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Statistical and Principal Component Analysis in the Design of Alkaline Methanol Fuel Cells

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Content

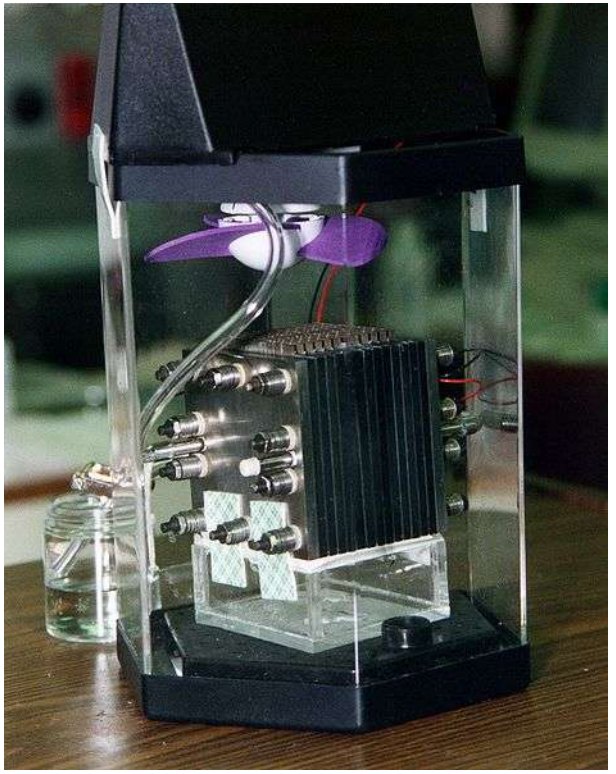
- Direct methanol fuel cells
- Modeling of electrochemical kinetics
- Fitting of model to experiment

- Statistical and Principal Component Analysis
  - sensitivity matrix
  - its singular value decomposition
  - analysis of error propagation

Electrochemical kinetics of the direct methanol fuel cells

- Fuel cell – similar to galvanic cell but with refilling reagents
- Direct fuel cell – avoids formation of hydrogen

Fuel	Gibbs energy [kJ / mol]	potential [V]	energy density [MJ / kg]
methanol	702	1.213	21.9
ethanol	1325	1.145	28.7
1-propanol	1853	1.067	30.9
2-propanol	1948	1.122	32.4
n-butanol	2602	1.124	35.2
dimethyl ether	1387	1.198	30.3
ethylene glycol	1181	1.224	19.0
formic acid	270	1.400	5.6
glycerol	1622	1.201	16.1



