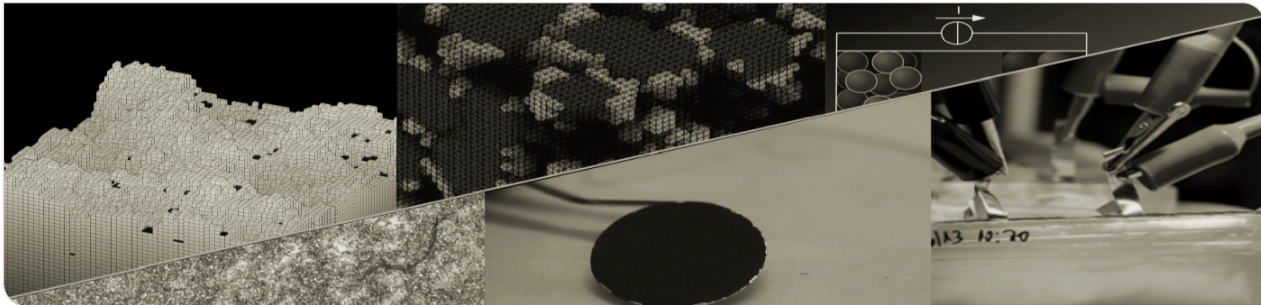# Model-assisted Analysis and Design of Electrochemical Processes

Energy Systems Initiative Fall Seminar, Carnegie Mellon University, online

Ulrike Krewer and Team | October 17, 2024

Content

Content

Challenge: Fluctuation of Renewable Energies
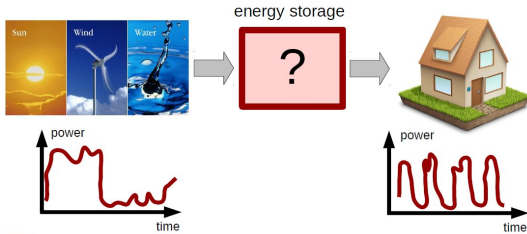
energy storage

- Energy supply and demand are fluctuating.
- Efficient and dynamic energy storages needed.
- Electrochemical storages (batteries) cover short and mid term range;
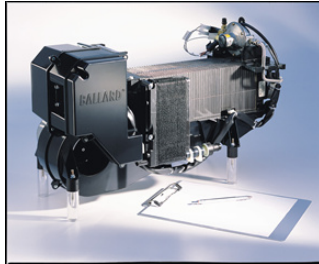- Chemical storages (fuel) cover long term range.
- Option: Power-to-chemicals!

[Behrens, Schlögl]
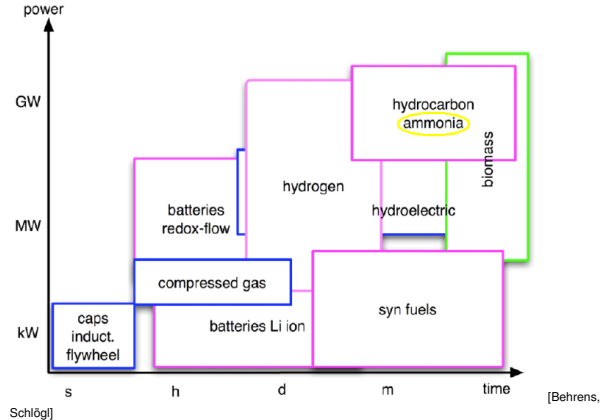
Electrochemical (Energy) Processes - Some Basics

Galvanic cell

[Ballard]

- Chemicals/fuels $\rightarrow$ electricity (+ chemicals)
- Example: H_2 fuel cell
- + Continuous & dynamic operation

Electrolyser

[Enertrag]

- Electricity $\rightarrow$ fuel (e.g. H_2), chemicals
- + Continuous & dynamic operation
- Reverse process to fuel cell

Batteries, redox flow cells

- Chemical energy $\leftrightarrow$ electricity
- + Reversible reaction
- o Not continuous, but highly dynamic

