Charged interface and its effects on heterogeneous electron transfer: experimental information creating challenges and verification tools for theory.

3. Analogies in electrocatalysis

- Hydrogen evolution (HER), from mercury to transition metals
- Hydrogen reactions, organic molecules oxidation, and oxygen reduction (ORR): certain information on reaction zone is available, but....
- CO₂ reduction: puzzle, no information on reaction zone
- Oxygen evolution (OER): puzzle complicated by electrode material transformations



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This lecture presents mostly thoughts and feelings, as well as suggestions.

Methodology: from simpler electrochemical kinetics to electrocatalysis

Outer-sphere electrode reactions:

- free electrode charge (*non-local EDL effects*),
- adsorption of the background electrolyte ions (*local EDL effects*).



G.A. Tsirlina, J. Solid State Electrochem. 21 (**2017**) 1833 - 1845 Inner-sphere electrode reactions:

- the same,
- + specific adsorption,

+ charge- and ions-affected solvent structure at the interface.



Electrocatalysis:

the same,

+ chemosorption, incl. dissociative adsorption,

+ charge- and ions-affected solvent structure at the interface,

+ complex multi-step reaction pathway.

Reaction zone is the area with inhomogeneous charge and substance distribution.

Concentrations of reactants in this zone (coming into kinetic equations) can be only estimated with account for electrostatic interactions.

Problem 1. We cannot be sure that all declared effects are reproducible

Commercial 'high purity' substances contain a lot of impurities. Purification of **cesium** salts is a special challenge, and even for potassium and sodium salts additional purification is sometimes required. Perchlorates and hydroxides purification is more tricky than of other salts.

Pay attention to Supplementary information on purification (if any).

Do not trust immediately the effects declared by only one group.....

Problem 2. We have a pile of published data, but we hardly have the complete set of data to solve crossword puzzles:

- data for electrocatalysis in solution(s) more or less comparable with that ones, for which direct free charge/adsorption data exist,
- data for relative reactions under exactly the same conditions (e.g., ORR and HPRR, or CO₂ and CO reduction),
- data for different reactions occuring in the same potential interval, collected for solutions of identical composition.





Cations inhibit hydrogen evolution on Hg in acid, Herasymenko-Šlendyk (1930) and Frumkin (1933)

10 - 6

 10^{-5}

10 - 4

 10^{-3}



	– Poter	 Potential vs. NCE at constant current density 							
Normalität des Salzzusatzes	LiCl	Na Cl	KCl	Rb Cl	$MgCl_2$	$Sr Cl_2$ $Ba Cl_2$			
	Volt	Volt	Volt	Volt	Volt	Volt			
0		The second	1.2	286		in the			
10^{-4} 10^{-3}	1.299	1.306	1.306	1.308	1.313	1.316			
10 ⁻² 10 ⁻¹ norm.	1.308 1.339	1.321 1.350	1.326 1.360	1.329 1.372	1.364 1.387	1.368 1.393 1.395			
Tabelle 4	0.01	norm S	Salzsäu	re					
A CONCARC A		II O'L III.	o terriste te						

1.286

1.307

1.331

1.355

1.390

1.307

1.315

1.339

1.365

149

5

Cations effects on hydrogen evolution and anions reduction on Hg, activation energies as diagnostic tool for local (short-range) interactions

Indifferent electrolyte	ln k _{rc} (25°C)	α (25°C)	ΔH_b^{\neq} /kJ mol ⁻¹	The same for peroxodisulfate reduction
	HER			Li⁺ 95
0.1 M NaCl	-10.35 (E $-\phi^{d} = -1.4$ V)	0.52	98.7	Na⁺ 86
0.1 M KCl	-10.41 (E - $\phi^{d} = -1.4$ V)	0.51	100.8	
0.1 M CsCl	- 10.76	0.50	96.9	Cs+ 66
	$(E - \phi^d = -1.4 V)$ $H_3 IO_6^{2-}$	reduction	Data fro articles discusse	om rarely available in Russian, ed by Fawcett
0.2 M NaOH	-5.42 SCE (E $-\phi^{d} = -0.5$ V)	0.24	103.4	
0.2 <i>M</i> KOH	-5.55 (E- $\phi^{d} = -0.5$ V)	0.26	92.0	
		Г	Deacrease of	an apparent activati

