5. Электрокатализ – окисление мочевины

Выделение кислорода на оксидах и окисленных металлах

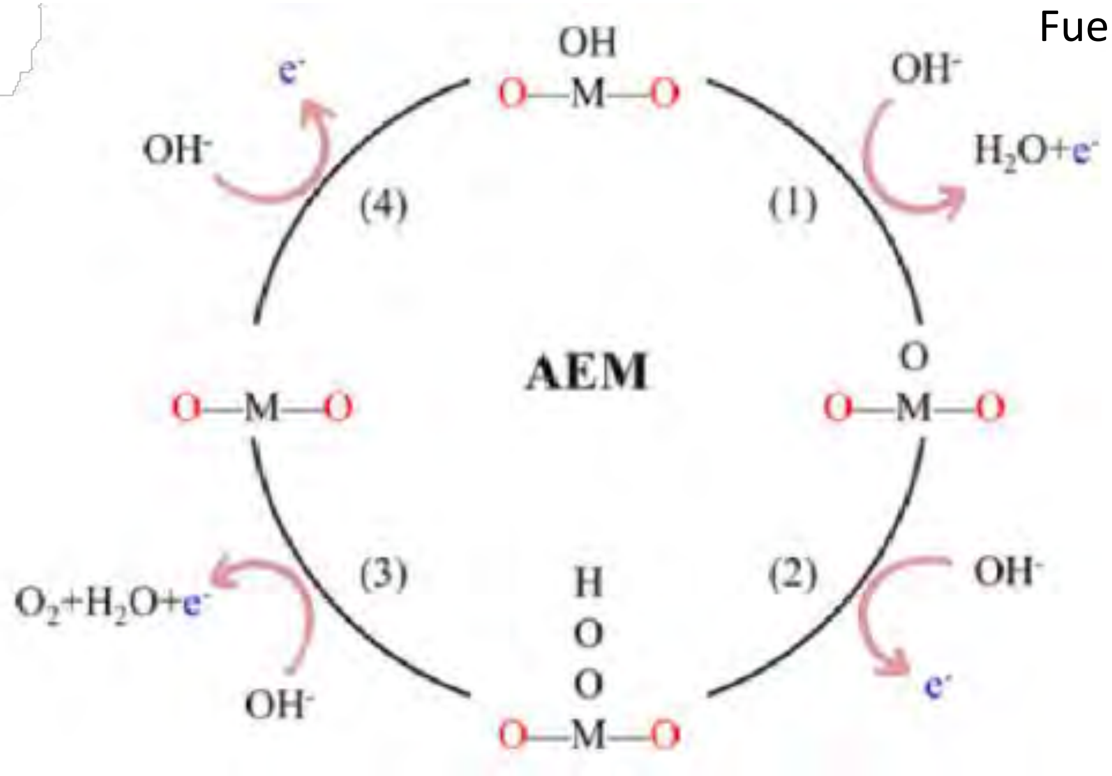
Оксидно-никелевый электрод – выделение кислорода и окисление органики

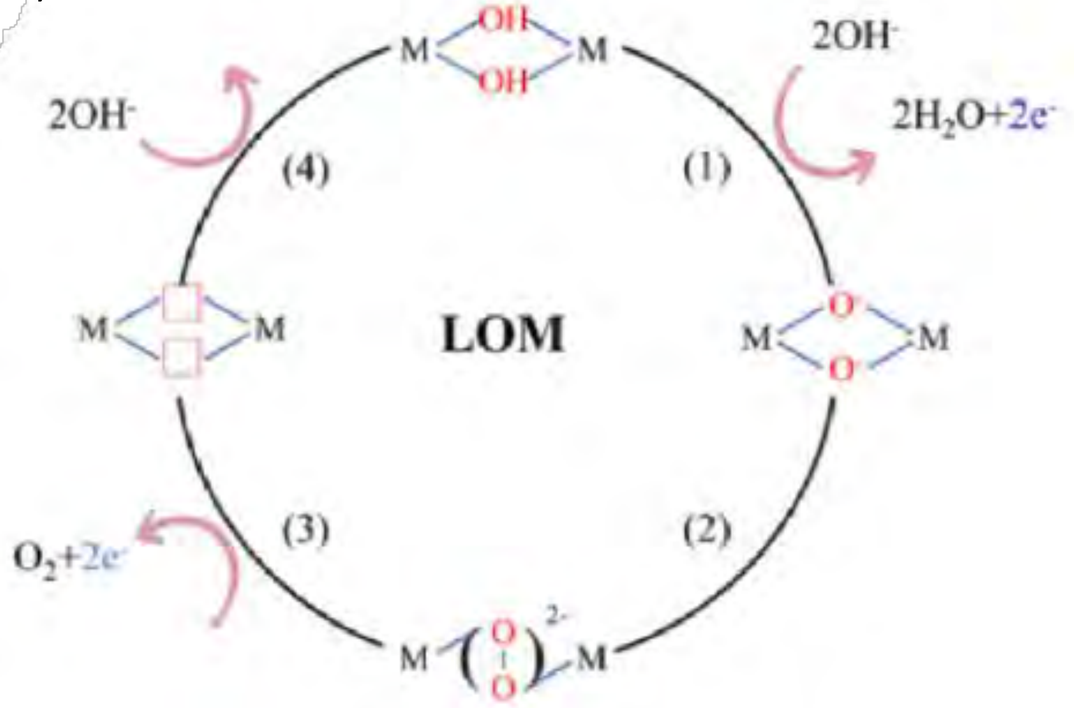
Стадийные схемы окисления мочевины

Попытки создания мочевинных топливных элементов

OER: схемы <механизмы> adsorbate evolution (AEM) и lattice oxygen oxidation (LOM)

Fuel 369 (2024) 131741





Доклады АН СССР 111 (1956) 637-639

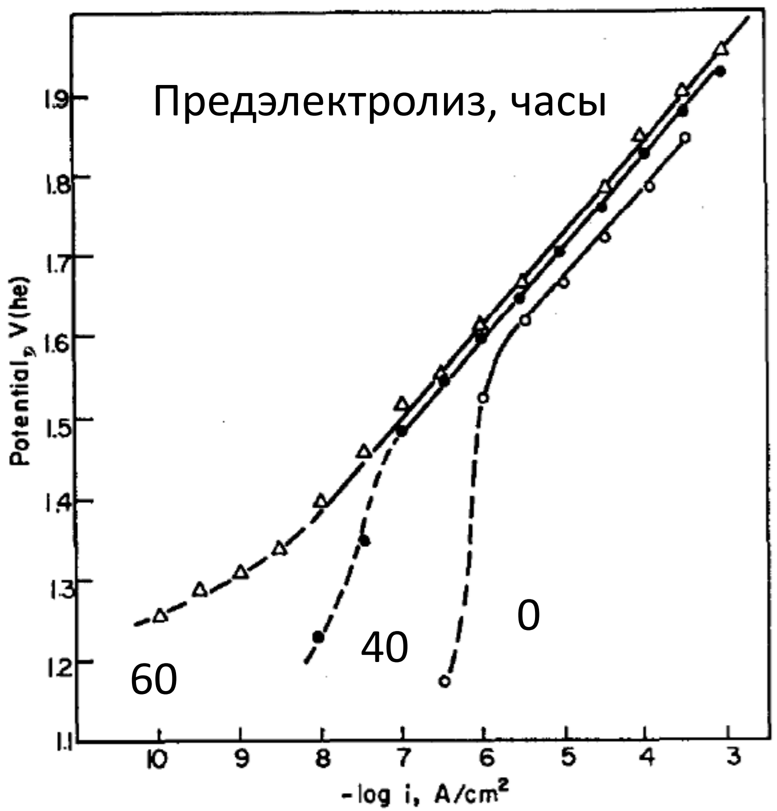
<Ag: Ж. физ. хим. 35 (1961) 2670-2675>

К. И. РОЗЕНТАЛЬ и В. И. ВЕСЕЛОВСКИЙ

ИЗУЧЕНИЕ МЕХАНИЗМА ЭЛЕКТРОХИМИЧЕСКОГО ВЫДЕЛЕНИЯ КИСЛОРОДА НА ПЛАТИНОВОМ ЭЛЕКТРОДЕ С ПОМОЩЬЮ ИЗОТОПА КИСЛОРОДА O^{18} <изотоп в оксиде>

$$Pt\text{-}PtO[O] + H_2O = Pt\text{-}PtO + O_2 + 2H^+ + 2e$$

OER: механизм на платине



Критерии для выбора из 14(!) возможных стадийных схем

SUMMARY OF DIAGNOSTIC CRITERIA

Diagnostic criteria	Anodic		Cathodic	
	acid	alkaline	acid	alkaline
$\frac{\partial \eta}{\partial \ln i}$	$2RT/F$[6,19,25–28,40,41]	RT/F[7,19] at low η $2RT/F$ at high η	$2RT/F$[8,19]	RT/F[7,19]
$\frac{\partial \eta}{\partial \mathrm{pH}}$	30[6] mV	−110 mV at high η −65 mV at low η	0	−30 mV
$\left(\frac{\partial \ln i}{\partial \ln p_{O_2}}\right)_\eta$	0·14	0·22	*ca* 0·30	*ca* 0·24
ν	~3·6[6] ~3·5	~2[7] ~1·8		

- Изменение состояния электрода
- Переход к другой стадийной схеме
- Изменение природы медленной стадии
- Изменение заполнения поверхности интермедиатом

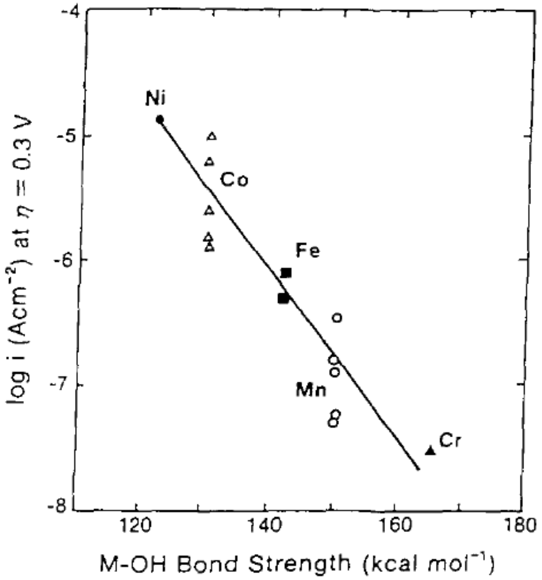
→ Два тафелевских участка

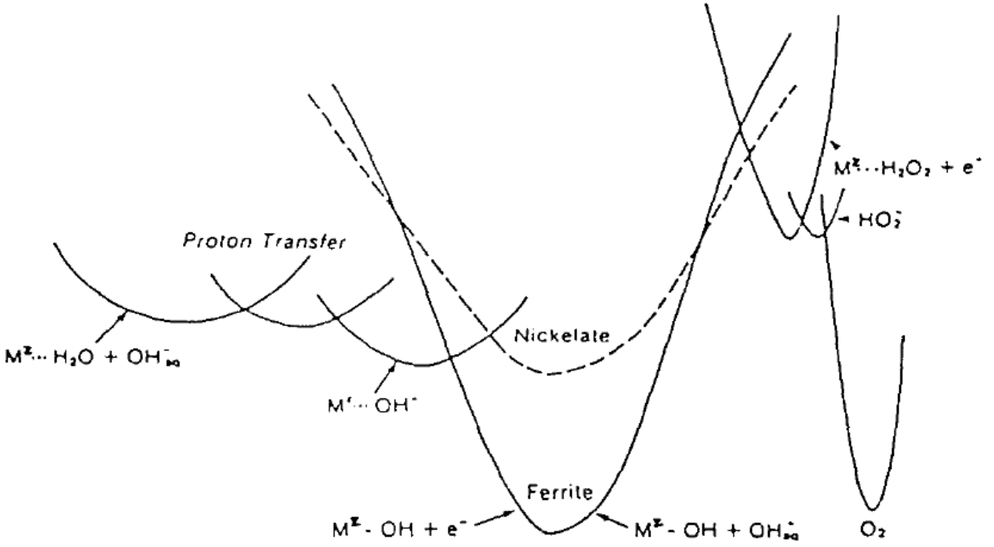
Electrochim. Acta 11 (1966) 791-814; J. Chem. Phys. 24 (1956) 817-827