Example (NASA JPL): direct methanol fuel cell

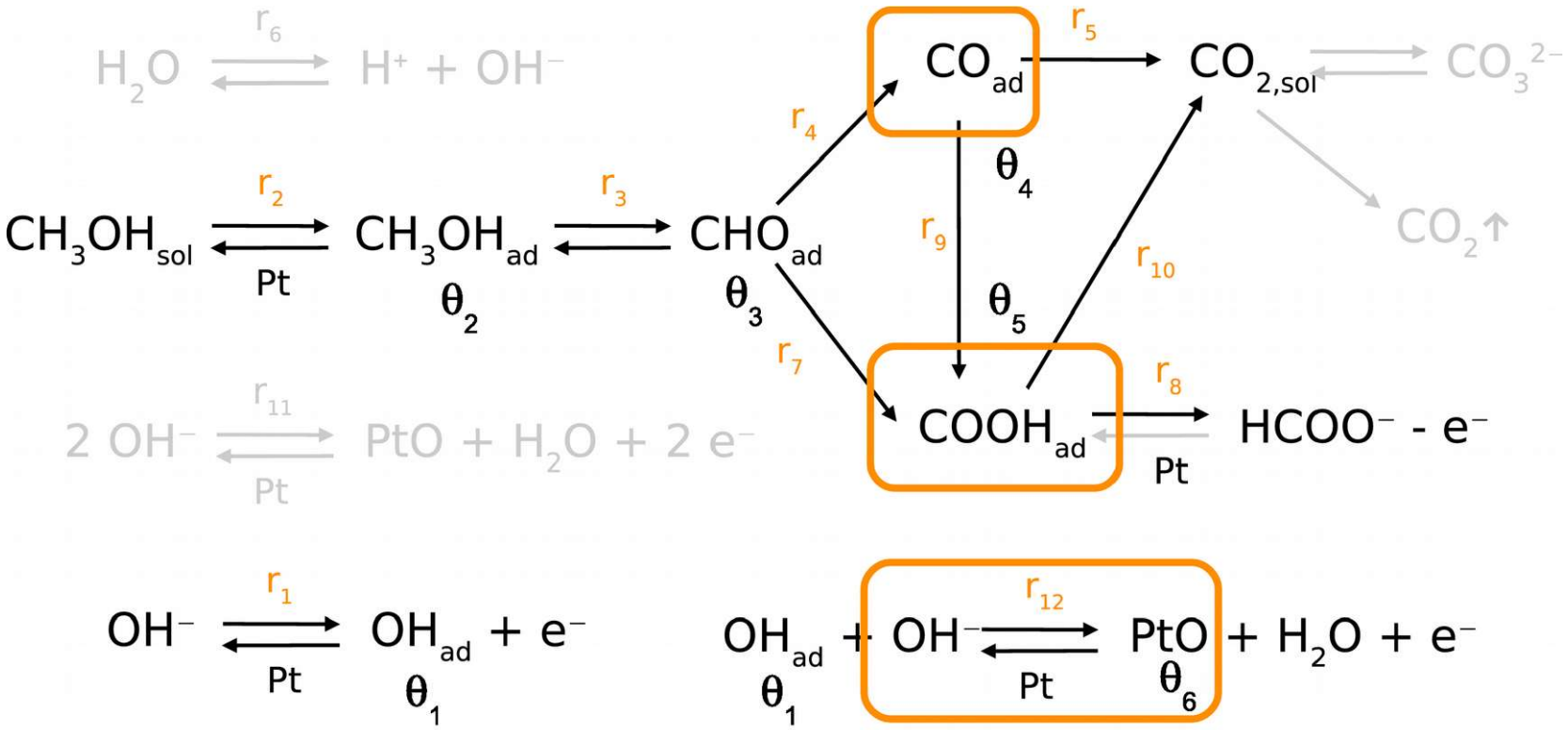
Ref: U.Krewer et al, Electrochemical Oxidation of Carbon-Containing Fuels and Their Dynamics in Low-Temperature Fuel Cells, ChemPhysChem 2011, 12, 2518-2544

Modeling of electrochemical kinetics

- reactions form a hypergraph $reaction_i = \sum_j a^L_{ij}\, g_j - a^R_{ij}\, g_j$,

  where a^L_{ij} , a^R_{ij} – incidence matrices multiplied to stoichiometric coefficients, for the left and right hand side of the reaction, g_j- reagents
- hypergraph is a generalization of graph where an edge can join any number of vertices, a_{ij} – incidence matrix for ending vertices (j) entering in an edge (i)
- reagents, variables, constants, parameters are listed
- hypergraph is translated to reaction rates $r_i = k^L_i \prod_j \theta_j^{\,a^L_{ij}} - k^R_i \prod_j \theta_j^{\,a^R_{ij}}$
- reaction rates are assembled to molar balance description
- ODEs are formed
- templates for fitting on stationary state and on dynamic system are prepared
- L_2 -norm distance between experiments and the model is minimized

Mechanism of methanol oxidation: reaction graph



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Mechanism of methanol oxidation: reactions

$$
\begin{aligned}
r_1&: \quad OH^- + Pt \leftrightarrow OH_{ad} + e^- \\
r_2&: \quad CH_3OH + Pt \leftrightarrow CH_3OH_{ad} \\
r_3&: \quad CH_3OH_{ad} + 3OH_{ad} \leftrightarrow CHO_{ad} + 3H_2O \\
r_4&: \quad CHO_{ad} + OH_{ad} \rightarrow CO_{ad} + H_2O \\
r_5&: \quad CO_{ad} + 2OH_{ad} \rightarrow CO_2 + H_2O + 2Pt \\
r_7&: \quad CHO_{ad} + 2OH_{ad} \rightarrow COOH_{ad} + H_2O + Pt \\
r_8&: \quad COOH_{ad} + e^- \leftrightarrow HCOO^- + Pt \\
r_9&: \quad CO_{ad} + OH_{ad} \rightarrow COOH_{ad} + Pt \\
r_{10}&: \quad COOH_{ad} + OH_{ad} \rightarrow CO_2 + H_2O + 2Pt \\
r_{11}&: \quad 2OH^- + Pt \leftrightarrow PtO + H_2O + 2e^- \\
r_{12}&: \quad OH^- + OH_{ad} \leftrightarrow PtO + H_2O + e^-
\end{aligned}
$$