Institute for Applied Materials - Electrochemical Technologies

Typical Electrochemical Cell Designs

- Cells with separator between neg. and pos. electrode typical for fuel cells, electrolysis, batteries
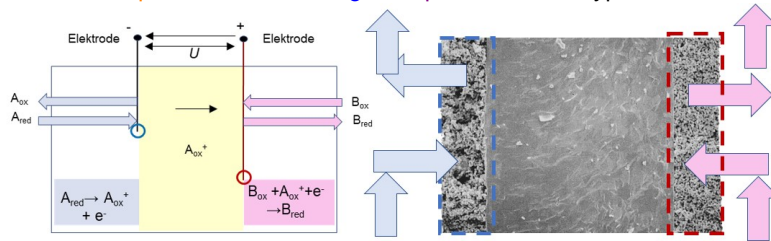
- Cells with reactant and electrolyte flow between neg. and pos. electrode; typical for electrosynthesis
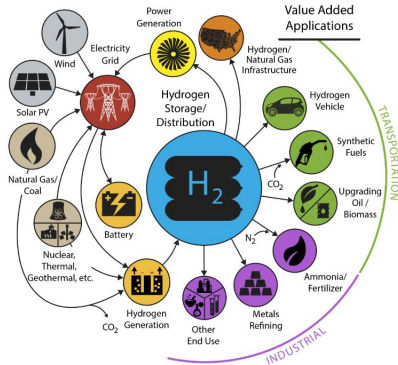
How to Defossilise Society with Electrochemical Technologies
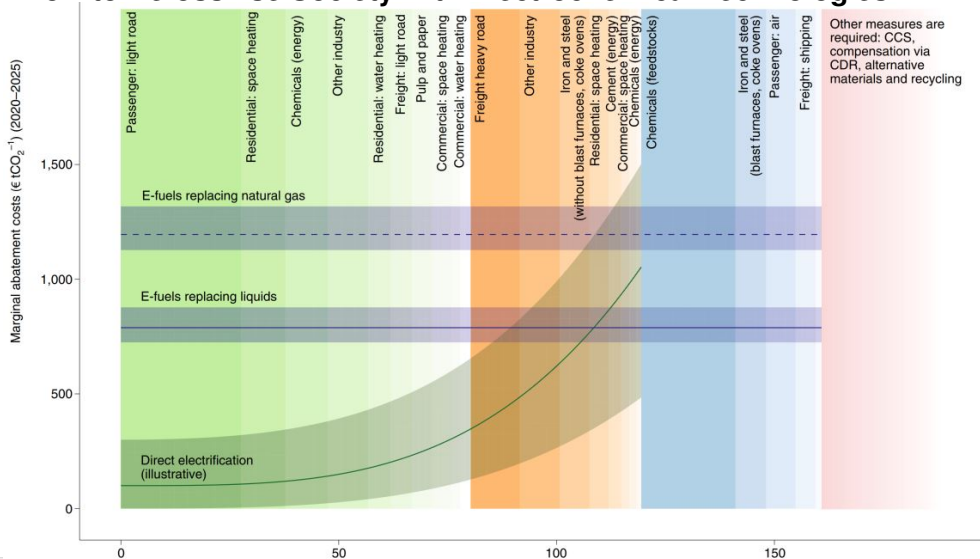
- **Direct electrification (incl. battery) cheapest**: building heating, transport, low T industrial processes

- **Electrosynthesis of H_2, E-fuels, chemicals indispensible**: feedstocks, aviation/shipping, ...
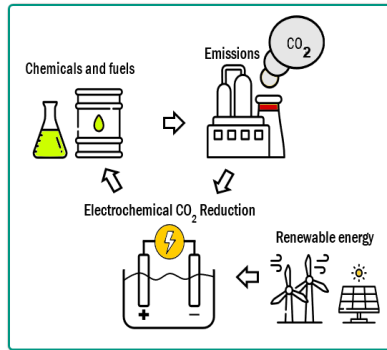
Electrosynthesis of Chemicals and Fuels

- Electrochemistry offers myriads of options to electrify and defossilise chemical processes
- Besides H_2 and CO_2 valorisation, also bulk and fine chemicals can be electrochemically produced!
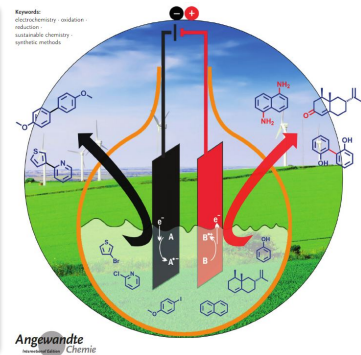
H_2 production & usage