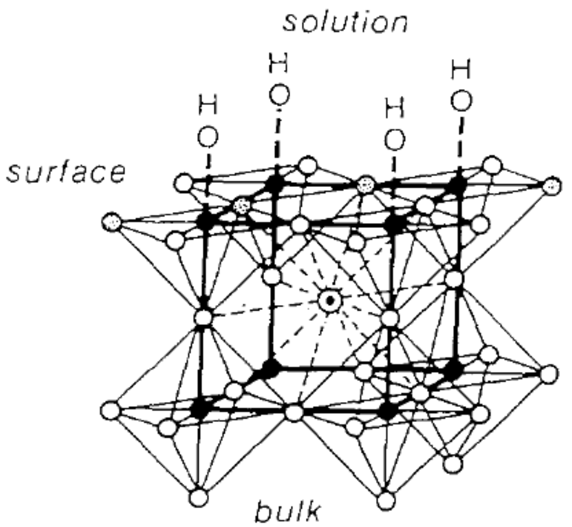
OER, перовскиты

Int. J. Hydrogen Energy 17 (1992) 423-444

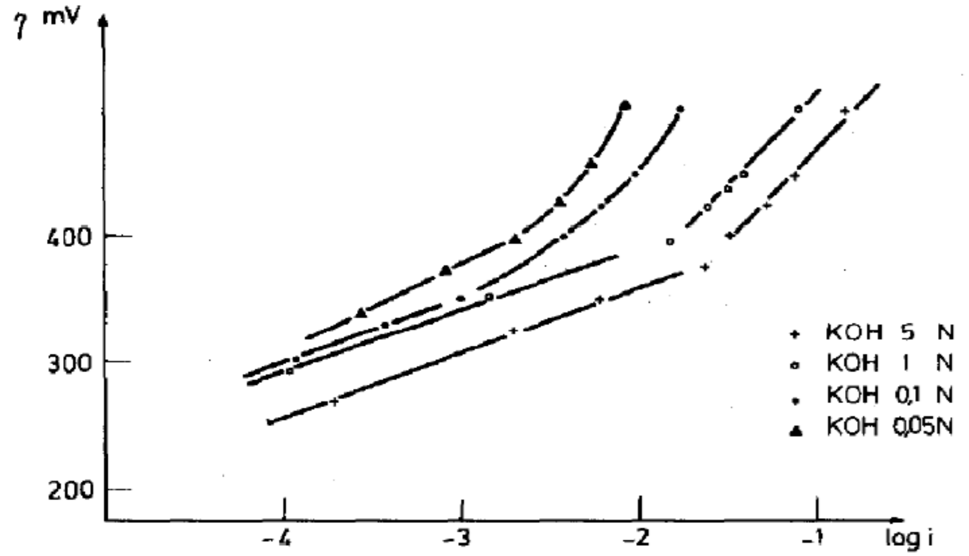
		Langmuir				Temkin				
		$\partial V/\partial \ln i$		$(\partial \ln i/\partial \ln C_{OH^-})_{V,\zeta}$ [c]		$\partial V/\partial \ln i$				
rate-determining step	ν [b]	$\theta \to 0$	$\theta \to 1$	$\theta \to 0$	$\theta \to 1$	NA [d]	A [e]	NA [d]	A [e]	condition
(I) Bockris's Oxide Path										
1. $M + OH^- \to MOH + e^-$	4	$2RT/F$		1						
2. $2MOH \to MO + M + H_2O$	2	$RT/2F$	∞	2	0	$2RT/F$		0.5		$r_{OH} \sim r_O$
						RT/F		1		$r_{OH} >> r$
3. $2MO \to 2M + O_2$	1	$RT/4F$	∞	4	0	$RT/2F$	RT/F	2	1	$K_2 \sim 1$
						$RT/4F$	$RT/3F$	2	1	$K_2 << 1$
(II) Bockris's Electrochemical Path										
1. $M + OH^- \to MOH + e^-$	2	$2RT/F$		1						
2. $MOH + OH^- \to MO + H_2O + e^-$	2	$2RT/3F$	$2RT/F$	2	1	$2RT/F$		1		$r_{OH} \sim r_O$
						RT/F		1.5		$r_{OH} >> r$
3. $2MO \to 2M + O_2$	1	$RT/4F$	∞	4	0	$RT/2F$	RT/F	2	1	$K_2 \sim 1$
						$RT/4F$	$RT/3F$	4	3	$K_2 << 1$

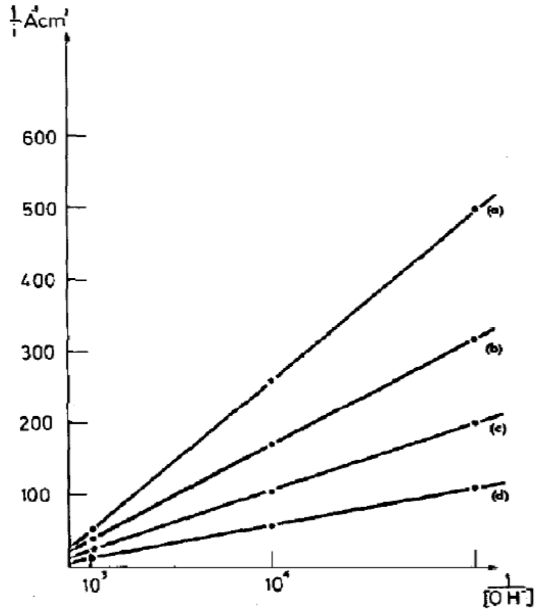






OER, никель





$$OH^- \rightleftharpoons OH_{ads} + e^-$$

$$OH_{ads} + OH^- \rightleftharpoons O^-_{ads} + H_2O$$

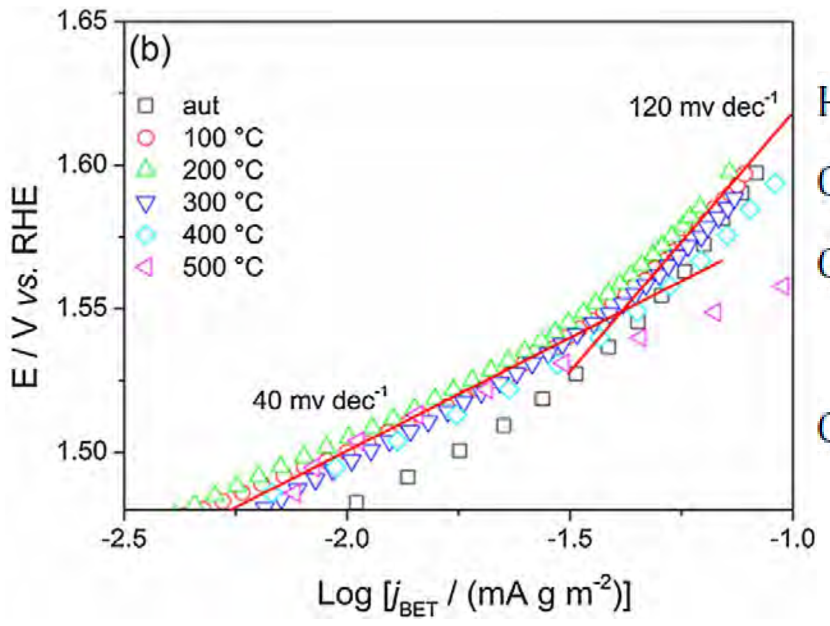
$$O^-_{ads} \rightleftharpoons O_{ads} + e^-$$

$$2O_{ads} \rightleftharpoons O_2$$

Electrochim. Acta 25 (1980) 973-976

OER, иридий и рутений

Catal. Today 262 (2016) 170-180



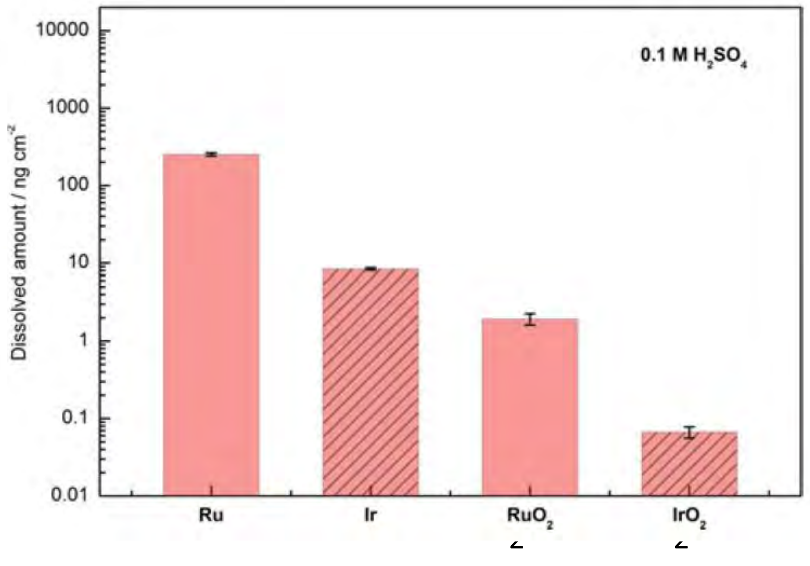
$$H_2O + * \rightleftharpoons OH_{ad} + H^+ + e^- (120\,mV\,dec^{-1}),$$

$$OH_{ad} \rightleftharpoons O_{ad} + H^+ + e^- (40\,mV\,dec^{-1}),$$

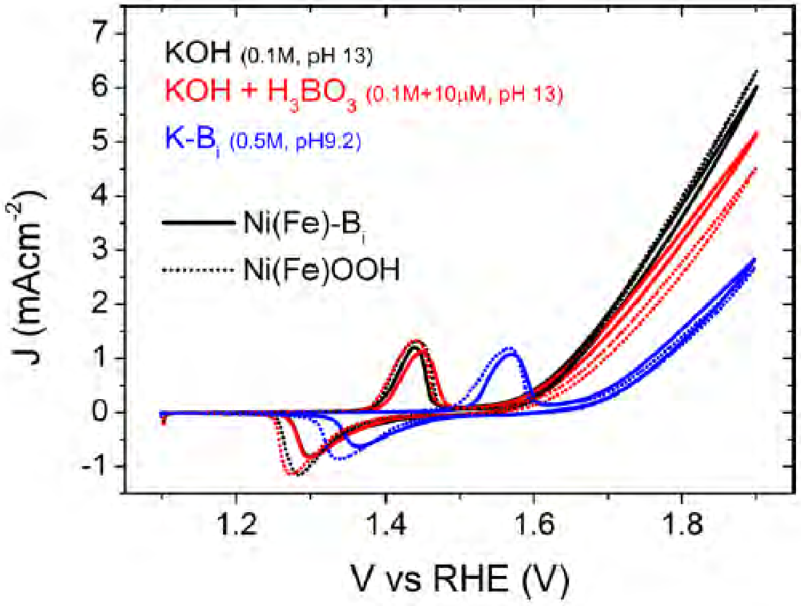
$$O_{ad} + H_2O \rightleftharpoons OOH_{ad} + H^+ + e^-,$$