Mechanism of methanol oxidation: model parameters

model constants

Constant, units	*Value*
F, C/mol	$9.649 \cdot 10^4$
R, J/(K mol)	8.314
A, m^2	$2.376 \cdot 10^{-5}$
C_{dl}, F	$1.899 \cdot 10^{-4}$
C_{act}, mol/m^2	$8.523 \cdot 10^{-5}$
α	0.5

Faraday const
gas const
surf.area
capacity
activity const
charge transfer coefficient

Variables		*Constants*	
θ_1	OH_{ad}		
θ_2	CH_3OH_{ad}	c_1	OH^-
θ_3	CHO_{ad}	c_2	CH_3OH
θ_4	CO_{ad}	c_3	H_2O
θ_5	$COOH_{ad}$		
θ_6	PtO		

surface coverages

volume concentrations

abs.temperature: *T, K*

voltage: η, *V*

current: Icell, A

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Mechanism of methanol oxidation: reaction rates

reaction rates r_i, mol/(m²s)

reaction constants k_i, mol/(m²s)

$$r_1 = k_1 c_1 \theta_0 - k_{-1}\theta_1,\ r_2 = k_2 c_2 \theta_0 - k_{-2}\theta_2,$$
$$r_3 = k_3 \theta_2 \theta_1^3 - k_{-3}\theta_3 c_3^3,\ r_4 = k_4 \theta_3 \theta_1,$$
$$r_5 = k_5 \theta_4 \theta_1^2,\ r_7 = k_7 \theta_3 \theta_1^2,\ r_8 = k_8 \theta_5,$$
$$r_9 = k_9 \theta_4 \theta_1,\ r_{10} = k_{10}\theta_5 \theta_1,$$
$$r_{11} = k_{11} c_1^2 \theta_0 - k_{-11} c_3 \theta_6,$$
$$r_{12} = k_{12} c_1 \theta_1 - k_{-12} c_3 \theta_6,$$

probability that 1CO meets 2OH

$$k_1 = k_1^0 \exp(\alpha\beta\eta),$$
$$k_{-1} = k_{-1}^0 \exp(-(1-\alpha)\beta\eta),$$
$$k_8 = k_8^0 \exp(-(1-\alpha)\beta\eta),\ \beta = F/(RT),$$
$$k_{11} = k_{11}^0 \exp(2\alpha\beta\eta),\ k_{12} = k_{12}^0 \exp(\alpha\beta\eta),$$
$$k_{-11} = k_{-11}^0 \exp(-2(1-\alpha)\beta\eta),$$
$$k_{-12} = k_{-12}^0 \exp(-(1-\alpha)\beta\eta)$$

k^0_i, k_i – fitting parameters

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Mechanism of methanol oxidation:
molar balance

$$
\begin{aligned}
F_1 &= (r_1 - 3r_3 - r_4 - 2r_5 - 2r_7 - r_9 - r_{10} - r_{12})/C_{act}, \\
F_2 &= (r_2 - r_3)/C_{act}, \\
F_3 &= (r_3 - r_4 - r_7)/C_{act}, \\
F_4 &= (r_4 - r_5 - r_9)/C_{act}, \\
F_5 &= (r_7 - r_8 + r_9 - r_{10})/C_{act}, \\
F_6 &= (r_{11} + r_{12})/C_{act}, \\
F_7 &= (-r_1 + r_8 - 2r_{11} - r_{12}) \cdot FA/C_{dl},
\end{aligned}
$$

