Near-surface ion distribution and buffer effects during electrochemical reactions

MIR@W day: Modelling and simulation of electrochemical flows in Lithium-ion batteries

Dr. Michael AUINGER

MIR@W day
Zeeman Building, University of Warwick
Coventry CV4 7AL, United Kingdom
30th November, 2015

The Beauty of Thermochemical Simulations

MIR@W day: Modelling and simulation of electrochemical flows in Lithium-ion batteries

Dr. Michael AUINGER

MIR@W day
Zeeman Building, University of Warwick
Coventry CV4 7AL, United Kingdom
30th November, 2015

The Steels Processing Group

Prof. S. Seetharaman
Physical Metallurgy

C. Davis
Mechanics

B. Shollock
Coatings

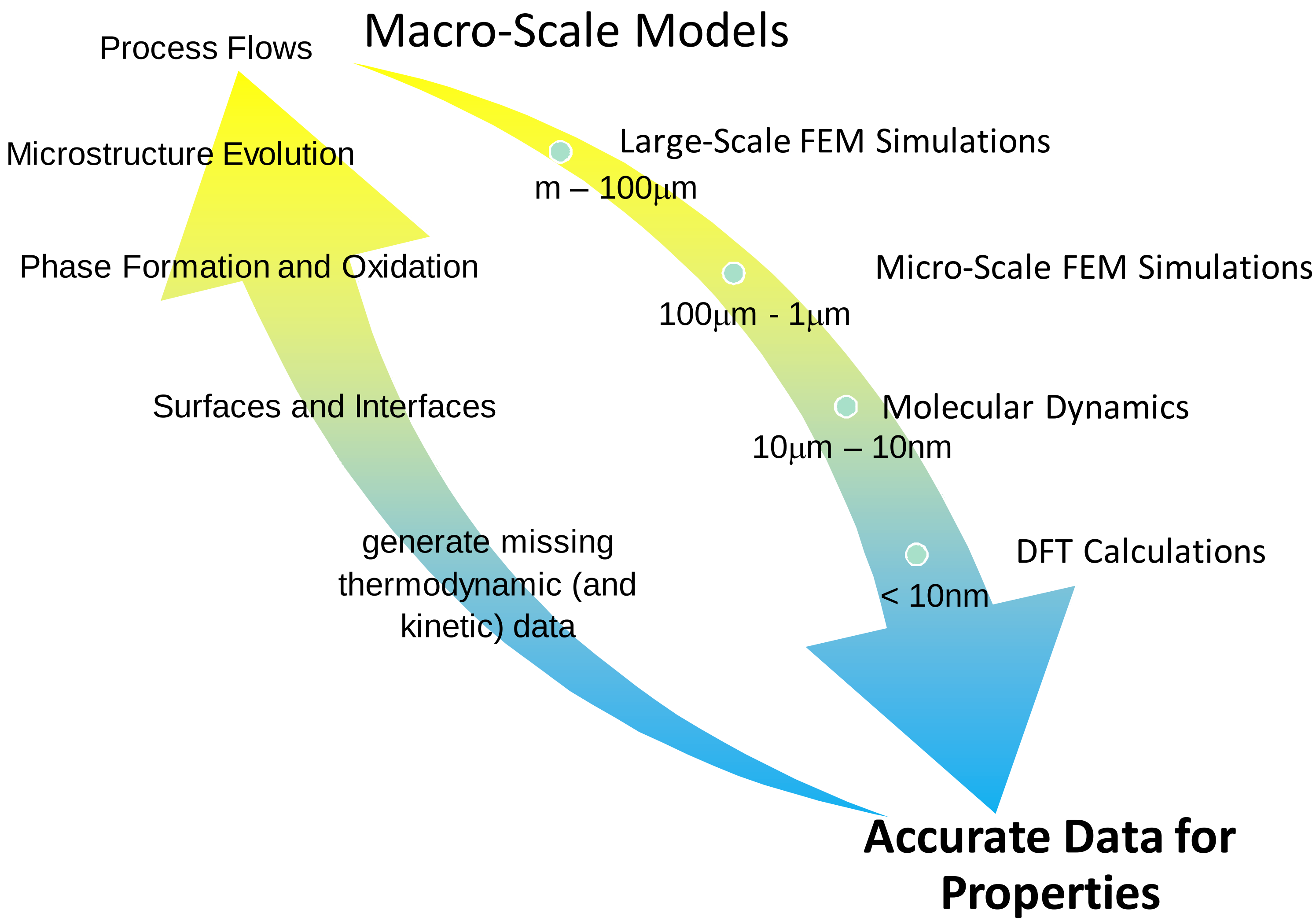
R. Dashwood
Director

P. Srirangam
in-situ

R. Bhagat
EChem.

M. Auinger
Modelling

The Hierarchy of Modelling



Theoretical Model and Discussion

WMG THE UNIVERSITY OF WARWICK

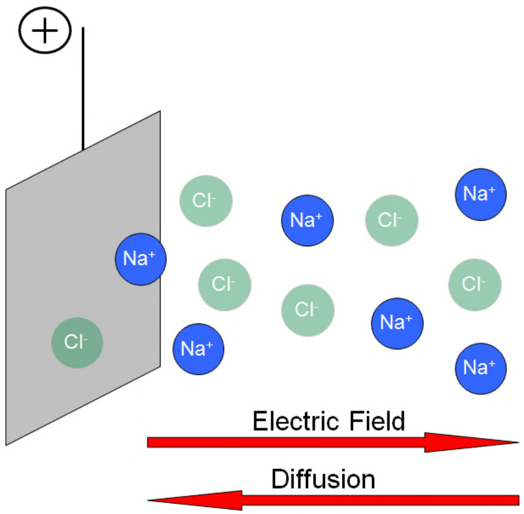
$$\left\{\frac{\partial c_i}{\partial t} = \mathrm{div}\left(D_i \nabla c_i + \frac{D_i z_i e_0}{k_{\mathrm{B}} T} c_i \nabla \varphi + c_i v_i\right)\right\} \quad (i = \mathrm{A, B, C, D})$$

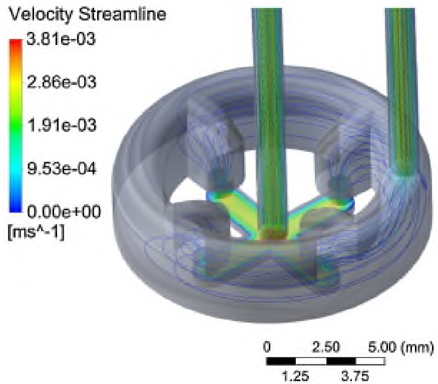
ion diffusion

migration in an electric field

$$K = \frac{c_{\mathrm{C}} c_{\mathrm{D}}}{c_{\mathrm{A}} c_{\mathrm{B}}}$$

chemical equilibrium





convection

P. Skladal, *Analytica Chimica Acta* **727** (2012) 41– 46.

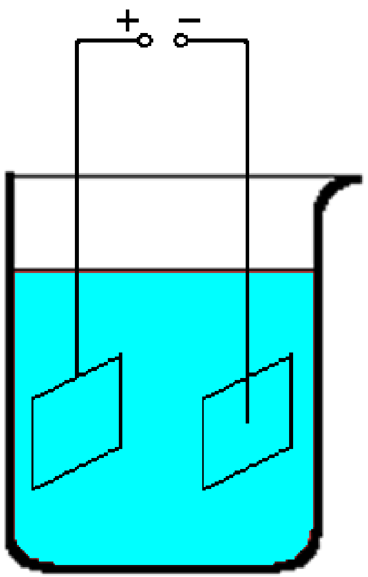
PCCP **13** (2011) 16384-16394.