$$OOH_{ad} \rightleftharpoons * + O_2 + H^+ + e^-$$

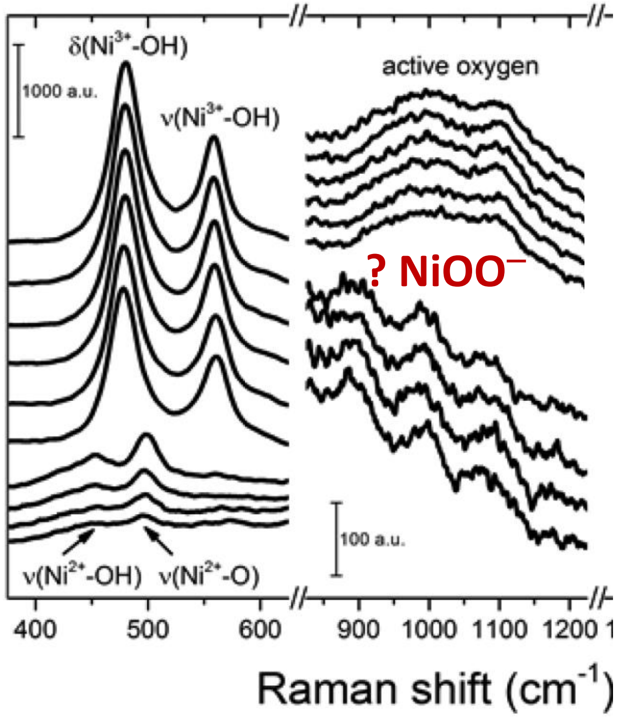
Appl. Catal. B 218 (2017) 287-297

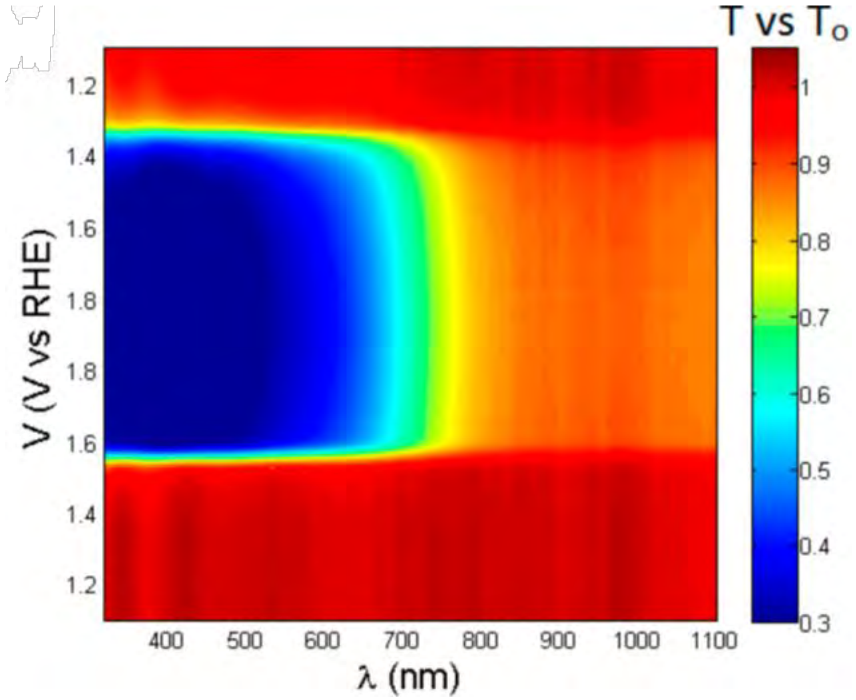


OER, катализаторы: метагидроксид и борат (B_i) Ni/Fe на подложке FTO – ‘active oxygen’ интермедиат



J. Amer. Chem. Soc. 137 (2015) 15112-15121

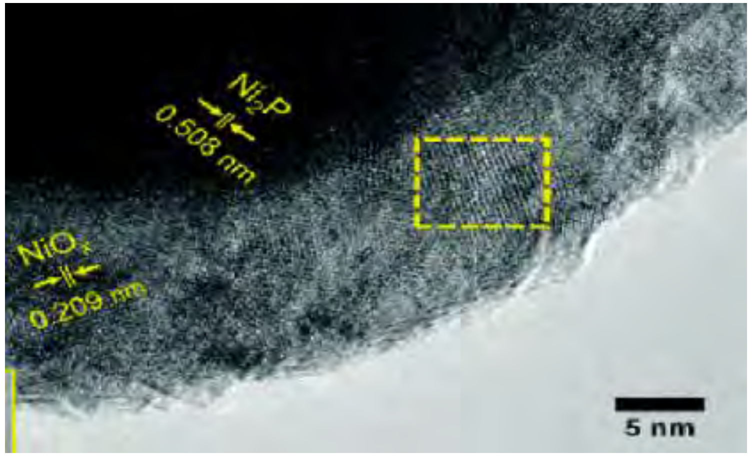


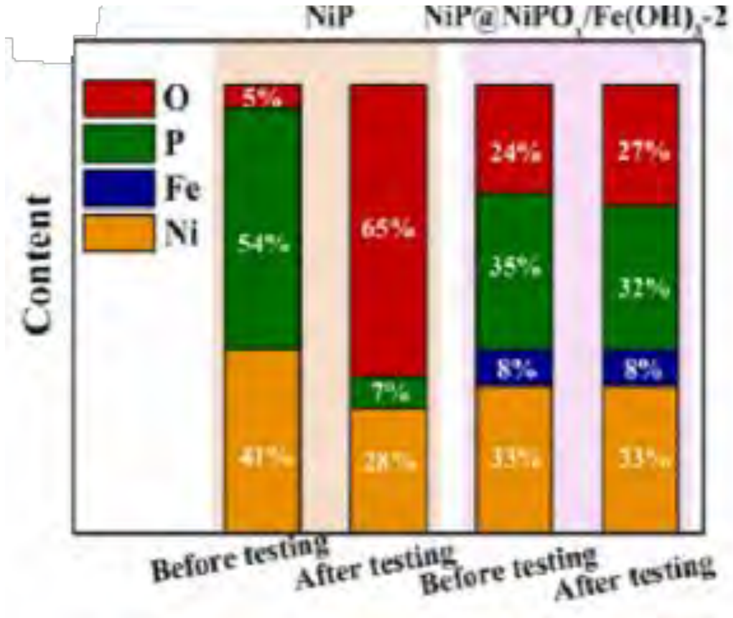


OER, другие Ni-содержащие катализаторы

Фосфиды переходных металлов (как и все кроме оксидов) в поверхностном слое становятся оксидами