Possible origin of cations effects:

Non-local electrostatics (expected to be the same for **both** types of reactions)

Local ion pairing/association (expected to affect **anions**)

Effect on water structure

- Hydrogen bonds
- Reorganization energy
 (expected to be the same for **both** types of reactions)

Local hydrolysis (*expected to affect HER*) acrease of an apparent activation energy from Na+ to Cs+

B.G. Chauhan, W.R. Fawcett, T.A. McCarrick, J. Electroanal. Chem. 58 (**1975**) 275-288

Cations effects on hydrogen evolution on Au and Pt, impressive qualitative effect



What can be guessed concerning HER reaction zone on Pt (alkaline solutions)



- (1) At 0 RHE, Cs⁺ adsorption is above 20 μ C/cm², but it can decrease at more negative potentials.
- (2) Na⁺ adsorption is lower than for Cs⁺, but surely above 15 μ C/cm² at 0 RHE.
- (3) Cs⁺ competition with Na⁺ is stronger than on Hg,
 i.e. Cs⁺ specific adsorption is stronger than on
 Hg, so more than a half of Cs⁺ can be located in
 the 'dense layer'.
- (4) Both cations compete with H_{ad}, so they are expected to inhibit recombination.
- (5) If discharge step becomes slow, H_{ad} coverage is expected to decrease. So, at higher overpotentials cations adsorption finally starts to increase again.

Hypotheses on the origin of HER promotion by cations

Schemes A....D are from Y.-S. Hsu, S.T. Rathnayake, M.M. Waegele, J. Chem. Phys. 151 (**2019**) 160902



All hypotheses A....D operate with **cations in the dense part**, and should **also** account for **non-local electrostatic effects** of cations at reaction plane.

Cation surface coverage and location are crucial for all A....D schemes. OH presence on Pt (A) looks less probable at HER potentials.

M.C.O. Monteiro, F. Dattila, N. López, M.T.M. Koper, J. Amer. Chem. Soc. 144 (**2022**) 1589-1602