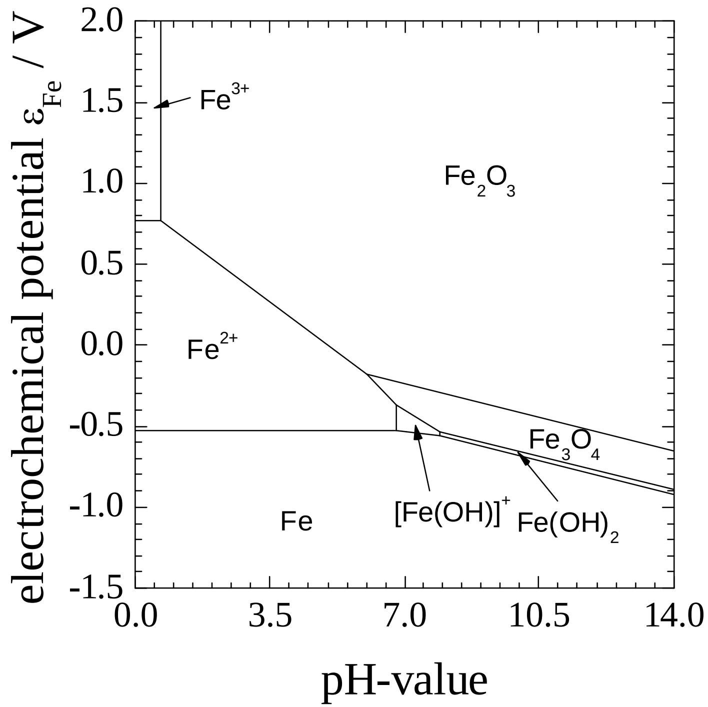
Programme Algorithm

element transport ⇄ chemical reaction

CHEMAPP

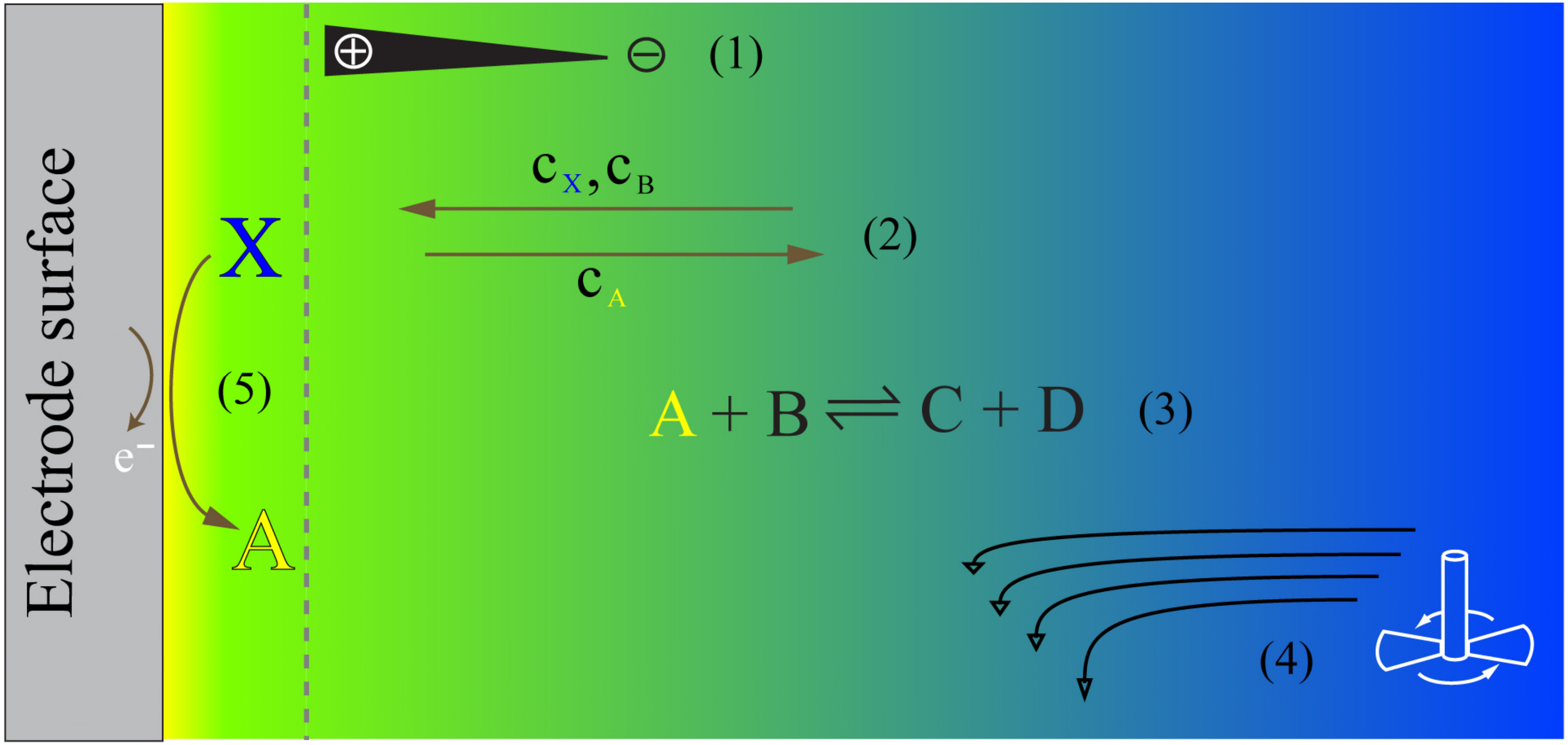
$$\frac{dc_{i(x,t)}}{dt} = \mathrm{div}\left(D_{i(x,T)}.\nabla c_{i(x,t)} + z_i.\mu_{i(x,T)}.c_{i(x,t)}.\nabla\phi_{(x,t)}\right)$$





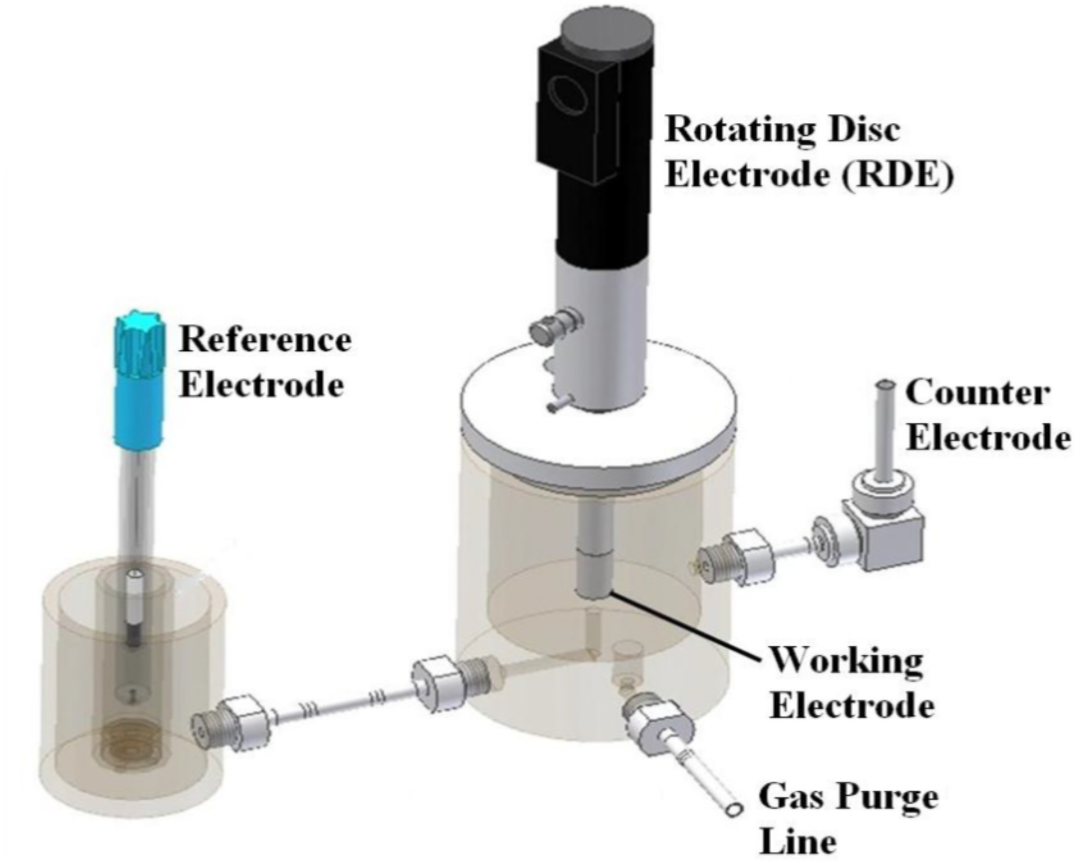
Oxid. Met. **76** (2011) 247-258.

Electrochemistry & surface pH-values



PCCP **13** (2011) 16384-16394.