Fuel 369 (2024) 131741



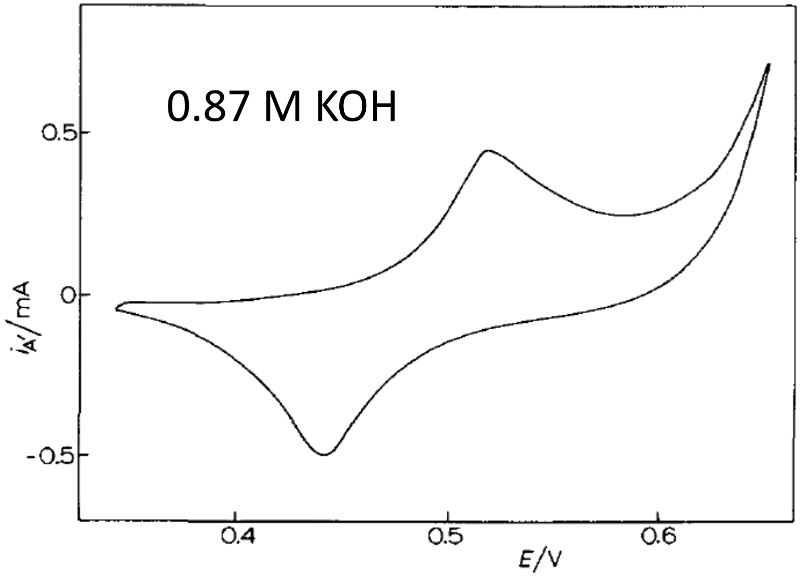


Окисление органики на никеле

THE OXIDATION OF ORGANIC COMPOUNDS AT A NICKEL ANODE IN ALKALINE SOLUTION

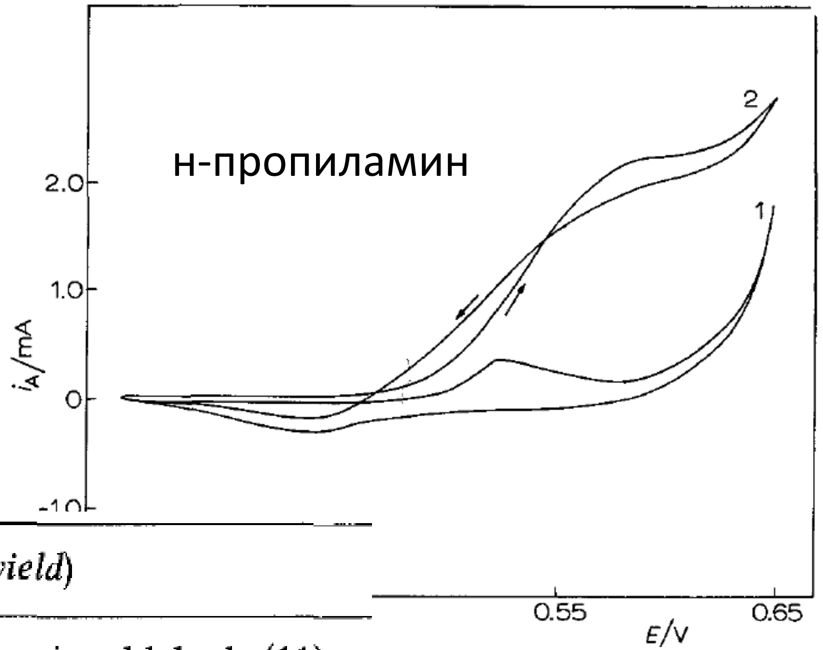
J. Electroanal. Chem. 31 (1979) 39-49

M. FLEISCHMANN, K. KORINEK AND D. PLETCHER
Department of Chemistry, The University, Southampton (England)

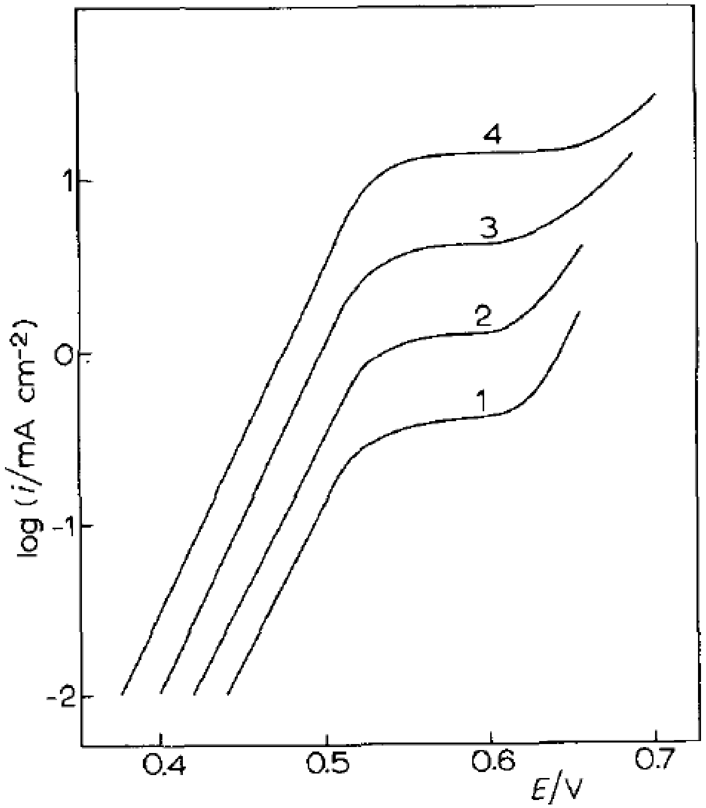


Potential vs. HgO/Hg

н-пропиламин



н-бутиламин, разные концентрации



Substrate	*Product (% current yield)*
n-propylamine	ethyl cyanide (84), propionaldehyde (11)
n-butylamine	propyl cyanide (85), n-butyraldehyde (6)
isopropylamine	acetone (80)
diethylamine	acetonitrile (40)
ethanol	acetic acid (98)
propanol	propionic acid (95)
isopropanol	acetone (90)
pyrrolidine	trimer of 1-pyrroline

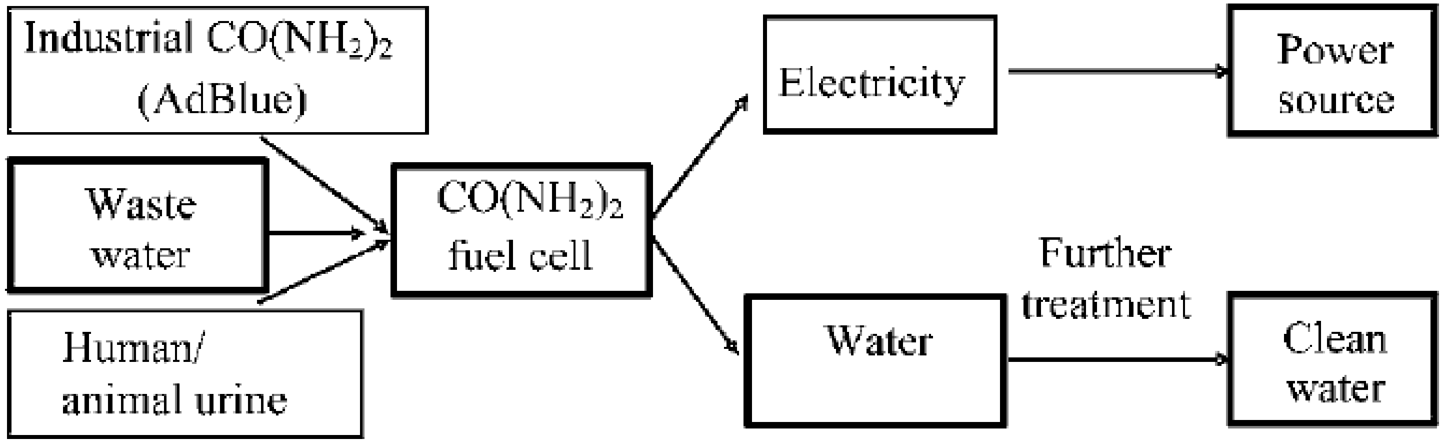
$$Ni(OH)_2 \xrightarrow{\text{fast}} NiO(OH) + e + H^+$$

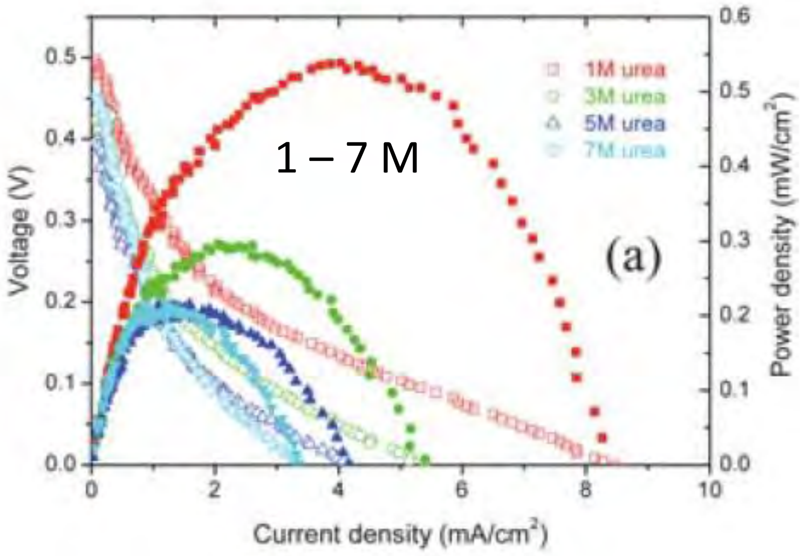
$$NiO(OH) + \text{organic compound} \xrightarrow{\text{slow}} Ni(OH)_2 + \text{product}$$

A direct urea fuel cell – power from fertiliser and waste†

Energy Environ. Sci. 3 (2010) 438–441

Rong Lan,[a] Shanwen Tao*[a] and John T. S. Irvine[b]

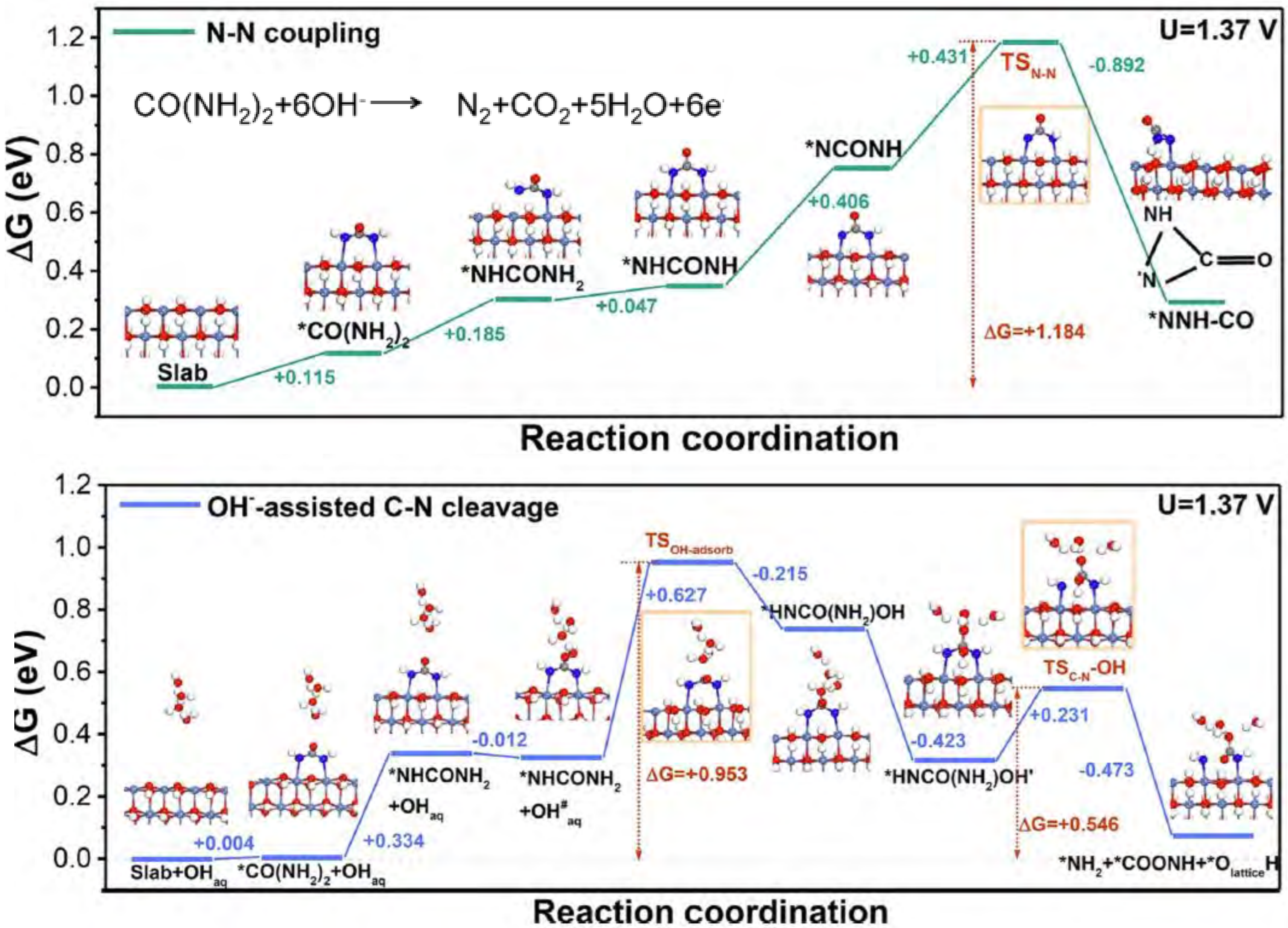




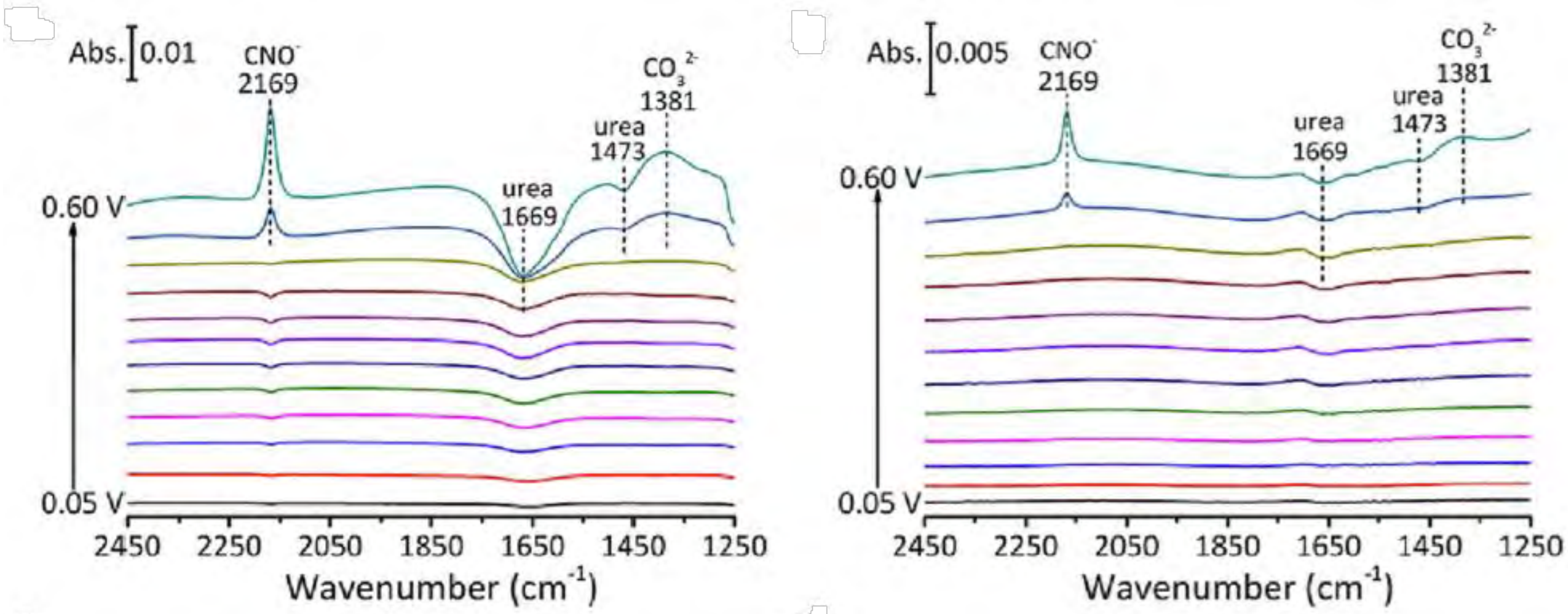
$$O_2 + 2H_2O + 4e' \rightarrow 4OH^- \text{(cathode reaction) } E^0 = +0.40V$$

$$CO(NH_2)_2 + 6OH^- \rightarrow N_2 + CO_2 + 5H_2O + 6e' \text{(anode reaction)}$$
$$E^0 = -0.746V$$