cation acidity / Z² r⁻¹

Promotion affected by bulk

cation concentration



Comments on hypotheses C and D: these two can

Comments on hypotheses C and D: these tw					o can			<i>m</i> /mol•kg	−1 Li ₂ SO ₄	m/mol·kg ⁻¹ MgSO ₄
work only	simult	aneously	NaCl, N	Л	Saturat	ed so	lutions	0.0000	1.33248	0.0000 1.33248 0.2096 1.33762
25 C, 632.	8 nm		0.01	1.331 26		w %		0.4681	1.34096	0.3448 1.34072
Conen]	Refractive Index	x 0.02	1.331 40	NaCl	26 34	1.37958	0.7337	1.34534	0.5911 1.34594
M	NaCl	KCl	- 0.03 0.05	1.331 51 1.331 72	KCl	26.05	1.36905	<u>0.9917</u> 1.2447 1.4685	1.35316	0.7832 1.35009 0.9997 1.35438 1 1898 1 35810
1	1.34329	1.34253	0.10	1.332 16	RbCl	48.54	1.38851	1.7564	1.36011	1.3786 1.36174
0.5	1.33817	1.33786	0.20	1.333 13	CsCl	65.47	1.41963	1.7573	1.36015	1.6214 1.36613
0.2 0.1	$1.33502 \\ 1.33405$	$1.33496 \\ 1.33399$	0.50 1.00	1.336 28 1.341 30	R. Meng	g, S. L	i, Q. Zhai,	1.9387 2.1241	1.36242	1.8675 1.37039 2.1201 1.37469
0.05	1.33361	1.33340	1.45		Y. Jiang,	H. LE	е, н.	2.3061	1.30091	2.3603 1.37853
0.03	1.33340	1.33321	1.50		Zhang, M	Μ. Ηι	i, J. Chem	2.3419	1.37243	2.8588 1.38613
0.02	1.33329	1.33302	1.920	1.349 3	Eng. Dat	ta 56	(2011)	2.9827	1.37442	3.0869 1.38927
0.01	1.33315	1.33296	5.302	1.364 1	4643-46	50		S. Urrejol	a, A. Sar	nchez, M.F. Hervello, J.
Pure water	1.3	33315	J.V. Leyend	ekkers, R.J.				Chem. En	g. Data !	55 (2010) 482-487
R.N. O'Brien	, J. Chem.	Eng. Data	Hunter, J. C	Chem. Eng.						. ,
13 (1968) 2-	5		Data 22 (1	977) 427-43	31					
(C) Positioning	and	(D) Altering Solver	nt Pek	ar factor 1	l/n ² – 1/	ε is r	nostly	2.5 - solvent red energy, eV	organization	
Orienting h	20	Reorganization	 det	ermined b	y n valu	e, wł	nich is	2.0ε in the dens	e//// ro	eactant size 0.15 nm
~	2	$\varepsilon_{\rm solvent}({\rm cation})$) inc	reasing wit	th conce	ntra	tion for	10 //	///	
		ALL	ALL cations; λ change cannot			not	1.5 - 5	chan	ging both reorganization	
- 7		P P	ехс	eed 1-2%.				1.0 - 3	ener	gy and
T		×>>	• But	: H-bondin	g can aff	fect r	reactant	2	📫 elect	rode/reactant overlap.
<u> </u>	ch May 2025	locture 2	loca	ation, Þ	-			0 distance along	0.4 the normal to	0.6 0.8 11 0.6 <i>the surface</i> , nm



Hydrogen evolution on metals with low pzfc, surface pretreatment problem

Very old explanation of HER dependence on cation concentration (nickel):

$$Na^+ + e \longrightarrow Na(I)$$

 $Na(I) + H_2O \longrightarrow H(a) + Na^+ + OH^-$

T. Ohmori, A. Matsuda, J. Res. Inst. Catal. Hokkaido Univ. 15 (**1967**) 201-206





(I means Intermediate)

A.G. Oshchepkov, A. Bonnefont, E.R. Savinova, Eletrocatalysis 11 (**2020**) 133–142



P. Lukowzew, S. Lewina, A. Frumkin, Acta Physicochim. URSS 11 (**1939**) 21-44

Hypothesis (A) is the most promising for these metals.

Hydrogen oxidation in alkaline solutions: inversion of cation effect?



Greeley, V.R. Stamenkovic, N.M. Markovic, Nature Chem. 1 (**2009**) 466-472

At what potential adsorbed cations turn to Obonded? Closer to 1 V RHE?

Cations effects on ORR, and on hydrogen and organic molecules oxidation are similar



Any organic molecule oxidation suffers from self-poisoning, steady-state data are required



Markovic, Electrochim. Acta 152 (2015) 38-43

For organic molecules oxidation, low potentials are most important. Separation of parallel reactions is highly desirable. Smooth electrodes. including single crystalline. can be



Smooth electrodes, including single crystalline, can be hardly used to study the kinetics in desired region.

Cations effects for **PtRu** are of interest, as ca. 0.2 V RHE potentials can be studied, at which cations adsorption surely takes place at any pH.

Why adatoms are forgotten?