Experimental RDE-Setup



Working electrode:
polycrystalline Pt disc
(0.196 cm^2), embedded in Teflon

Counter electrode:
graphite rod

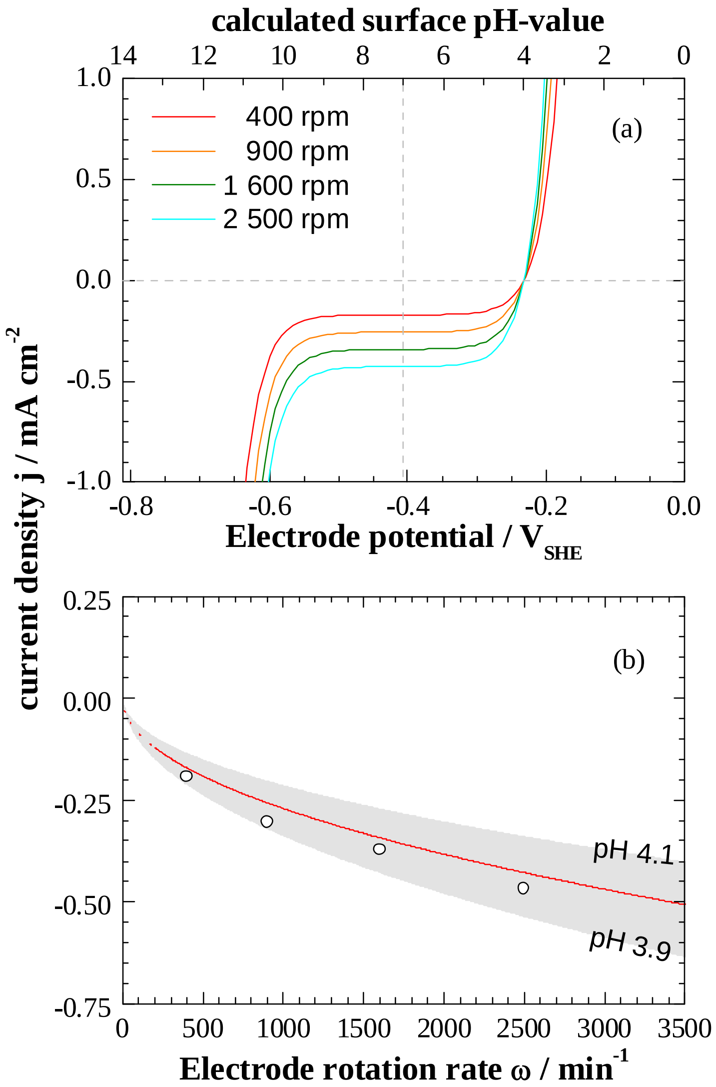
Reference electrode:
saturated Ag/AgCl

50ml Teflon 3-compartment cell

Uncompensated resistance < 2Ω

parameters controlled via LabVIEW

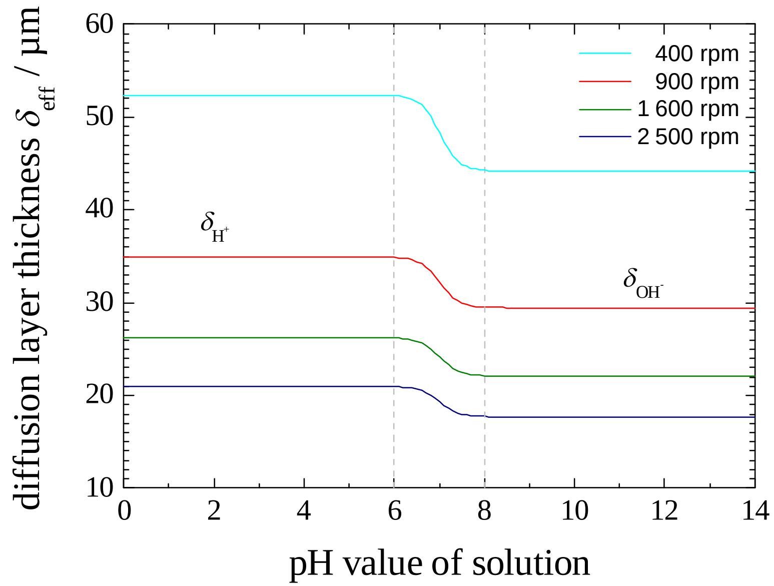
Parameters and Diffusion Layer



Levich Equation:

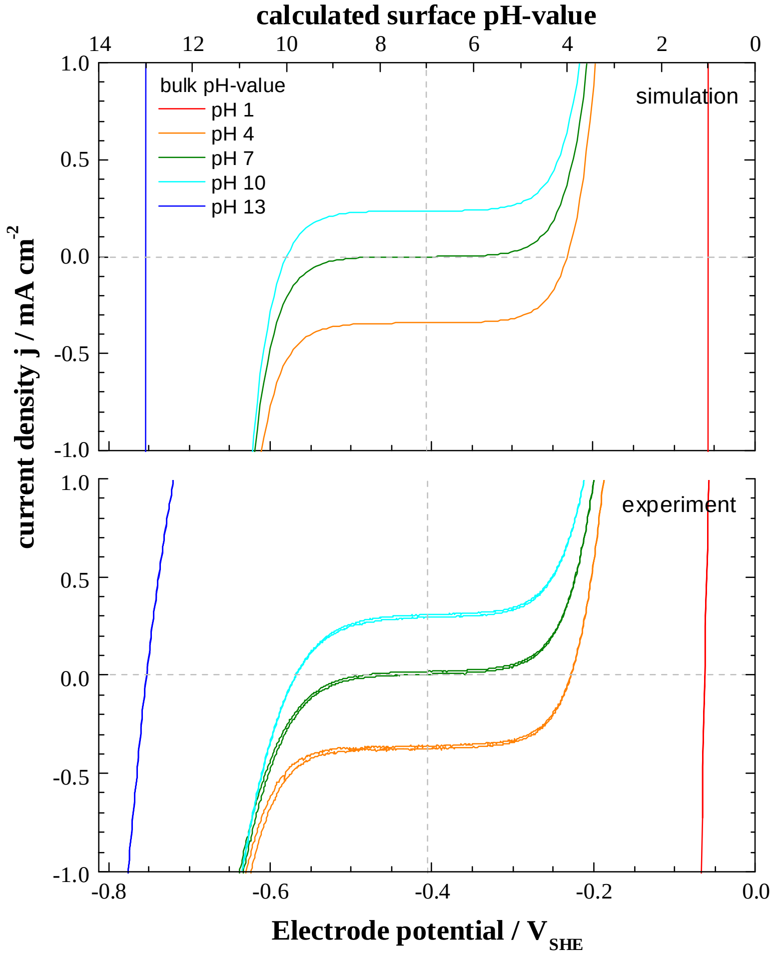
$$\delta_i = 1.6126\, D_i^{\frac{1}{3}}\, \nu^{\frac{1}{6}}\, \omega^{-\frac{1}{2}}$$

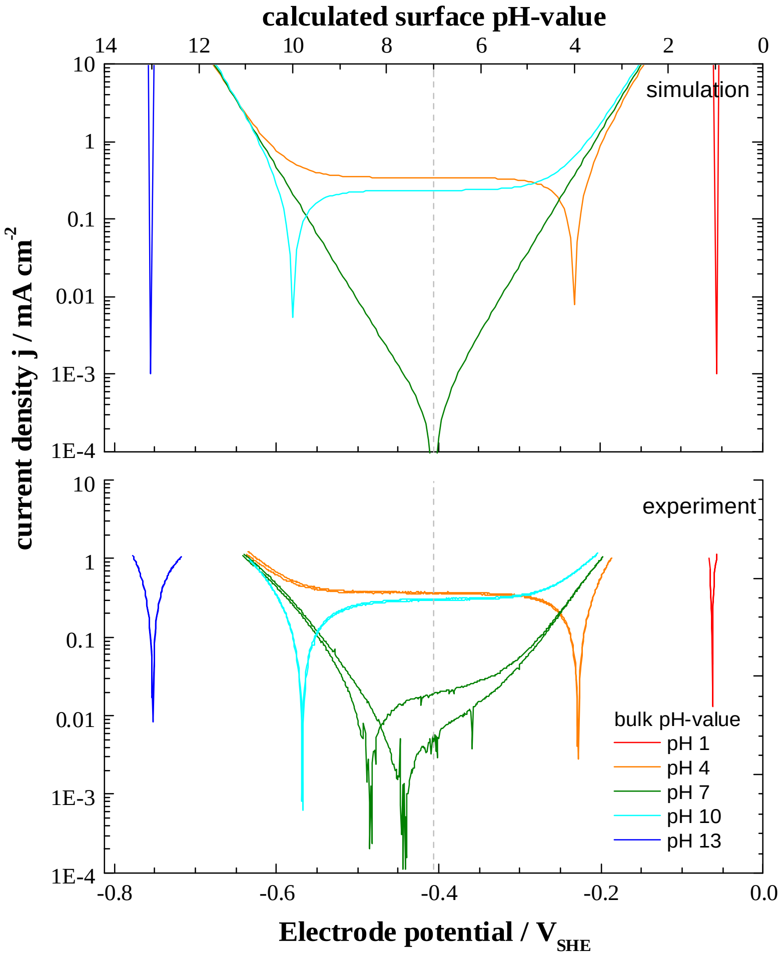
$$\delta_{eff} = \frac{c_{H^+}\,\delta_{H^+} + c_{OH^-}\,\delta_{OH^-}}{c_{H^+} + c_{OH^-}}$$



PCCP **13** (2011) 16384-16394.

Unbuffered Aqueous Solution





unbuffered solution:

$$j_{H^+/OH^-} = \frac{F}{\delta_{eff}}\left[D_{H^+}\left(c_H^{surface} - c_H^{solution}\right) - D_{OH^-}K_W\left(\frac{1}{c_H^{surface}} - \frac{1}{c_H^{solution}}\right)\right]$$

PCCP **13** (2011) 16384-16394.