→ electrons come out of here

Mechanism of methanol oxidation: problem formulation

ODEs describing the dynamics

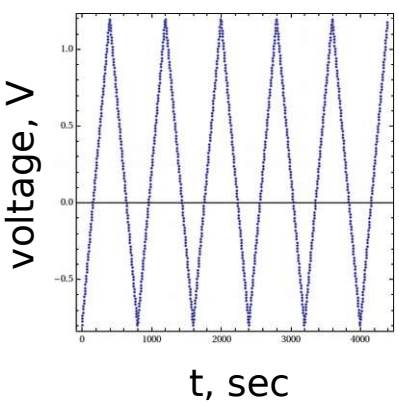
$$d\theta_i/dt = F_i(\theta, \eta),\ \ i = 1 \ldots n-1,$$
$$d\eta/dt = F_n(\theta, \eta) + I_{cell}/C_{dl}$$

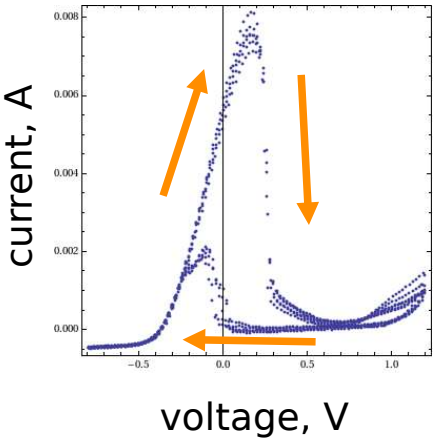
optimization problem: adjust 14 reaction consts *k* to fit experimental data, minimize $L_2^2 = \Sigma\,(Icell_i - Icell_{i,exp})^2$

stationary state: l.h.s. = 0, algebraic equations

Fitting of model to experiment

- the cell is probed with saw-like voltage profile
- high amplitude
- non-linear effects
- numerical integration of ODEs



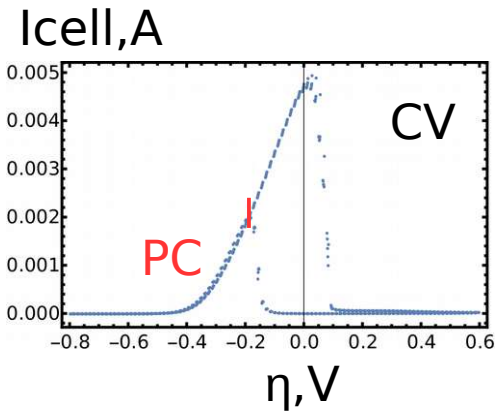


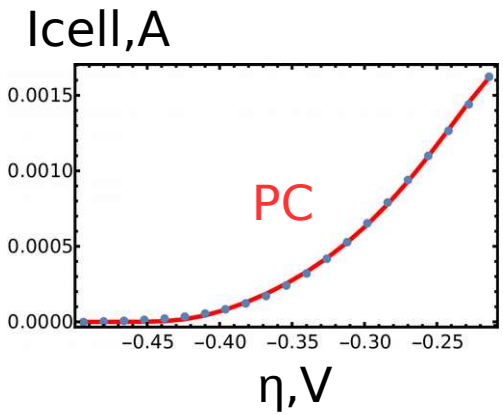
- teflon cell, deep vacuum to avoid external influence
- CO_2 is removed by permanent argon blow
- rotating electrode suppresses diffusion effects

experiments by TU Braunschweig

Fitting of model to experiment

- dynamical part: Cyclic Voltammogram (CV) described by ODE
- stationary part: Polarization Curve (PC) described by algebraic equations, will only be considered in this work
- **blue points** – experimental data
- **red line** – mathematical model
- **perfect fit!**





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Statistical and Principal Component Analysis

TABLE I
PARAMETER CENTRAL VALUES AND TRUST REGION OF LINEAR MODEL

p_j	0.949	-4.5	0.398	-0.563	4.72	-3.46	0.352	-0.101	1.2	-8.66	1.89	-1.08	-1.72	-7.82
dp_j	0.3	0.1	0.3	0.4	1.5	0.1	0.1	0.06	0.1	0.1	0.08	0.2	0.15	0.15