For larger organic molecules oxidation, cations do not affect products distribution



P. P. Lopes, D. Strmcnik, J. S. Jirkovsky, J. G. Connell, V. Stamenkovic, N. Markovic, Catal. Today 262 (**2016**) 41-47

V.Y. Yukuhiro, R.A. Vicente, P.S. Fernandez, A. Cuesta, J. Amer. Chem. Soc. 146 (**2024**) 27745-27754

ORR on Pt: two approaches to modeling



A.M. Gómez–Marín, E.A. Ticianelli, Curr. Opin. Electrochem. 9 (**2018**) 129-136

Or more general microkinetic simulation

J. Huang, M.H. Eikerling, Curr. Opin. Electrochem. 13 (2019) 157–165

Golden mean: first analyze 'double layer' effects on each step, then go to microkinetic modelling

To say, if Ox = O₂, z_{Ox} =0, $exp\left(\frac{(\alpha - z_{Ox})F\varphi_2}{RT}\right)$ easily explains pH effect

Highly desirable: to model ORR and HPRR simultaneously



R.Rizo, J.M. Feliu, E. Herrero, J. Catal. 398 (**2021**) 123-132

Hydrogen peroxide reactions, as affected by cations and pH

Pt(111)

E vs. SHE / V

1.7 mM H₂O₂

V. Briega-Martos, F.J. Sarabia, V. Climent, E. Herrero, J.M. Feliu, ACS Meas. Sci. Au 1 (**2021**) 48-55



MeF/HClO₄



Cations/pH effects are sensitive to surface crystallography, Pt(111) cannot model Pt poly

A. Goyal, S. Louisia, P. Moerland, M.T.M. Koper, J. Amer. Chem. Soc. 146 (**2024**) 7305-7312

C. Stoffelsma,..., N.M. Markovic, M.T.M. Koper, J. Amer. Chem. Soc.

Probably this is the time to separate fuel cell/electrolysis research (using the real catalysts) and basic research of 'double layer' effects for relatively simple electrocatalytic reactions: HER/HOR can help with ORR + HPOR, as reaction zone is the same as for HOR.



Large collection of the effects of surface crystallography: A.R. Fairhurst, J. Snyder, C. Wang, D. Strmcnik, V.R. Stamenkovic, Chem. Rev. 125 (**2025**) 1332-1419

Early CO₂ reduction: Hori assumed 'usual' Frumkin correction, with specific cation adsorption

Herasymenko/Šlendyk data for HER on Hg, cation concentration at constant <u>ionic strength</u>



Y. Hori, S. Suzuki, Bull. Chem. Soc. Jap. 55 (**1982**) 660-665

Single electron outer=sphere reaction is possible at least at -0.9 - -1.0 V RHE. Cation effects look very similar to that for anions reduction on Hg.

Cu, it is assumed that interfacial H⁺ concentration decreases from Li to Cs

	CC	D ₂ , 5 mA/cm	CO, 1.5 mA	/cm²		
Cation	Potential		Potential			
	Cation	V/SHE	H_2	V/SHE	H_2	C1/C2
-	Li+	-1.45	60.5	-1.40	60.5	1
	Na+	-1.45	25.1	-1.43	25.1	
	K+	-1.39	14.5	-1.37	14.5	
	Cs ⁺	-1.38	24.4	-1.31	24.4	

A. Murata, Y. Hori, Bull. Chem. Soc. Jap. 64 (1991) 123-127

However, this effects are hardly pronounced if pH in diffusion layer is changed, as Hori also assumed. Buffering effects of cations were addressed many times

reviewed, e.g., in F. Ni, K. Jia, Y. Chen, Y.Wen, S. He, Mater. Chem. Front. 7 (**2023**) 2750-2763

but why they do not manifest themselves, to say, in the effects of alkali metal cations on hydrogen evolution on Hg? (Buffering with multicharged cations is of course possible)

Activating CO₂⁻ dissociation is realistic hypothesis, but it should be balanced



Questions:

- (1) Cations in this scheme do not interact with metal, so the difference in *specific* adsorption cannot play any role?
- (2) Cations surface coverage is < c.a. 10% in any case, so there are no neighbor cations. How C2 products can form on Cu?
- (3) How to separate this and parallel outer-sphere pathways (also cation-dependent)?
- (4) How to separate this and subsequent steps (also cation-dependent)?