Local Corrosion Effects

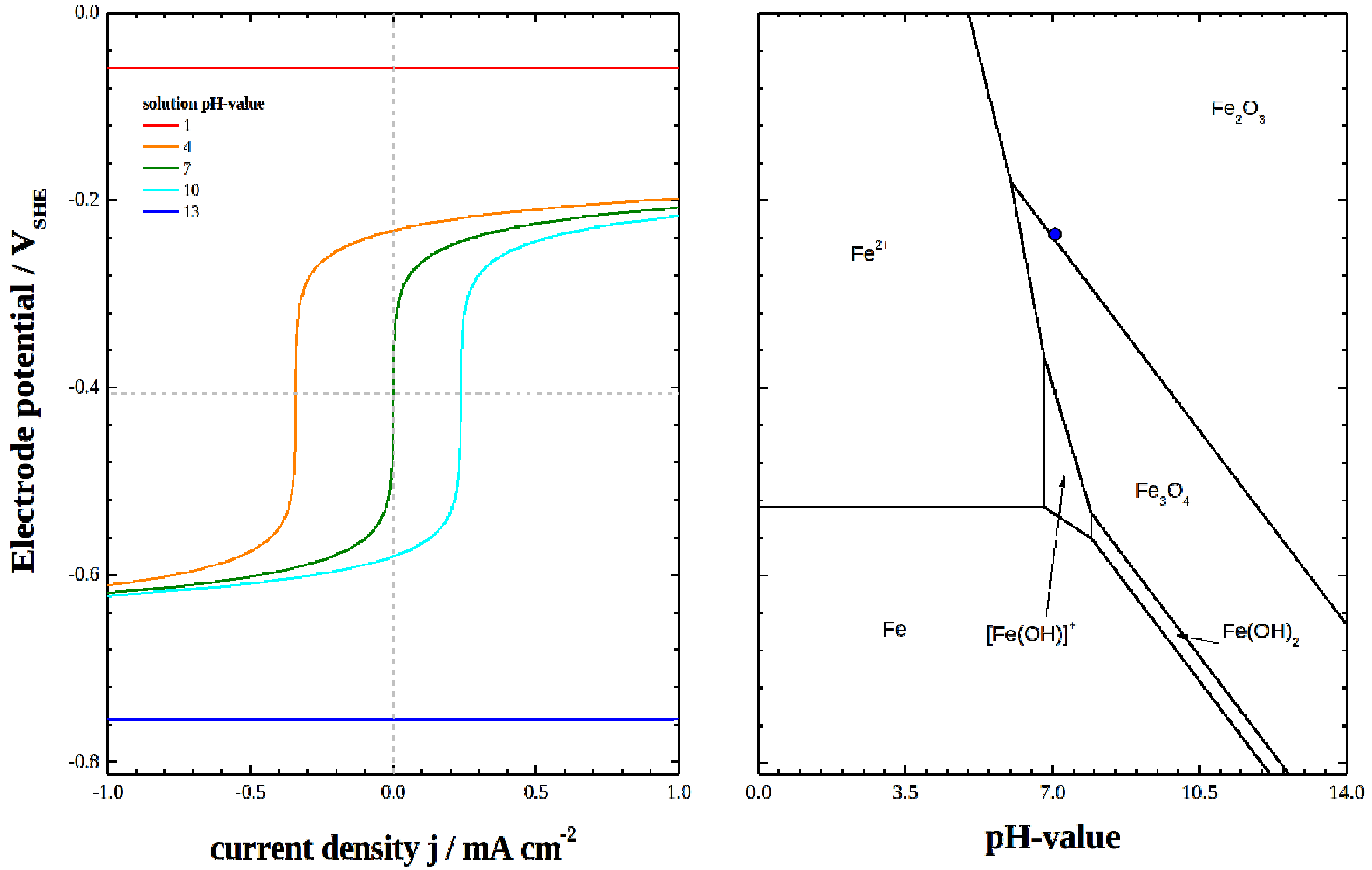


Figure: Cyclic voltammograms in unbuffered solutions of different pH-value.

Local Corrosion Effects

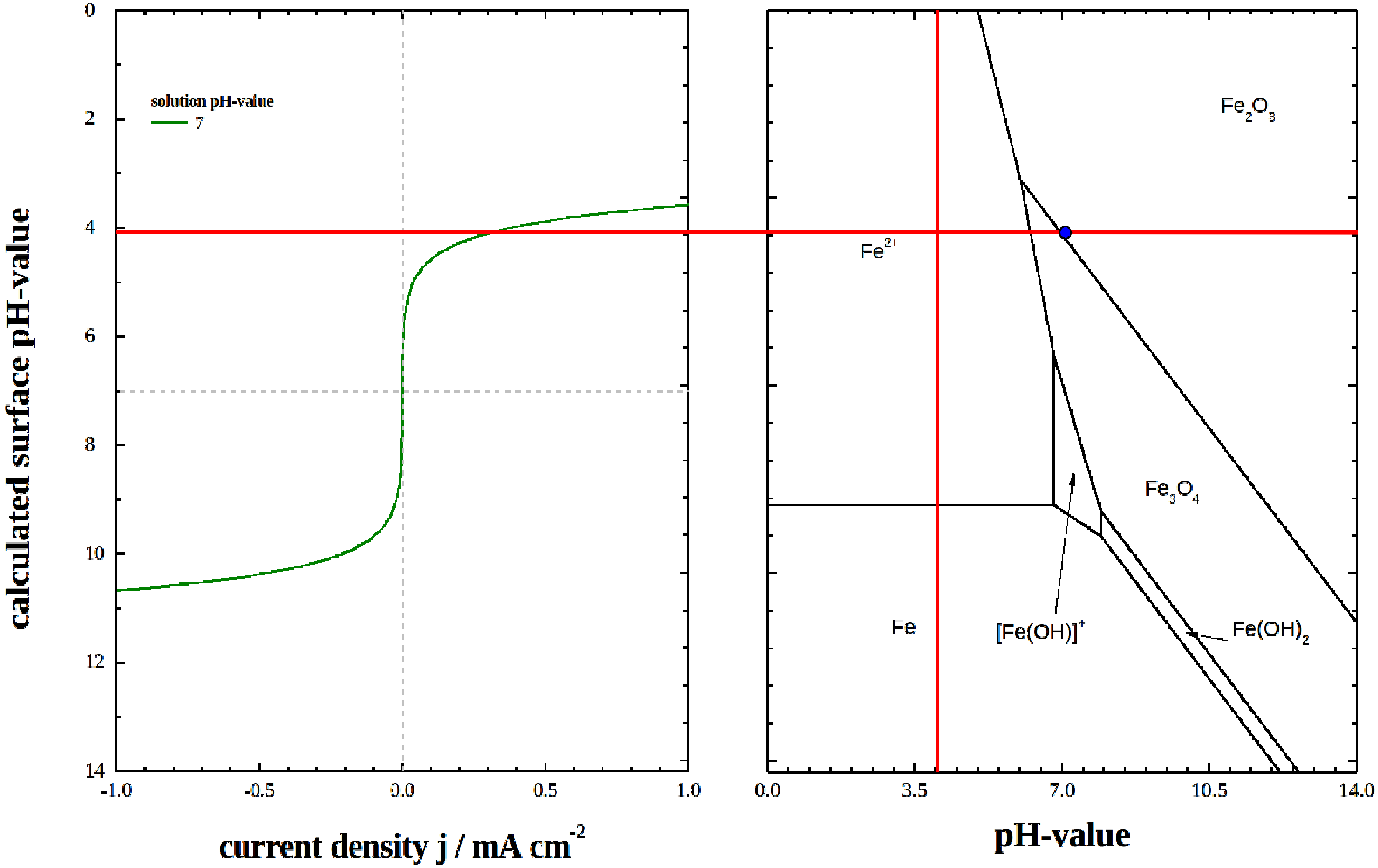


Figure: Cyclic voltammograms in unbuffered solution of pH 7.