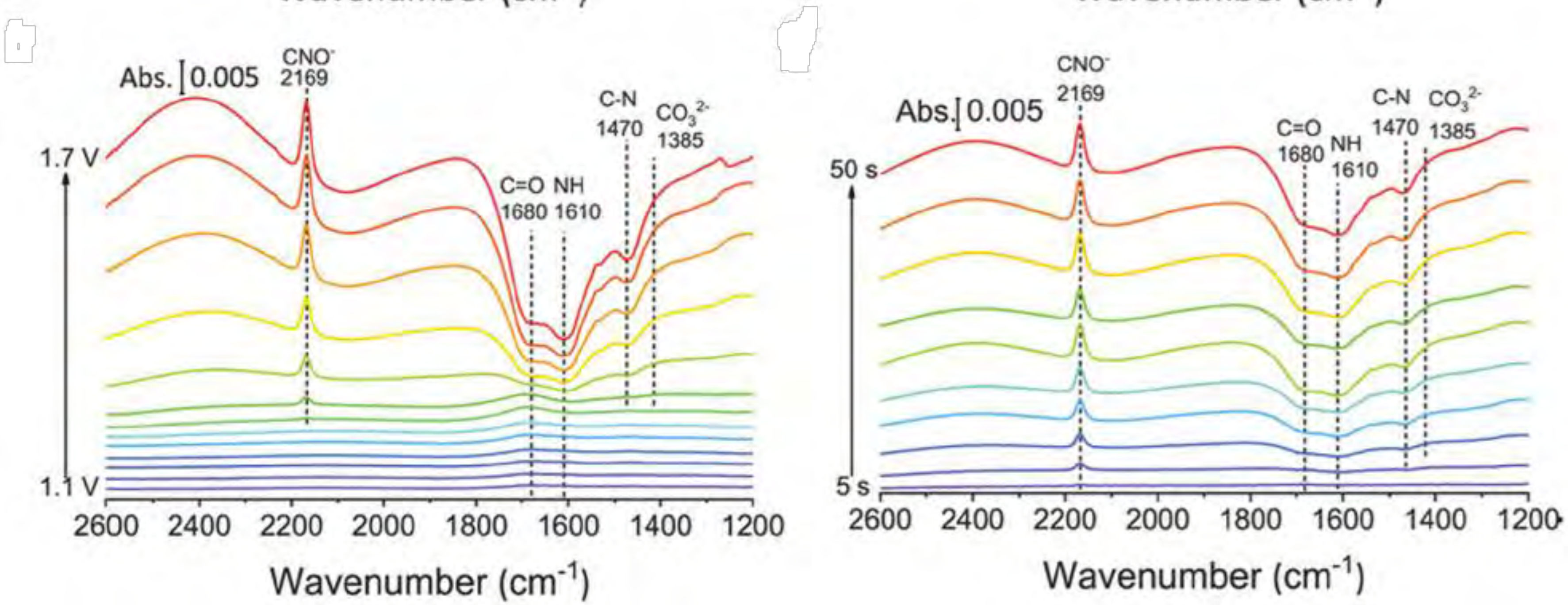
$$2CO(NH_2)_2 + 3O_2 \rightarrow 2N_2 + 2CO_2 + 4H_2O \text{(overall reaction)}$$
$$E^0 = +1.146V$$



Surfaces and Interfaces 41 (2023) 103230

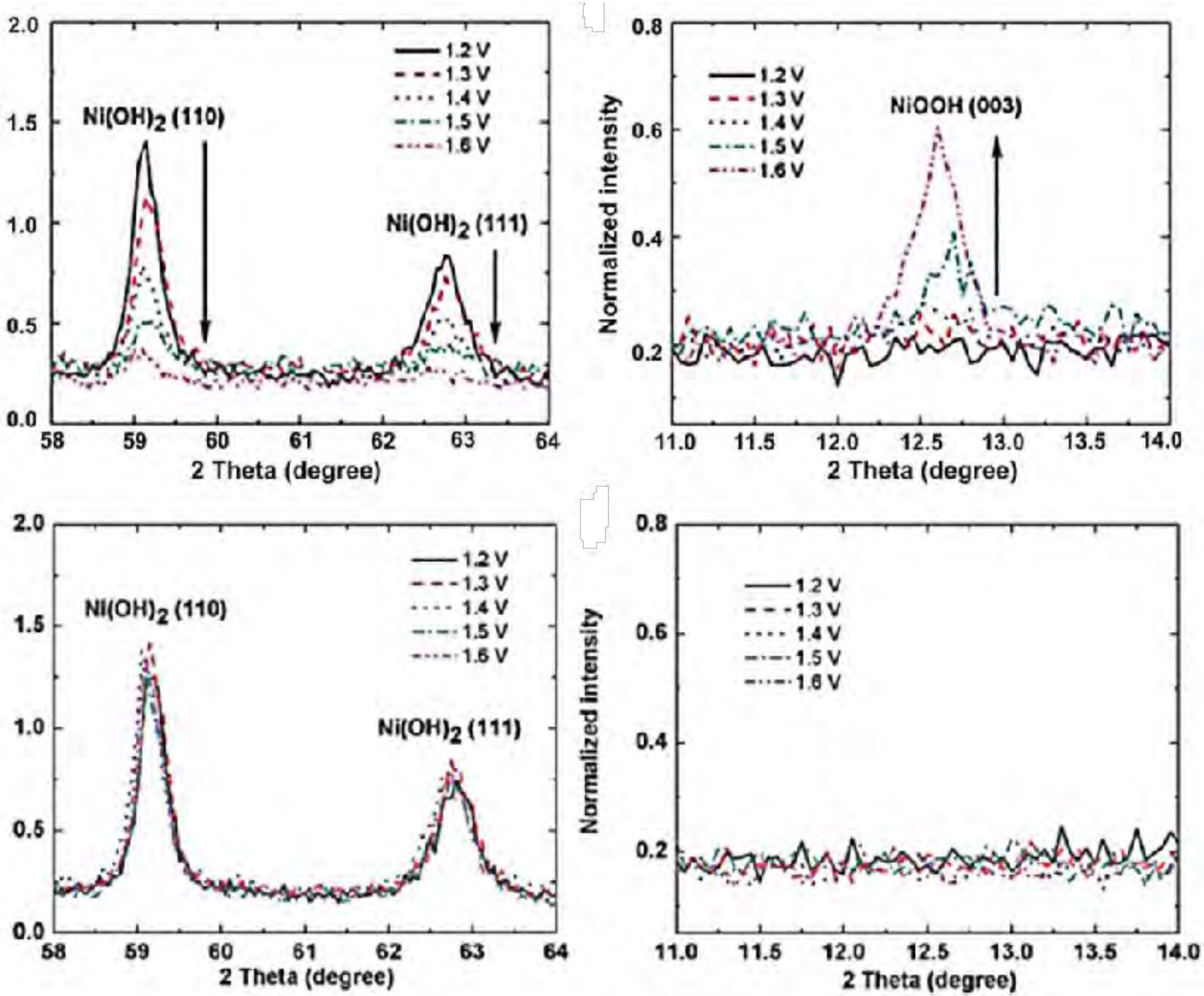


N-N coupling,
amorphous $NiWO_4$



C-N cleavage,
Fe-Co selenide/Fe-Co
double hydroxide

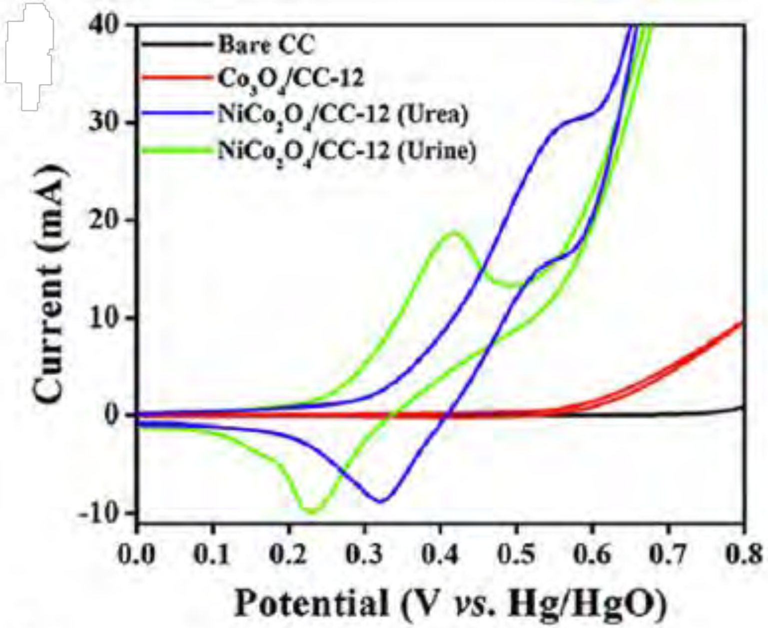
Surfaces and Interfaces
41 (2023) 103230