One more pathway: CO₂ reduction on dispersed Pd (also modified with Cu adatoms)

One cannot exclude participation of H_{ad} on Cu; it is crucial to study low negative RHE potentials using high surface area electrodes VIII group metals:

	Electrode	rode Pressure	Farad	aic efficiency	of CO ₂ r	duction p	roduct (%))				
		of CO_2/atm	CO	HCOOH	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	i-C ₄ H ₁₀	n-C ₄ H ₁	0 CO _{2tot}
	Fe	1 °	0	0	0	0	0	0	0	0	0	0
	Fe	50	6.7	3.7	1.61	1.32	0.05	1.53	0	0.19	1.01	16.0
CO and C2	Co	1°	1.2	t	0.31	0.2	t	0.19	0	t	0.09	2.0
annear at	Co	60	14.4	4.1	0.93	0.45	0.13	0.48	t	t	0.33	20.1
	Ni	1°	0	0.1	0.62	0	0.63	0.06	0	0	0	1.4
lower	Ni	60	10.4	23.2	1.78	0.88	0.44	0.41	0.06	t	0.3	37.5
potentials	Pd	1 ^c	5.3	4.4	0	0	0	0	0	0	0	9.7
	Pd	50	57.9	4.4	0	0	0	0	0	0	0	62.3
	Pt	1 °	0	0	0.02	t	0	0	0	0	0	0.02
	Pt	60	9.3	24.1	0.31	0.08	t	0.08	t	0	t	33.9
Copper:	c.a. –1	1.0 - —1.1 V F	(HE S	. Nakagaw	a, A. Kı	Ido, IVI. / Fai	Azuma, radaic ef	T. Sakata ficiency (a, J. Elec %)	troanal. (Chem. 30)8 (1991)
CO ₂ (atm)	E ^a (V) AgCl/Ag	CH4	C_2H_6	C_2H_4	C_2H_5O	н	co	HCOOR	H I	H_2 H	C _P C	O_2 red ^c
1	-1.57	Trace	Trace	0.01	\mathbf{nd}^{d}		nd	nd	98	3.7 (0.0	0.0
10	-1.61	2.5	0.02	0.56	nd		nd	0.8	91	1.8 3	3.1	3.9
20	-1.62	25.0	0.04	2.33	0.9		nd	3.1	58	3.7 28	3.3	31.4
30	-1.61	48.4	0.04	3.62	1.1	1	race	3.3	31	1.8 53	3.2	56.5
40	-1.03	04.4 49 5	0.08	3.34	1.1	1	race	9.D 0 0	10).9 D0 11 59	5.9 2 9	08.4
		444		() •				~ ~	-			n / I

-1.61c.a. -0.9 V RHE

K. Hara, A. Tsuneta, A. Kudo, T. Sakata, J. Electrochem. Soc. 141 (1994) 2097-2103

Julich, May 2025, lecture 3

Look for similarities: nitrate reduction on Pt (also modified with Cu adatoms) and on Cu



O.A. Petrii, T.Y. Safonova, J. Electroanal. Chem. 331 (**1992**) 897-912 Similarity of CO₂ and NO reduction is mentioned in H. Wan, A. Bagger, J. Rossmeisl, Angew. Chem. Int. Ed. 60 (**2021**) 21966-21972

Cations effect on OER formally agrees with inverted pzfc, known for oxide as well



Raman, Ni–O?

	240 mV	340 mV	440 mV
LiOH, left peak	480.43 ± 0.23	480.93 ± 0.20	481.27 ± 0.19
CsOH, left peak	478.87 ± 0.17	479.47 ± 0.15	479.77 ± 0.15
LiOH, right peak	562.07 ± 0.51	561.93 ± 0.47	561.13 ± 0.39
CsOH, right peak	557.03 ± 0.35	556.93 ± 0.27	556.57 ± 0.26

However, this effect is not very strong, mostly observed under nonsteady-state modes, and is not accompanied by oxide recharging studies.