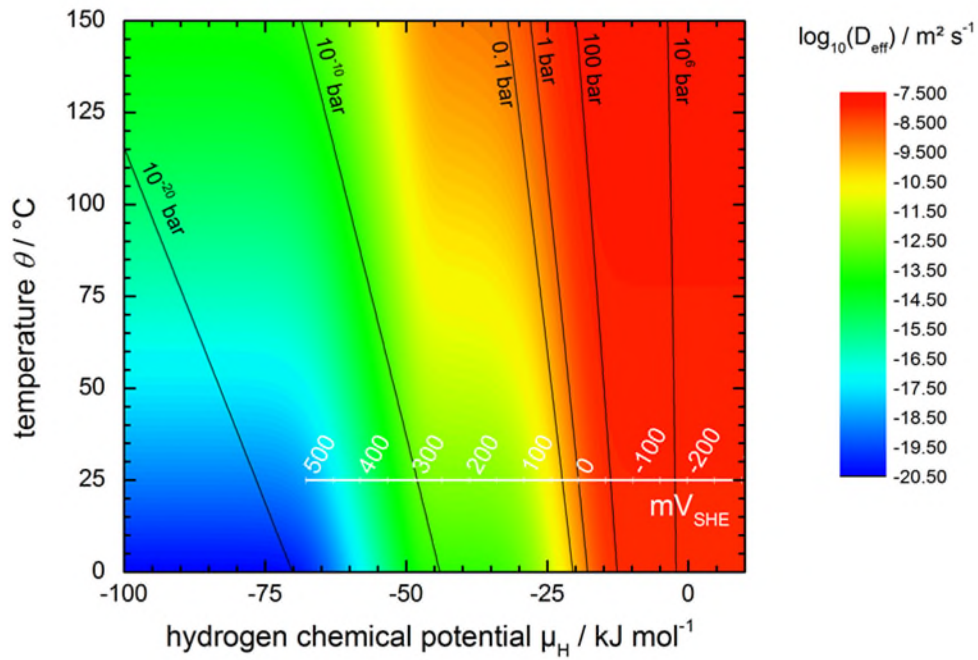
Electrochemistry & Pickling

$$Nernst\ Equation \quad E = E^o + \frac{RT}{zF} ln\left(\frac{a_{Ox}}{a_{Red}}\right)$$

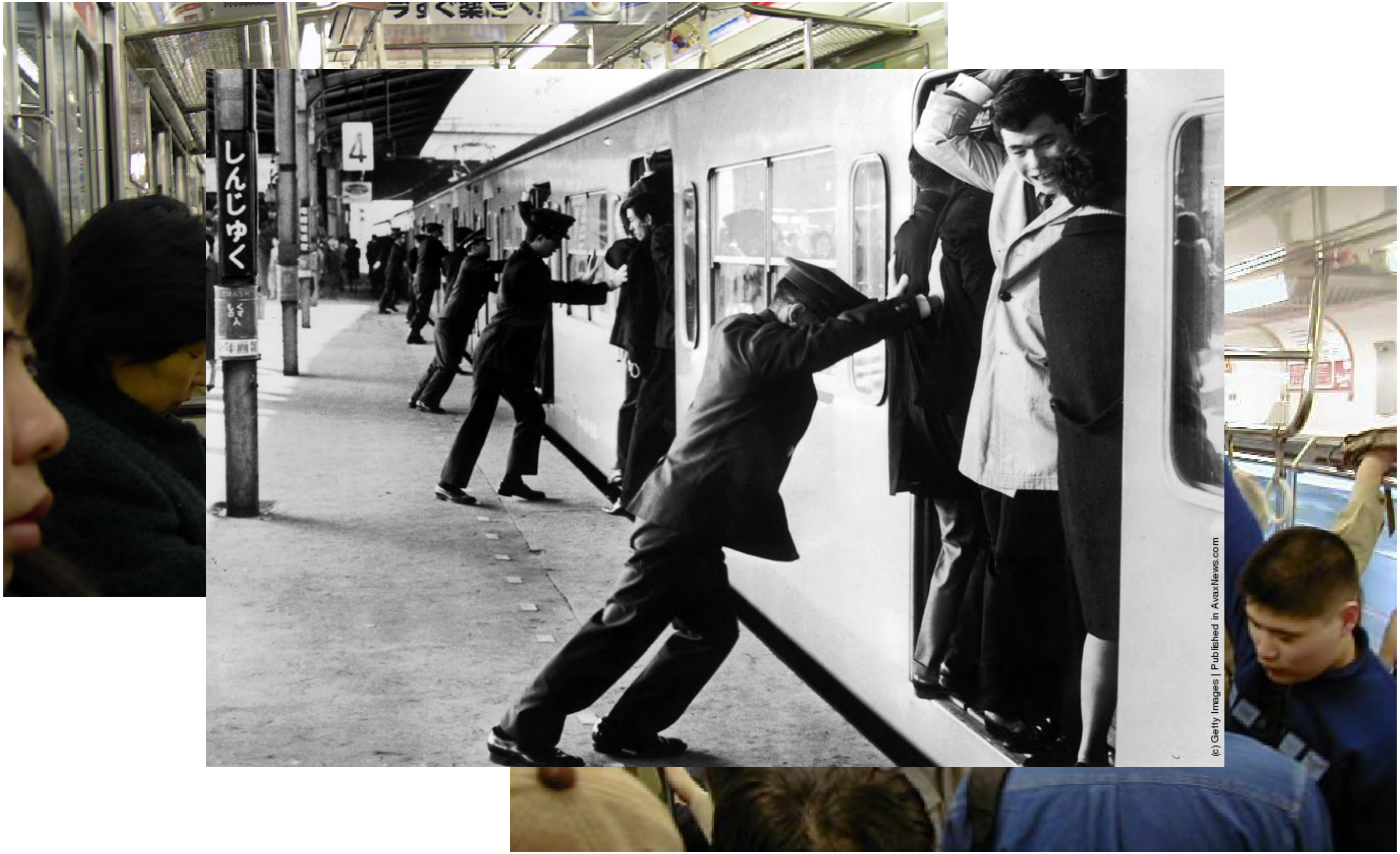
$$E = -58mV\,pH - (29mV\,\log(p(H_2)))$$

An applied voltage of -58 mV (vs SHE) corresponds to:

pH =	7 and	10^{-12} bar H_2
pH =	5 and	10^{-8} bar H_2
pH =	1 and	1 bar H_2
pH =	0 and	100 bar H_2