- fitting result (central values, $p=\log_{10}k$)
- the main question: **how precise are these values?**
- standard statistical method
- experimental error estimation $\varepsilon^2 = L_2^2/N_{dof}$, $N_{dof}=N_{pt}-N_{par}$

$$N_{pt} = 21,\ N_{par} = 14,\ N_{dof} = 7,$$
$$L_2^2 = 2.08 \cdot 10^{-9} A^2,\ \epsilon = 1.72 \cdot 10^{-5} A.$$

Statistical and Principal Component Analysis

$$X_{ij} = \partial f(\eta_i, p)/\partial p_j, \;\; cov = \epsilon^2 (X^T X)^{-1}$$
$$\sigma_i = (cov_{ii})^{1/2}, \;\; corr_{ij} = \sigma_i^{-1} cov_{ij}\, \sigma_j^{-1},$$

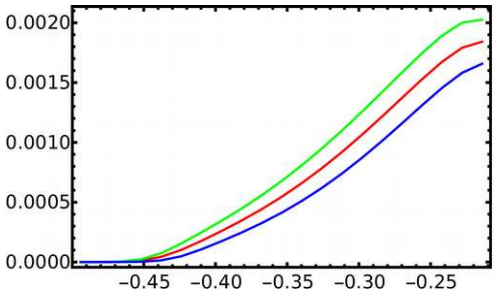
- sensitivity, covariance, correlation matrices
- diagonal of cov: squared errors of parameters

- the deviation of the curve (~20%) measures non-linearity of the model inside given dp-box

- surprise! X^TX is degenerate, cannot be inverted

- a deeper analysis is needed

X_{i1},A



η_i,V

sensitivity matrix (the first column) **red** – central diff scheme, **green**/**blue** – forward/backward diff schemes

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Statistical and Principal Component Analysis

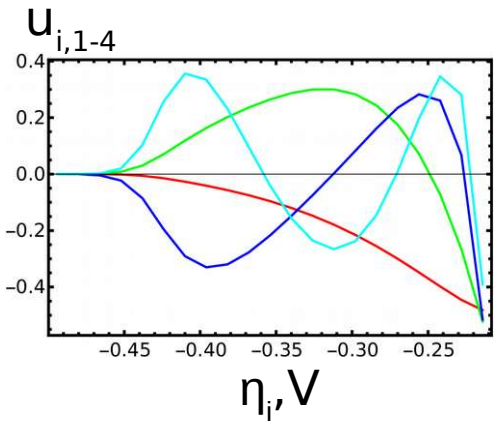
- trust region: box in parameter space, marking the applicability of linear model up to a given tolerance (e.g., 20%)
- error ellipsoid: one-sigma confidence region in parameter space, corresponding to the estimated Gaussian errors of experiment
- semi-axes of the ellipsoid that belong to trust region, correspond to parameter combinations, which can be measured precisely
- other directions are measured imprecisely

$$X = u\lambda v^T,\ u^T u = 1,\ v^T v = v v^T = 1,\ a_k = \epsilon/\lambda_k.$$

- Singular Value Decomposition (SVD):
  X is $N_{pt} \times N_{par}$ rectangular, u is $N_{pt} \times N_{par}$ semi-orthogonal,
  λ is $N_{par} \times N_{par}$ diagonal, v is $N_{par} \times N_{par}$ orthogonal,
  a_k values represent the semi-axes of the error ellipsoid

Statistical and Principal Component Analysis

- cont'd: columns of v-matrix represent directions of the axes of the ellipsoid in parameter space
- columns of u-matrix represent the profiles of principal components in the space of experiments
- these profiles show the variation of PC curve when the parameters are displaced along the axes of the error ellipsoid



u-profiles for the first four components, in **red**-**green**-**blue**-**cyan** order for $u_{i,1\text{-}4}$

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Statistical and Principal Component Analysis

- the main result: 4 directions are measured precisely, 9 imprecisely, 1 cannot be measured in principle (exact symmetry of the system)