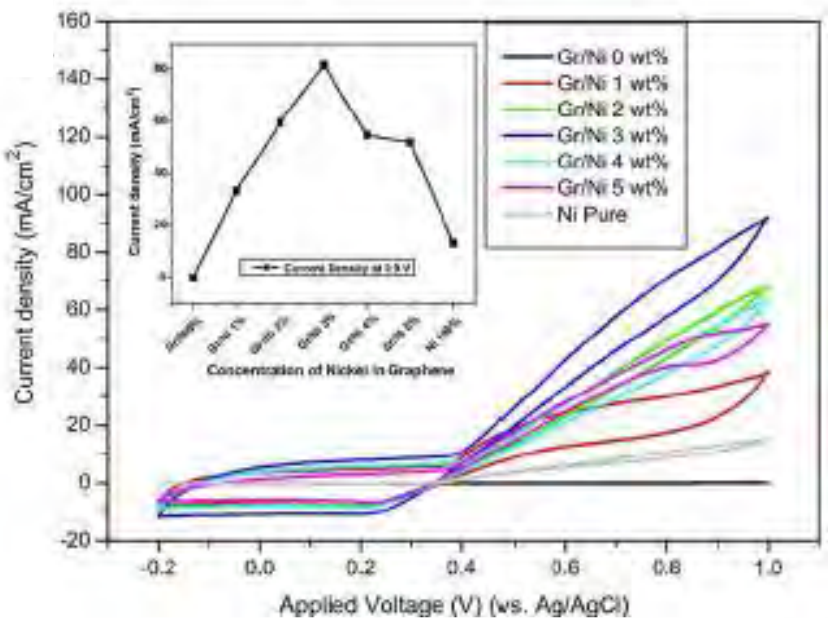


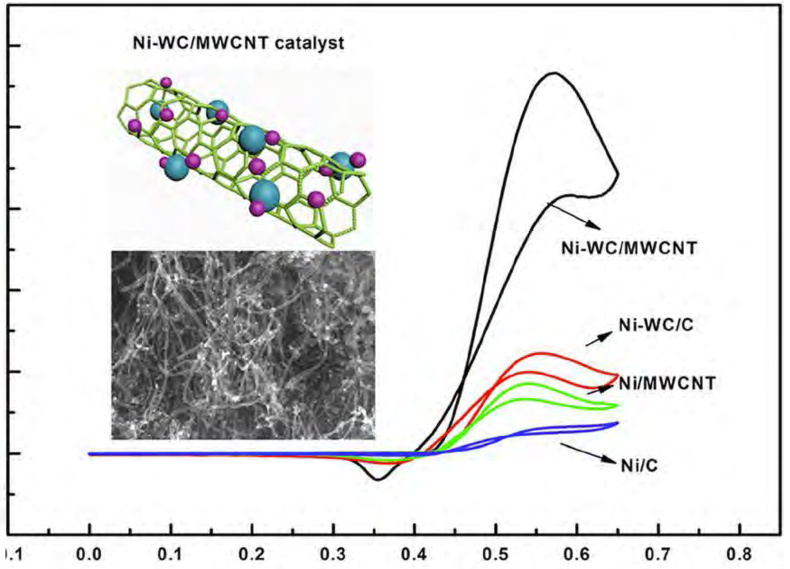
5 M KOH

5 M KOH + мочевина

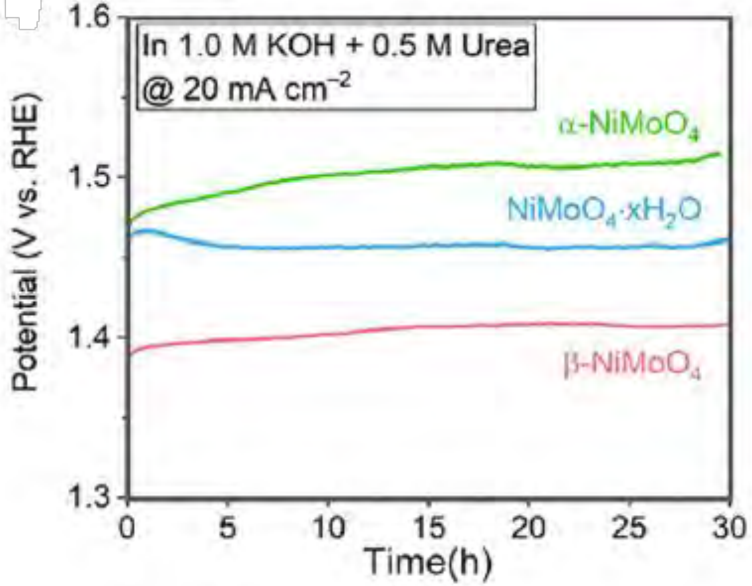
Surfaces and Interfaces 41 (2023) 103230