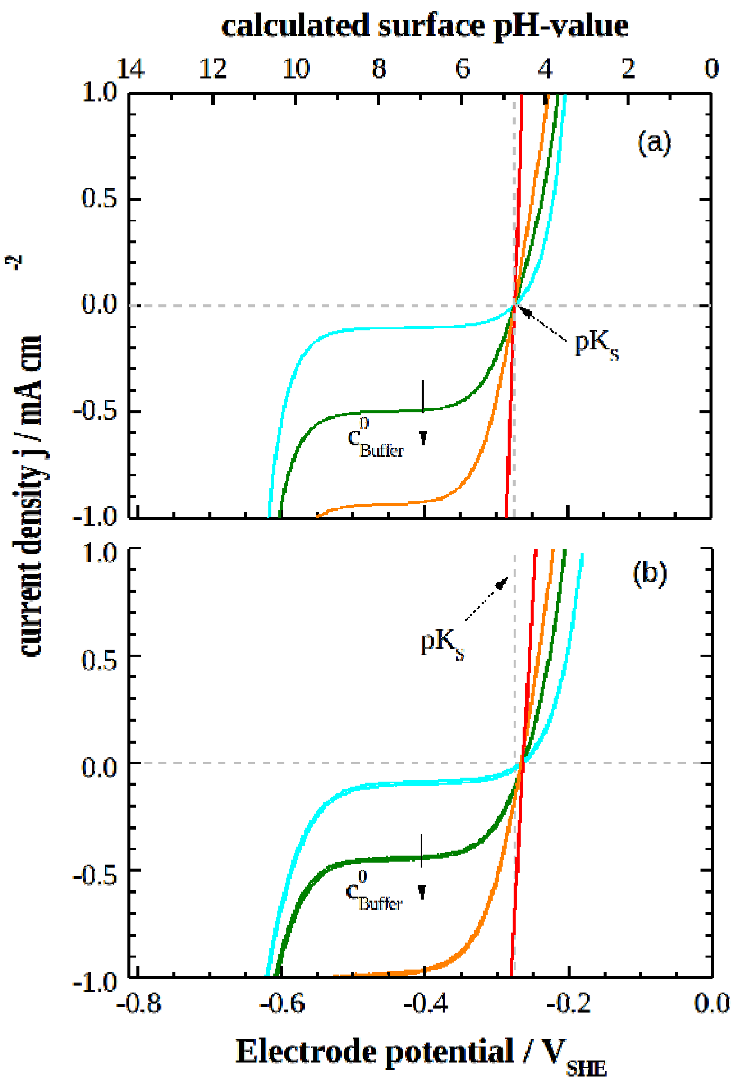


“Solubility” at extreme Conditions



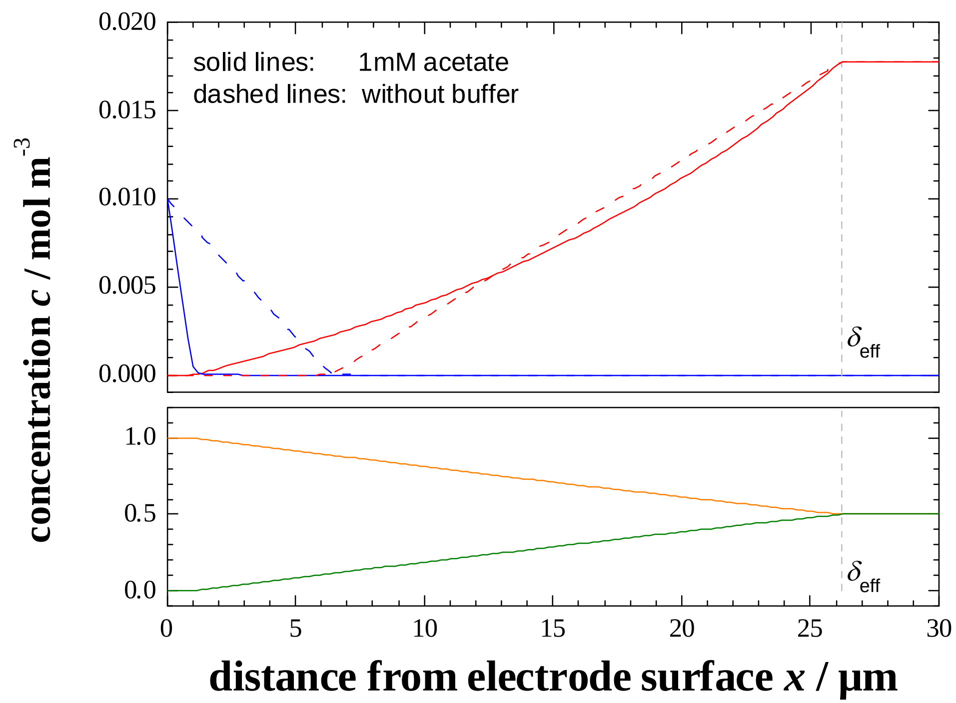
different internet sources – GOOGLE search

Acetate Buffered Solution



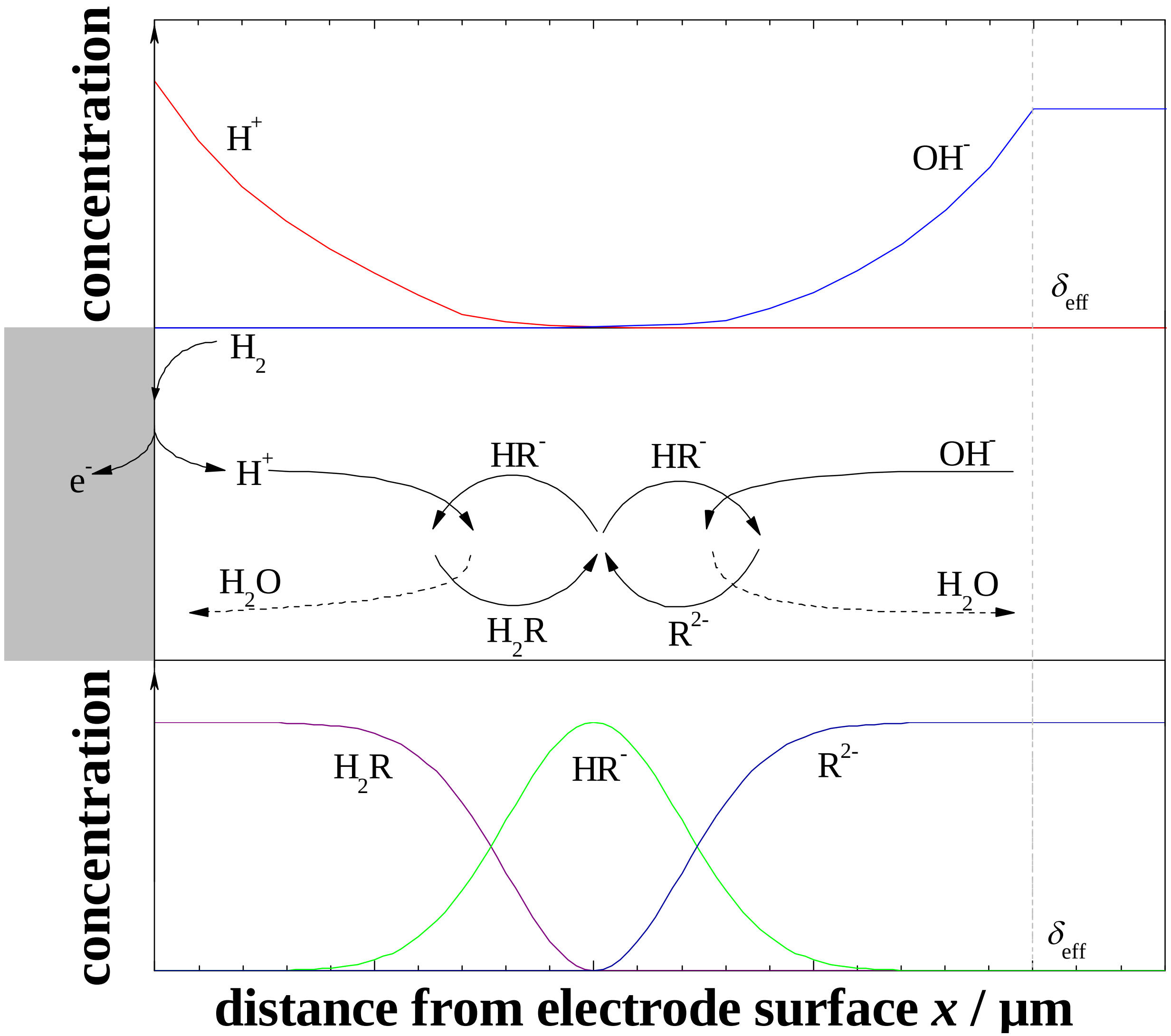
$$CH_3COOH \rightleftarrows CH_3COO^- + H^+$$

$$j = j_{H^+/OH^-} + \frac{c^0_{Buffer}\,F}{\delta_{eff}}\left[\frac{D_{HAc}\,c_H^{surface} - D_{Ac^-}\,K_S}{K_S + c_H^{surface}} - \frac{D_{HAc}\,c_H^{solution} - D_{Ac^-}\,K_S}{K_S + c_H^{solution}}\right]$$



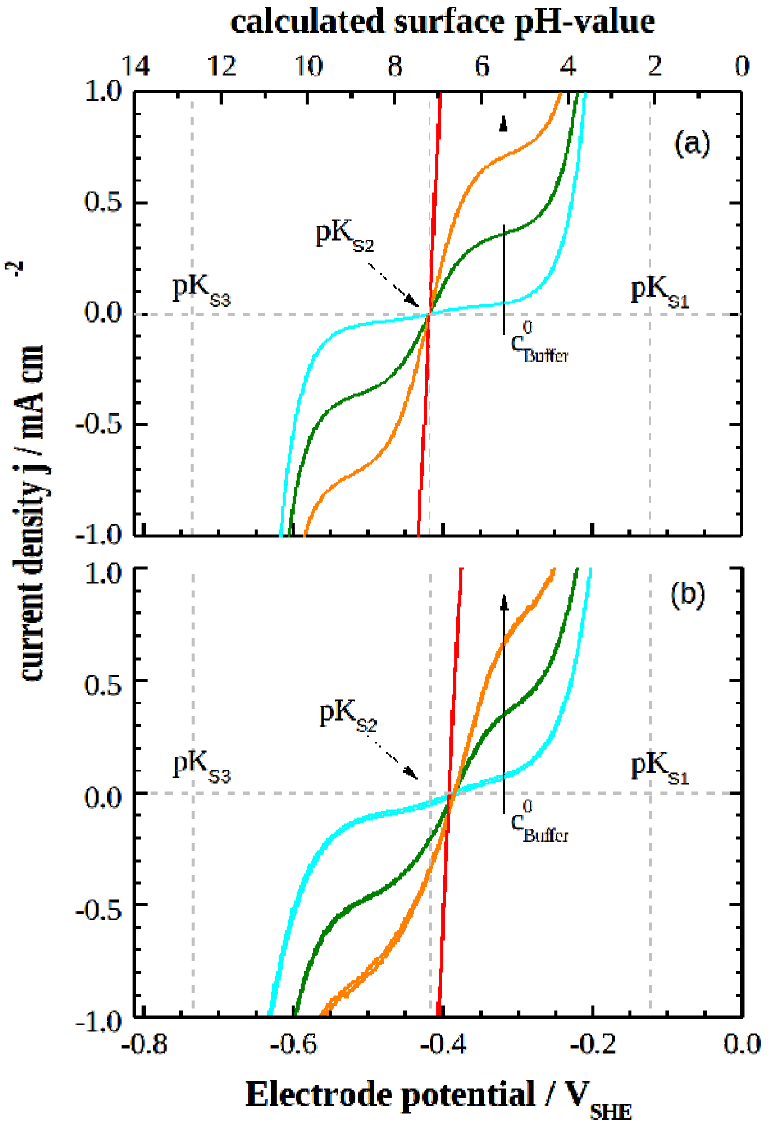
PCCP **13** (2011) 16384-16394.

