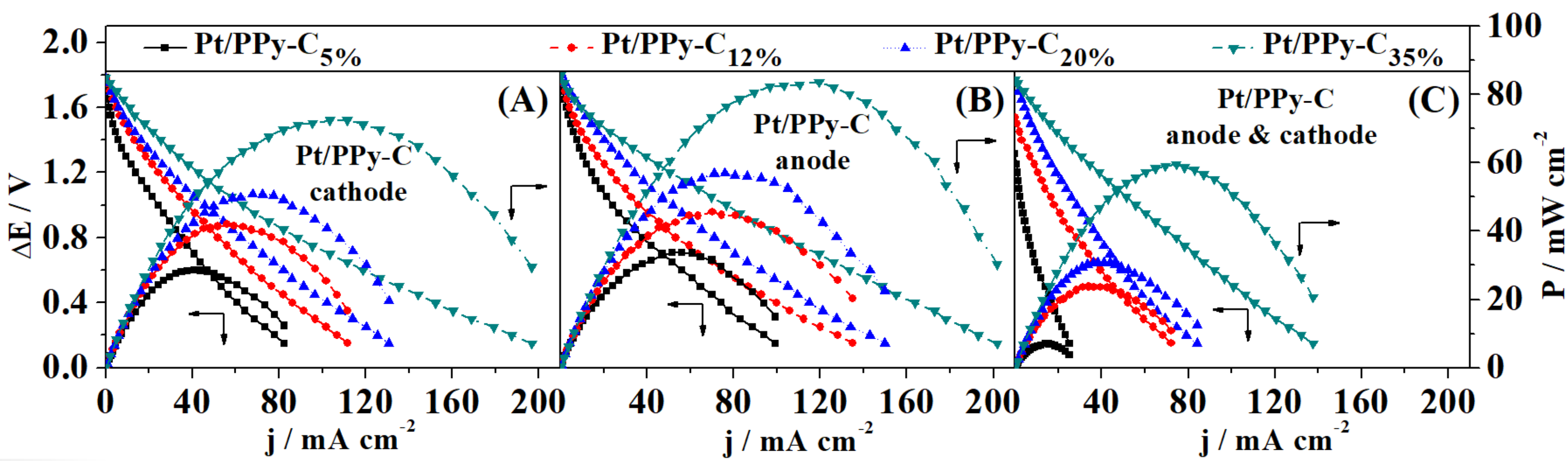


Electrocatalyst	n	E_a / kJ mol^{-1}	α
Pt/PPy-$C_{5\%}$	/	14	0.83
Pt/PPy-$C_{12\%}$	1.0	8	0.66
Pt/PPy-$C_{20\%}$	1.0	11	0.75
Pt/PPy-$C_{35\%}$	**2.0**	8	0.77

R.C.P. Oliveira, J. Milikić, E. Daş, A.B. Yurtcan, D.M.F. Santos, B. Šljukić, Appl. Catal. B, 2018 (in press)

DIRECT BOROHYDRIDE FUEL CELLS

Following the fundamental studies, the developed catalysts need to be tested in practical lab-scale borohydride fuel cells



Polarization and power density curves at room temperature for DBPFC laboratory test using: (A) Pt/PPy-C$_{x\%}$ (x = 5, 12, 20 or 35) cathode and Pt mesh anode; (B) Pt/PPy-C$_{x\%}$ anode and Pt mesh cathode; (C) Pt/PPy-C$_{x\%}$ as both anode and cathode.

R.C.P. Oliveira, J. Milikić, E. Daş, A.B. Yurtcan, D.M.F. Santos, B. Šljukić, Appl. Catal. B, 2018 (in press)

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for YOUR ATTENTION!