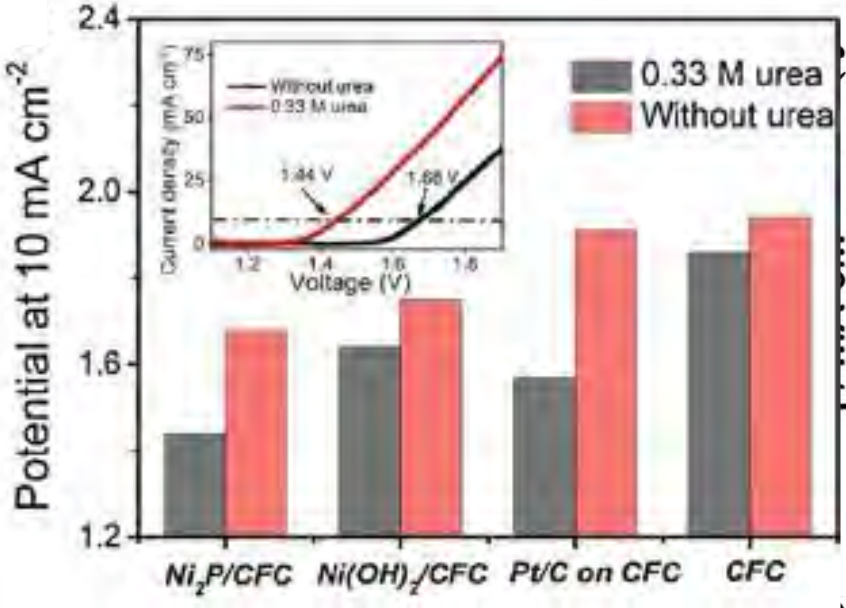


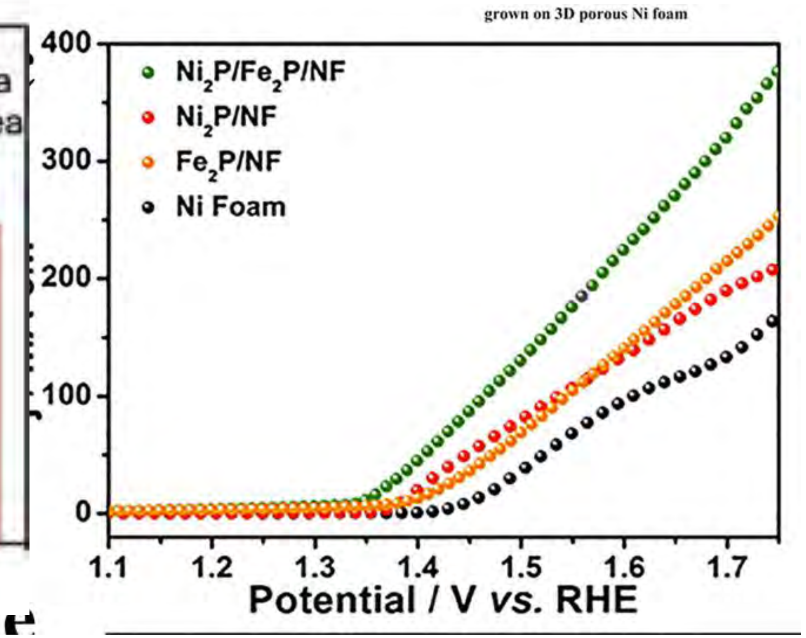




Surfaces and Interfaces 41 (2023) 103230

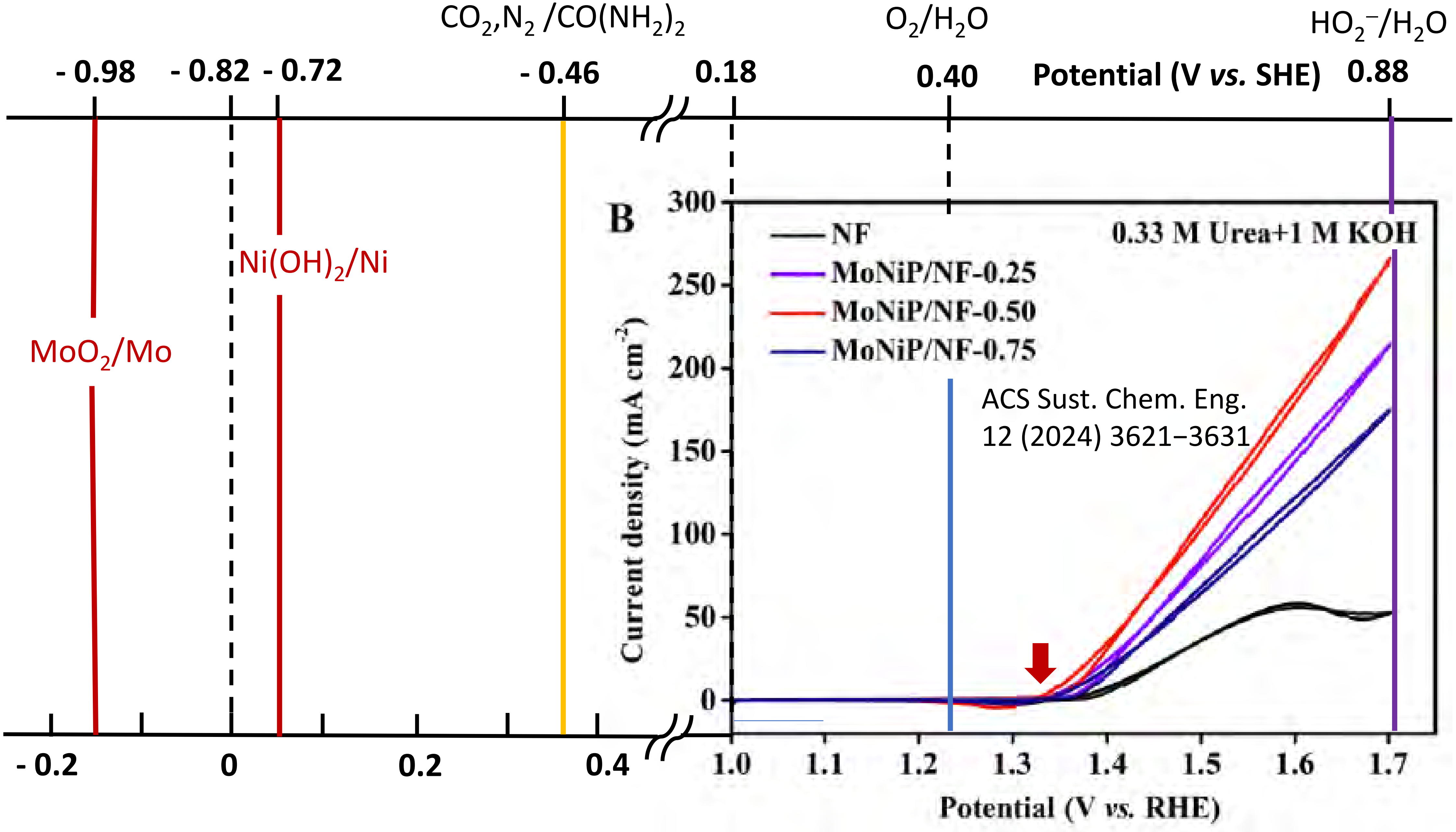




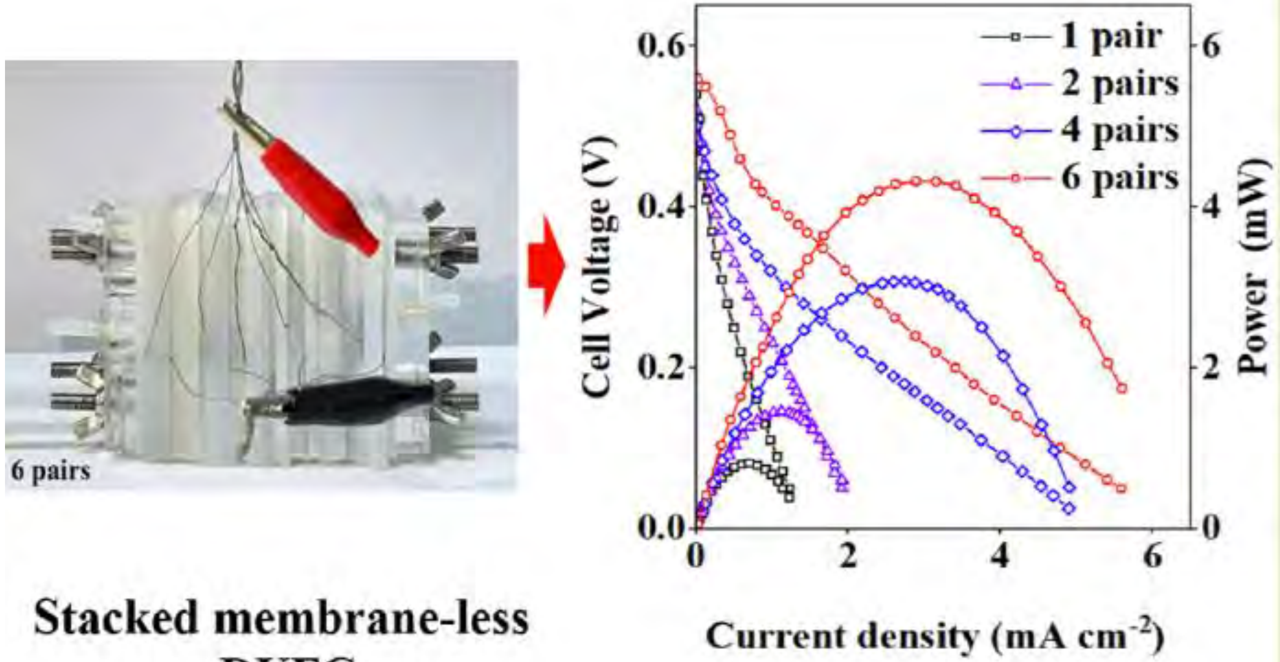


Ionics 29 (2023) 2969–2987

Окисление метанола и вообще органики: типичная ошибка при «поиске новых катализаторов»