J.D. Michael, E.L. Demeter, S.M. Illes, Q. Fan, J.R. Boes, J.R. Kitchin, J. Phys. Chem. C 119 (2015) 11475-11481 σ/C



RuO₂ .iOH Increasing 50 temperature Current density (µA/cm²) NaOF 50 0 KO 50 1.5 1.6 1.3 1.4 Potential (V vs RHE) R.R. Rao, Y. Shao-Horn, J. Phys. Chem. C 125 (2021) 819508207

This can be cation effect on oxide stoichiometry, and correspondingly on lattice-related OER pathways





Before answering this question, we need first to clarify what reaction we study. Peroxide yield?

Pt	Electrolyte	$\begin{array}{llllllllllllllllllllllllllllllllllll$		Electrolyte	$\mathrm{H}_{2}\mathrm{O}_{2}$ formed ($\mu\mathrm{g} \pm 1.0 \ \mu\mathrm{g}$)	Efficiency (%)
1 <i>M</i> NaOl 1 <i>M</i> NaOl 1 <i>M</i> NaOl 1 <i>M</i> NaOl 1 <i>M</i> NaOl	H H + 0.001 M CaCl ₂ ^b H + 0.001 M Sr(ClO ₄) ₂ H + 0.001 M Ba(ClO ₄) ₂	72.0 49-5 38.4 22.4	68.0 46.7 36.2 21.1	1 N H2SO4 1 N H2SO4 + 0.033 M KF 1 N H2SO4 + 0.033 M KCl 1 N H2SO4 + 0.033 M KBr 1 N H2SO4 + 0.033 M KBr 1 N HCl	15.0 18.7 32.8 55.2 39.2	14.2 17.6 30.5 52.0 36.9

EFFECT OF CATIONS IN I M NaOH

Effect of anions in 1 N H₂SO₄

A. Kozawa, J. Electroanal. Chem. 8 (1964) 20-39

We can expect some news from organic electrochemistry

Quantification of adsorbate formation steps can be very helpful



Considering more than one reaction occurring in the same potential interval, we can learn more about reaction zone.

As wide as possible potential interval is desirable, to judge about electrode charge induced changes of reaction zone.



16 0_{H*} = 0.05

C.-Y. Lin, H.D. Abruña, J. Suntivich, J. Electrochem. Soc. 172 (**2025**) 016503



Still unsolved most urgent issues (including experimental)

I. Reactions kinetics

Collect/measure electrocatalytic effects for solutions already characterized in respect to free charge and ionic adsorption.

Use traditional redox probes sensitive to cations, to estimate what effects take place for more or less outer-sphere reactions, and what effects are unique for electrocatalysis.

II. Analysis under assumption of equilibrium 'double layer'

Compare computed charge vs. potential dependence with "thermodynamic" experiments, to get more realistic parameters for further modeling of reaction.

Is it possible to model the interface for various free electrode charges fixed in advance?

Is it possible to estimate solvent reorganization or effective permittivity in the 'dense layer'?

Improve and complement 'double layer' knowledge: radiotracer and optical techniques

III. Choice of the next set of the most urgent issues

How to arrange the reliable experimental tests of the non-equilibrium 'double layer' effects?

Effect of catalyst particle size on free charge and adsorbates distribution?



S. Chen, A. Kucernak, J. Phys. Chem. B 108 (**2004**) 3262-3276

Vladimir S. Bagotsky (1920-2012)

Vladimir S. Bagotsky





ELECTROCHEMICAL POWER SOURCES

Batteries, Fuel Cells, and Supercapacitors



WILEY









Julich, May 2025, lecture 3