TABLE II
RESULTS OF PRINCIPAL COMPONENT ANALYSIS

λ_k, A	a_k	v_{jk}													
$8.12 \cdot 10^{-3}$	$2.12 \cdot 10^{-3}$	−0.531	0.014	0.461	−0.459	0.140	−0.013	−0.007	0	0	0	0	−0.522	0.032	−0.032
$1.21 \cdot 10^{-3}$	$1.43 \cdot 10^{-2}$	0.396	−0.159	−0.251	0.250	0.214	−0.010	−0.018	0	0	0.002	0	−0.769	0.167	−0.167
$2.71 \cdot 10^{-4}$	$6.36 \cdot 10^{-2}$	−0.078	0.639	−0.052	0.058	−0.402	0.065	−0.065	0	0	0.004	0	−0.052	0.451	−0.451
$1.24 \cdot 10^{-4}$	0.139	−0.066	−0.711	0.091	−0.074	−0.191	−0.058	0.066	0	0	−0.014	0	0.197	0.443	−0.443
$7.79 \cdot 10^{-6}$	2.21	0.305	−0.063	0.211	−0.123	−0.728	−0.290	0.277	0	−0.001	−0.113	0	−0.234	−0.206	0.206
$5.1 \cdot 10^{-6}$	3.38	0.546	0.214	0.540	−0.152	0.408	−0.204	0.205	0	0	−0.056	0	0.192	0.160	−0.160
$8.51 \cdot 10^{-7}$	$2.02 \cdot 10^{1}$	0.315	−0.066	0.148	−0.264	−0.163	0.336	−0.449	0.001	0.032	0.679	−0.003	−0.010	−0.033	0.033
$1.69 \cdot 10^{-7}$	$1.02 \cdot 10^{2}$	0.033	−0.083	0.508	0.459	−0.114	0.441	−0.349	−0.001	−0.029	−0.434	0.003	−0.033	−0.046	0.046
$2.52 \cdot 10^{-8}$	$6.84 \cdot 10^{2}$	0.240	−0.003	−0.304	−0.617	−0.003	0.439	−0.030	−0.003	−0.080	−0.518	0.012	0.021	0.013	−0.013
$7.81 \cdot 10^{-9}$	$2.21 \cdot 10^{3}$	0.047	−0.001	−0.075	−0.135	0.004	−0.582	−0.722	0.008	0.212	−0.257	−0.039	0.031	0.004	−0.004
$5.92 \cdot 10^{-10}$	$2.91 \cdot 10^{4}$	0	0	−0.002	−0.002	0	−0.165	−0.159	−0.037	−0.972	0.022	0.002	0.007	0	0
$9.35 \cdot 10^{-13}$	$1.84 \cdot 10^{7}$	0	0	0	0	0	0.024	0.024	0.485	−0.028	0	−0.874	0	0	0
$3.38 \cdot 10^{-13}$	$5.09 \cdot 10^{7}$	0	0	0	0	0	0.014	0.014	−0.874	0.028	0	−0.485	0	0	0
0	∞	0	0	0	0	0	0	0	0	0	0	0	0	0.707	0.707

Statistical and Principal Component Analysis

- exact symmetry of the stationary system
- revealed as a result of PCA
- variation $\delta p_{13}=\delta p_{14}$ corresponds to infinite scatter
- the result depends only on p_{13}-p_{14}, or on ratio of corresponding k's
- the source of degeneracy of $X^T X$ matrix

- Implementation in *Mathematica*
- `Nsolve` – to solve stationary algebraic system, real roots selected
- `Manipulate` – interactive change of parameters to find starting point
- `FindMinimum / Nminimize` – for local/global optimization
- `NonlinearModelFit` – fitting interface to the methods above
- `Gradient` – option to the fitting method to provide finite diff scheme
- `SingularValueDecomposition` – SVD/PCA

Conclusion

- the electrochemical alkaline methanol oxidation process is mathematically modeled
- an algorithm for reconstructing the reaction constants from the experimentally measured polarization curve is developed
- the approach combines statistical and principal component analysis
- formal criteria for reconstruction accuracy based on the estimate of the trust region for the linearized model are defined

Conclusion

- analysis shows that the described experiment allows to determine precisely not all 14 reaction constants, but only 4 their certain linear combinations
- of the remaining orthogonal combinations, one corresponds to the symmetry of the stationary system and is fundamentally indeterminate in the described experiment
- the remaining 9 combinations have insufficient reconstruction accuracy

- Further plans: other experiments should be involved in the analysis, including fully dynamic cyclic voltammetry and variations in the concentration of the main reagents.