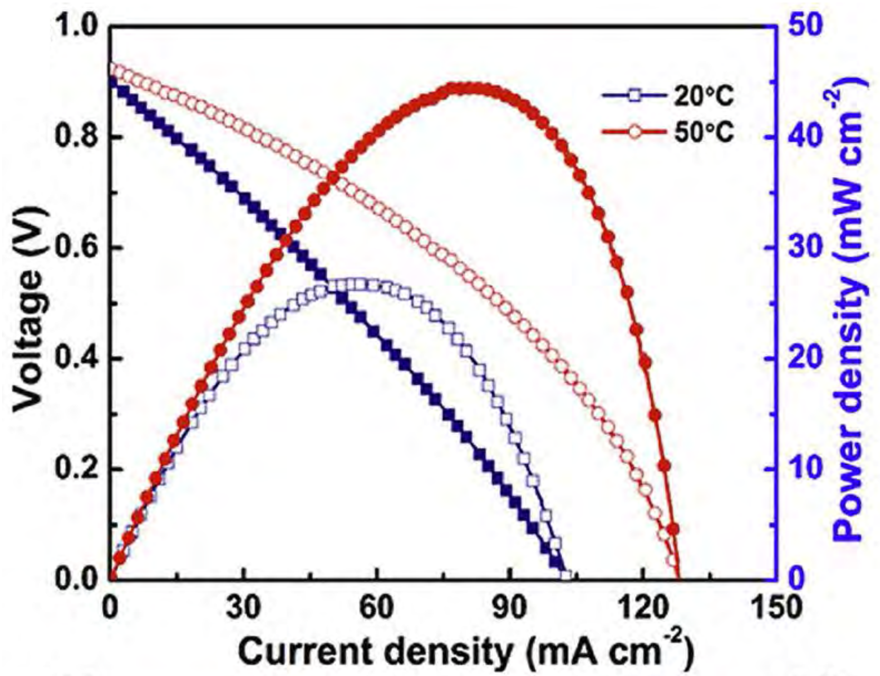


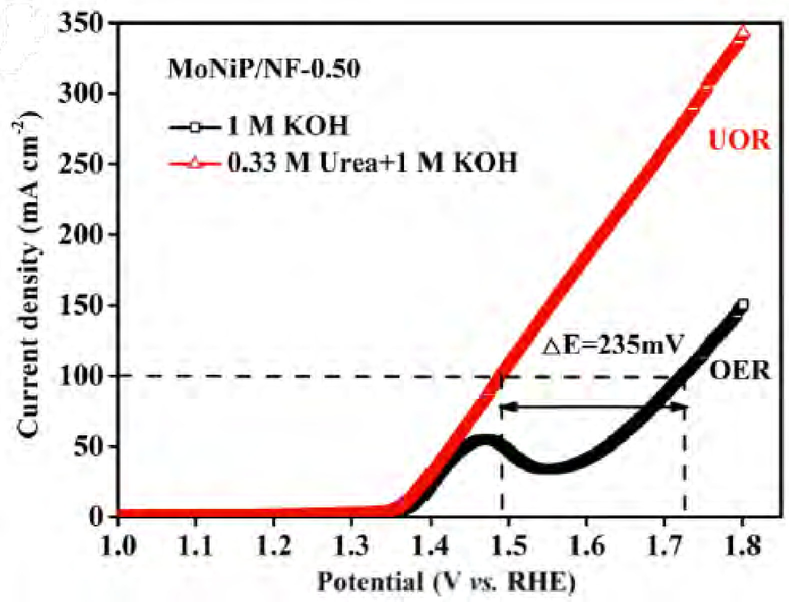
ORR

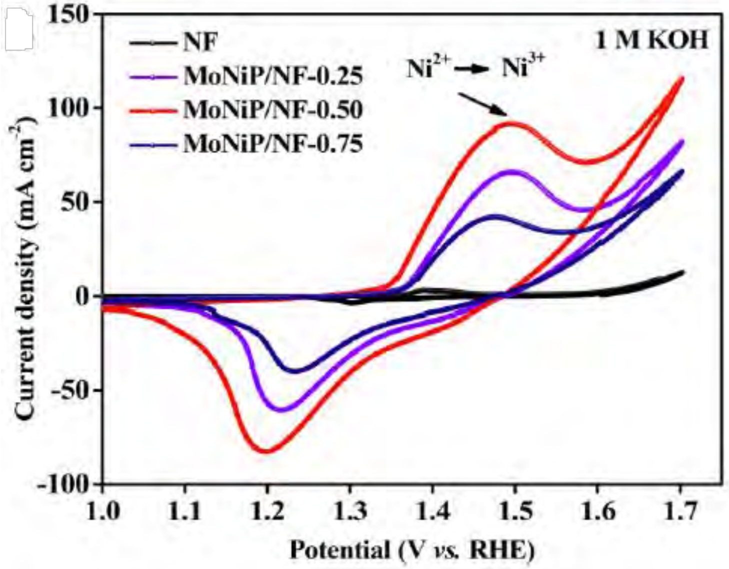


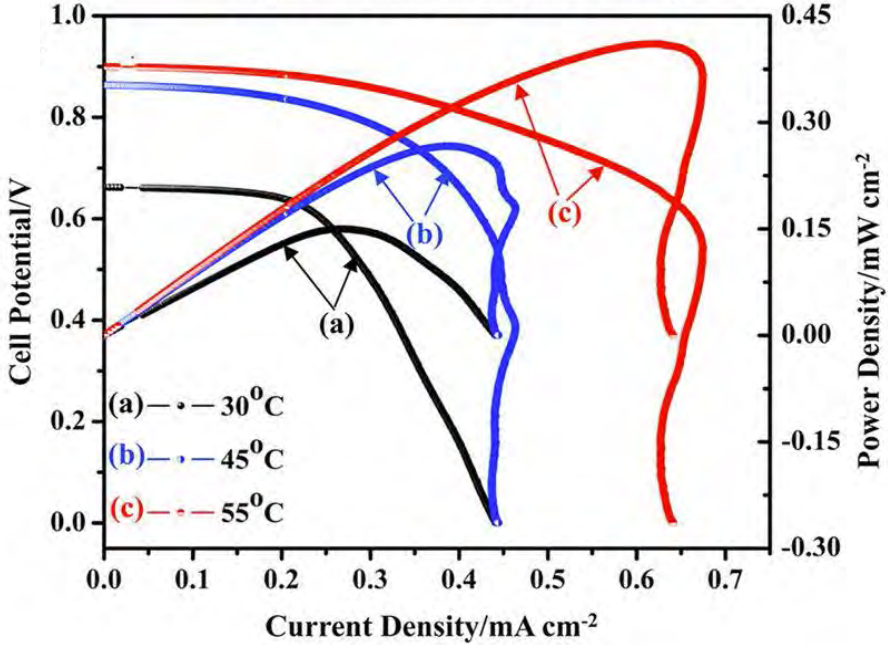
Stacked membrane-less DUFC

ACS Sust. Chem. Eng. 12 (2024) 3621−3631



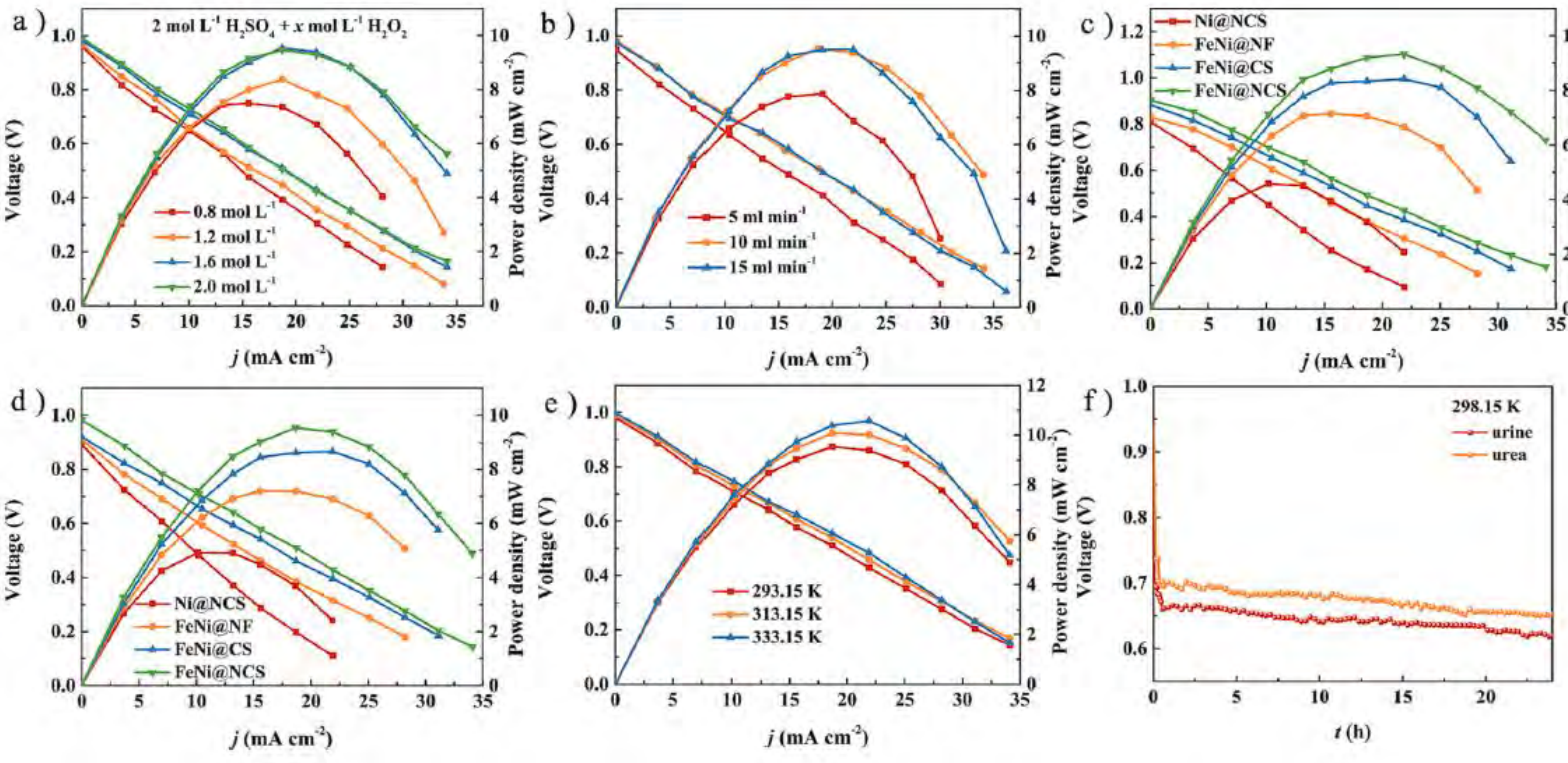




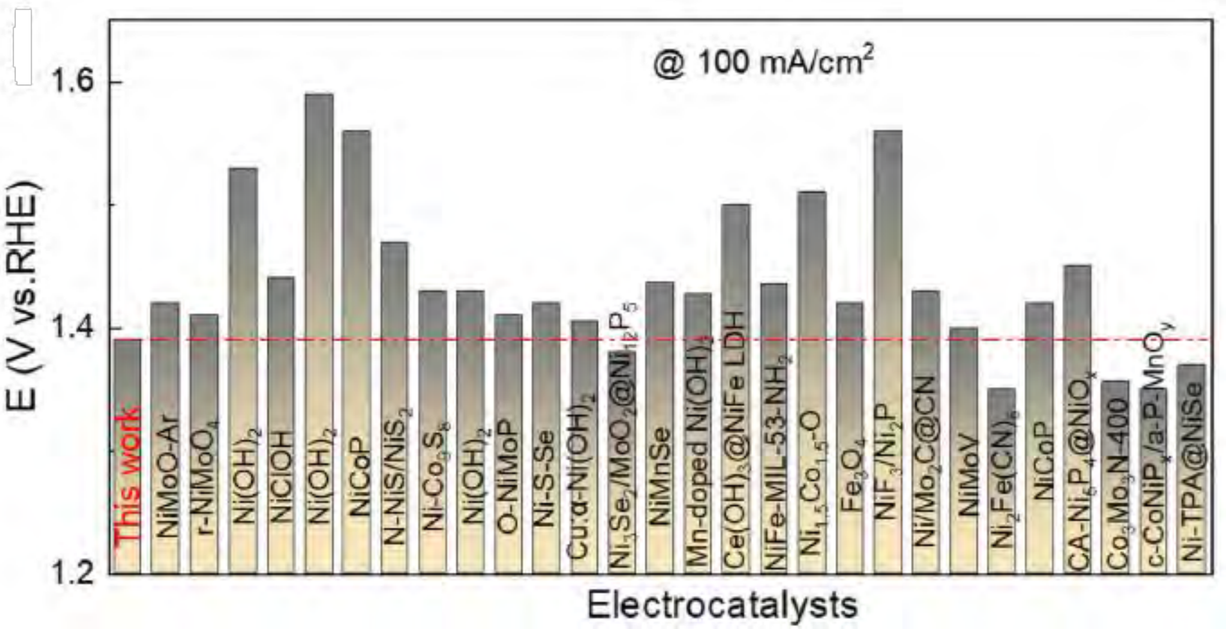


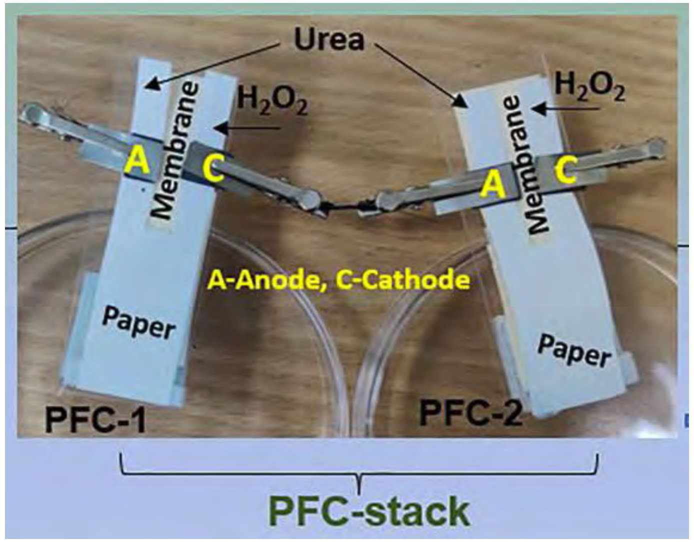
Ionics 29 (2023) 2969–2987

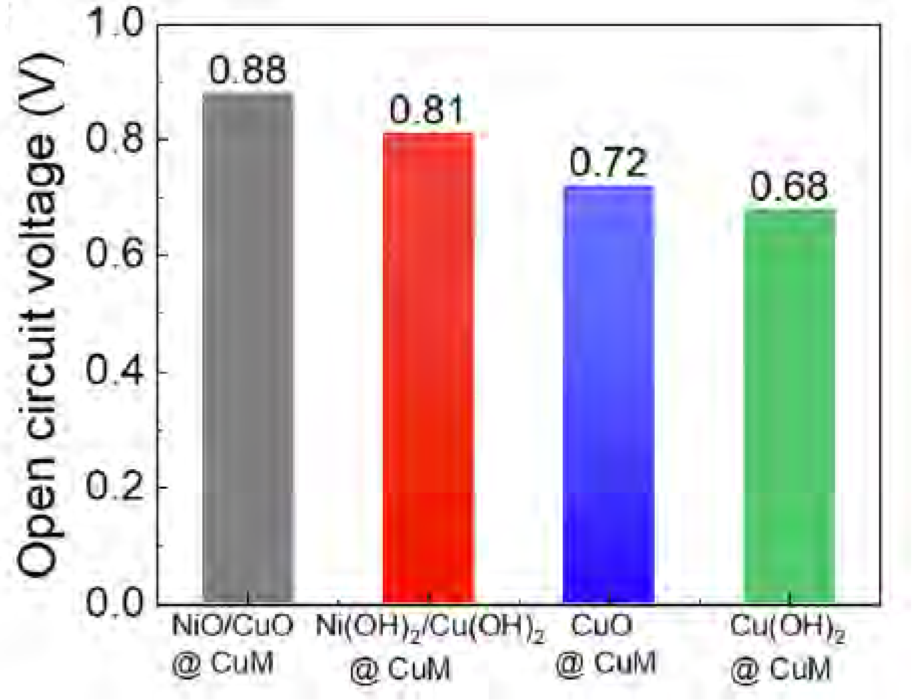
Окислитель - перекись

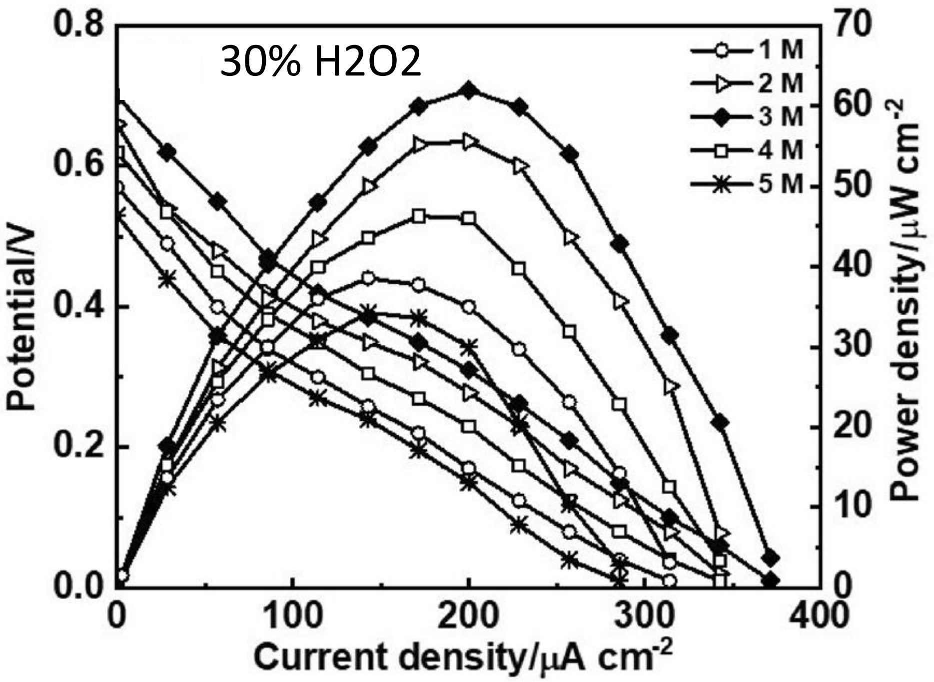


J. Colloid Interfac. Sci. 654 (2024) 36–45









Nano Energy
115 (2023) 108714

J. Appl. Electrochem. 2024
https://doi.org/10.1007/s10800-024-02105-z

Extraterrestrial Electrochemistry – Challenges and Opportunities for Electrolytic in-situ Resource Utilization (ISRU) on Mars

	EARTH	MARS
Average diurnal surface temperature range (K)	283 to 293	184 to 242
Average surface pressure (kPa)	101.400	0.636 (seasonally variable from 0.400 to 0.870)
Surface gravity (m/s^2)	9.79	3.71
Escape velocity (km/s)	11.19	5.03
Atmospheric composition	*Major (vol.%):* 78.08% N_2, 20.95% O_2, >1% H_2O (highly variable) *Minor:* 9340 ppm Ar, 410 ppm CO_2, 18.18 ppm Ne, 5.24 ppm He, 1.7 ppm CH_4, 1.14 ppm Kr, 0.55 ppm H_2	*Major (vol.%):* 95.1% CO_2, 2.59% N_2, 1.94% Ar, 0.16% O_2, 0.06% CO *Minor:* 210 ppm H_2O, 100 ppm NO, 2.5 ppm Ne, 0.85 ppm H-D-O, 0.3 ppm Kr, 0.08 ppm Xe

Solid oxide electrolyzer to produce O_2 from CO_2

$Mg(ClO_4)_2$ **brine** electrolyzer that runs at Martian ambient temperatures, with $Pb_2Ru_2O_{7-\delta}$ pyrochlore for OER

Electrochem. Soc. Interface 32 (2023) 47