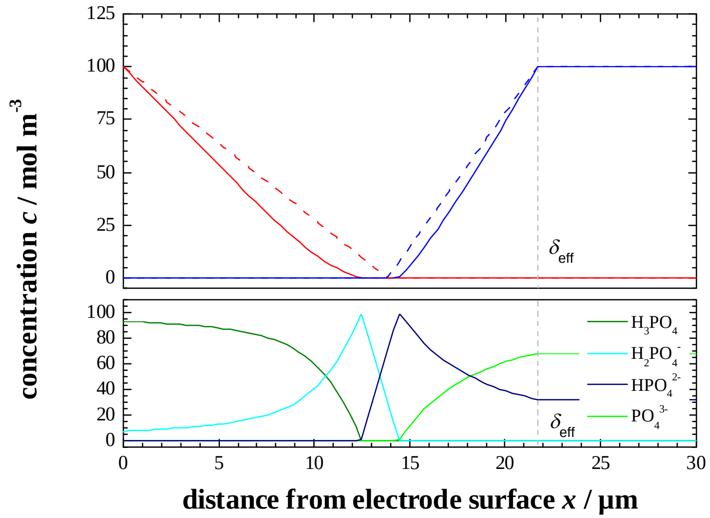
General Transport Scheme



PCCP **13** (2011) 16384-16394.

Phosphate Buffered Solution



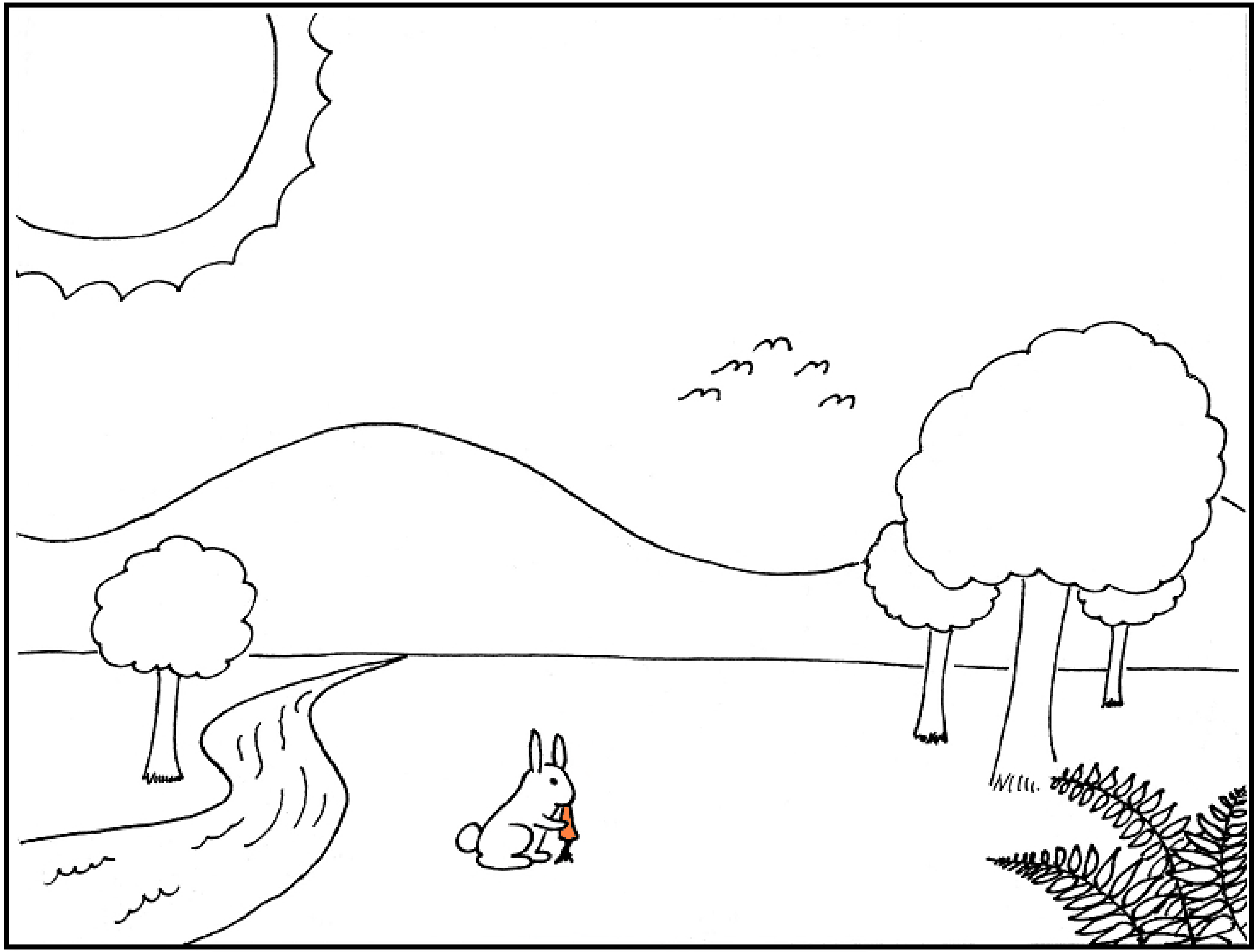


$$j = j_{H^+/OH^-} + j_{Buffer}$$

$$j_{Buffer} = \frac{c^0_{Buffer} F}{\delta_{eff}} \left(\frac{3D_1 + D_2 \frac{K_{S1}}{c_{(x),H^+}} - D_3 \frac{K_{S1} K_{S2}}{c^2_{(x),H^+}} - 3D_4 \frac{K_{S1} K_{S2} K_{S3}}{c^3_{(x),H^+}}}{1 + \frac{K_{S1}}{c_{(x),H^+}} + \frac{K_{S1} K_{S2}}{c^2_{(x),H^+}} + \frac{K_{S1} K_{S2} K_{S3}}{c^3_{(x),H^+}}} \right) \Bigg|_{x=\delta_{eff}}^{x=0}$$

PCCP **13** (2011) 16384-16394.

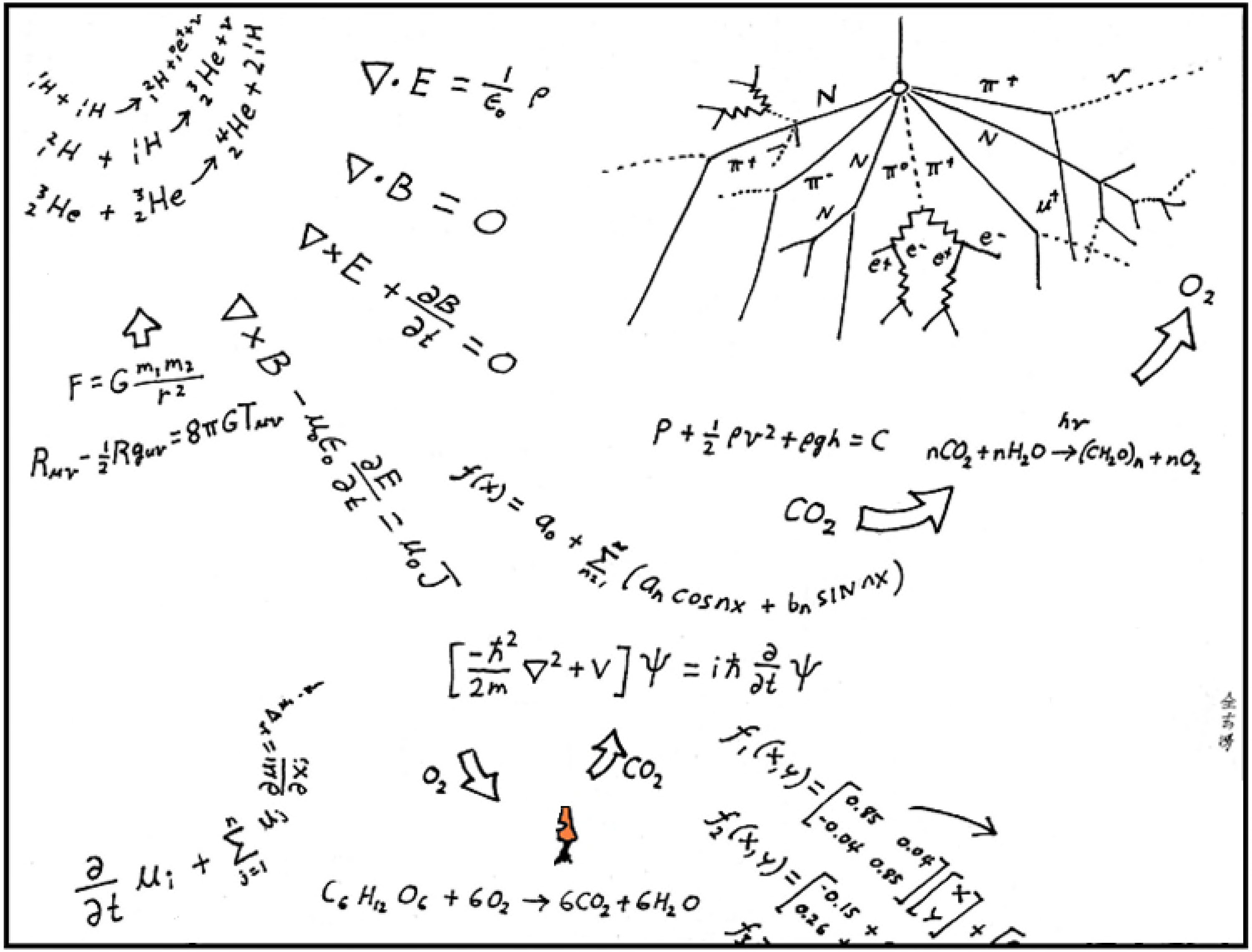
The Use of Mathematics



www.abstrusegoose.com

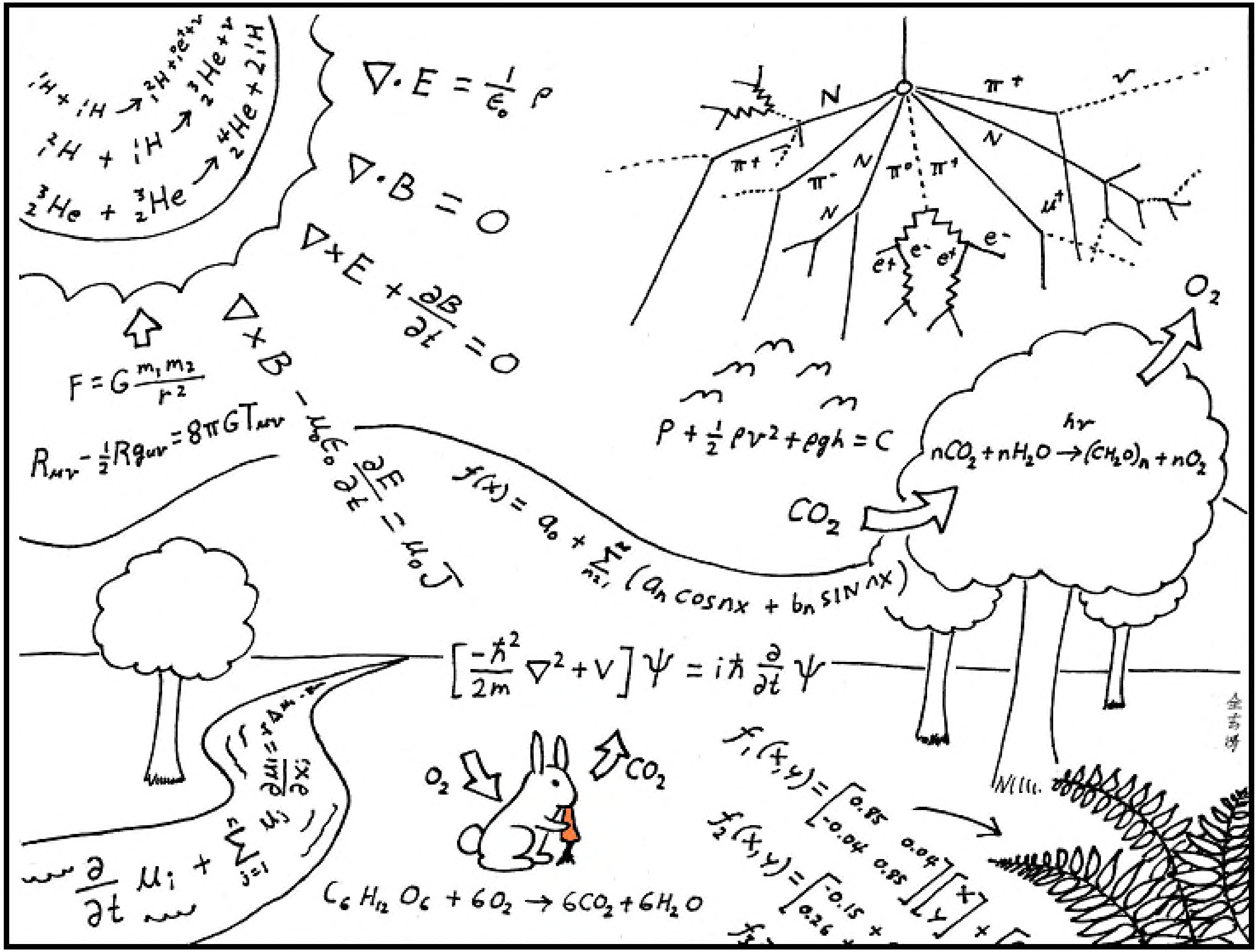
The Use of Mathematics

WMG THE UNIVERSITY OF WARWICK



www.abstrusegoose.com

The Use of Mathematics



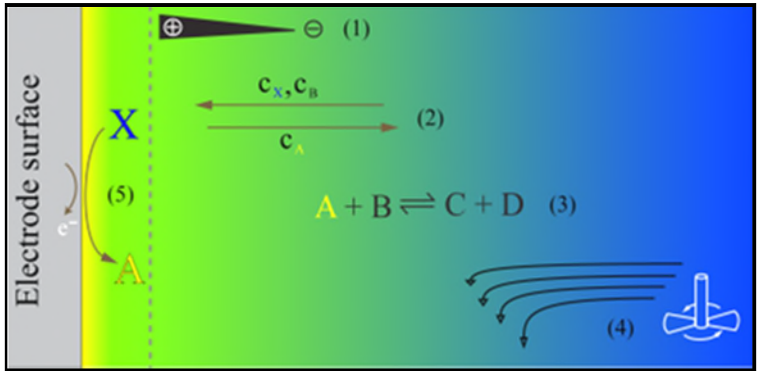
www.abstrusegoose.com

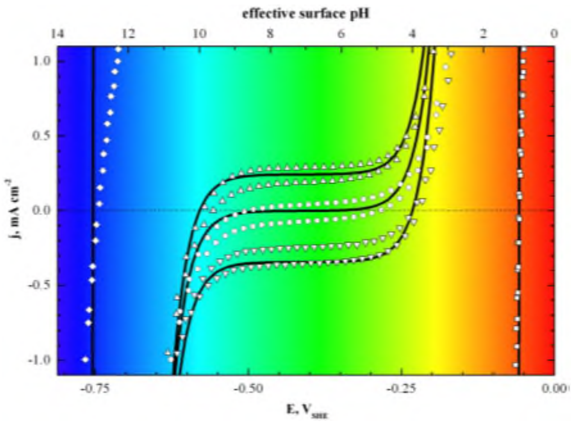
Summary

Near-surface ion distribution and buffer effects during electrochemical reaction

M. Auinger, I. Katsounaros, J.C. Meier, S.O. Klemm, P.U. Biedermann, A.A. Topalov, M. Rowherder, K.J.J. Mayrhofer

PCCP 13 (2011) 16384-16394.





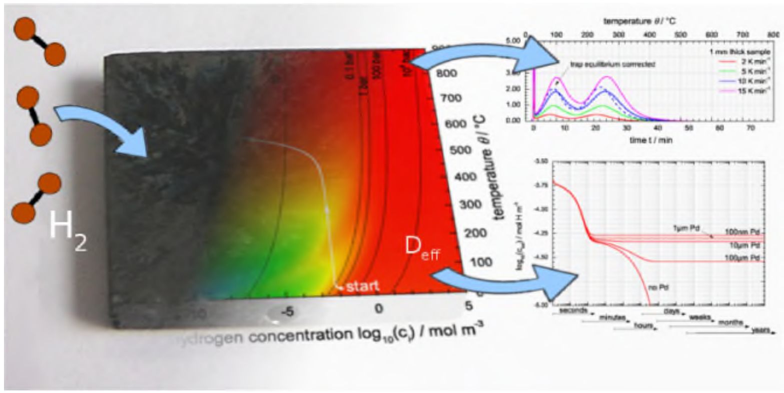
The effective surface pH during reactions at the solid-liquid interface

I. Katsounaros, J.C. Meier, S.O. Klemm, A.A. Topalov, P.U. Biedermann, M. Auinger, K.J.J. Mayrhofer

Electrochem. Commun. 13 (2011) 634-637.

Hydrogen Transport in non-ideal Crystalline Materials

M. Auinger, Chem. Phys. Chem. 15 (2014) 2893-2902.



Acknowledgement

K. Mayrhofer, J.C. Meier, A.A. Topalov, I. Katsounaros, D. Kurz, A. Mingers

Max-Planck-Institut für Eisenforschung GmbH

Christian Doppler Forschungsgesellschaft

FCI FONDS DER CHEMISCHEN INDUSTRIE

voestalpine EINEN SCHRITT VORAUS.


warwick arts centre