[Satyapal, H2@scale, Dept. of Energy, US, 2017]

CO_2 electroreduction

Electroorganic synthesis

[Wiebe, ..Waldvogel, Angew. Chem.'18]

Myriad Synthesis Options as Counter Electrode for CO₂ Reduction
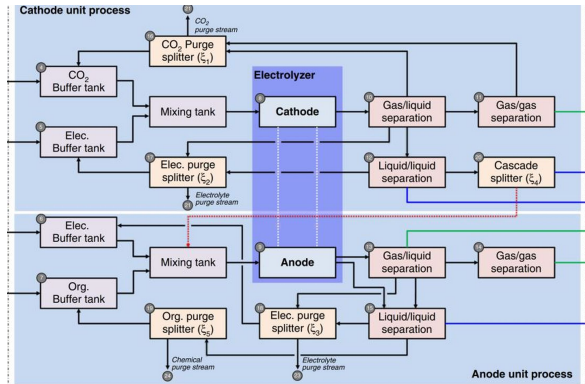
[Na et al., Nat. Comm.'19]
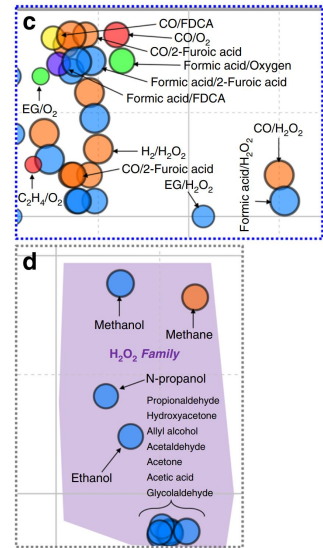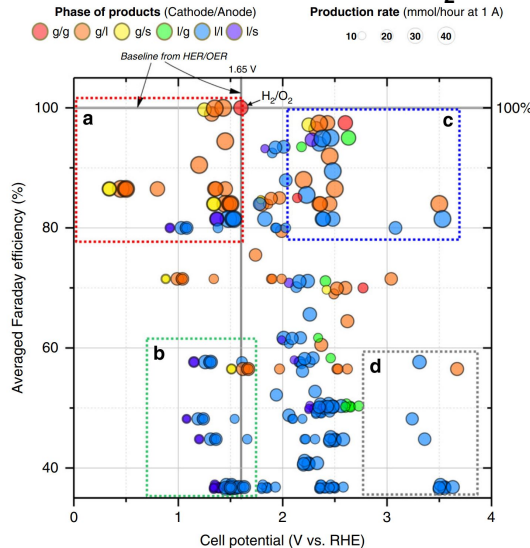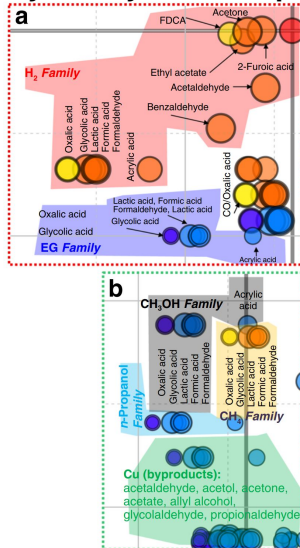
Debottlenecking for Successful Electrolysis Technologies

- Roadblocks to overcome: cost competitive, (energy) efficiency, available technical scale reactors/cells, robustness

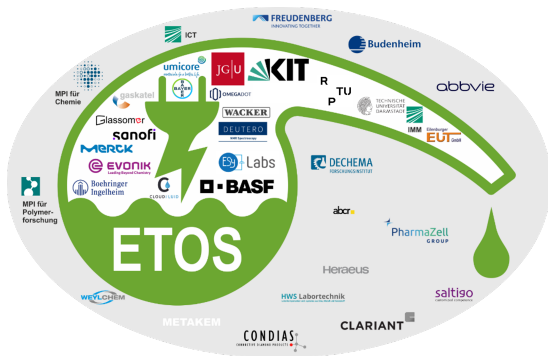- Wide-spread application requires prior quantitative understanding and assessment of technologies!
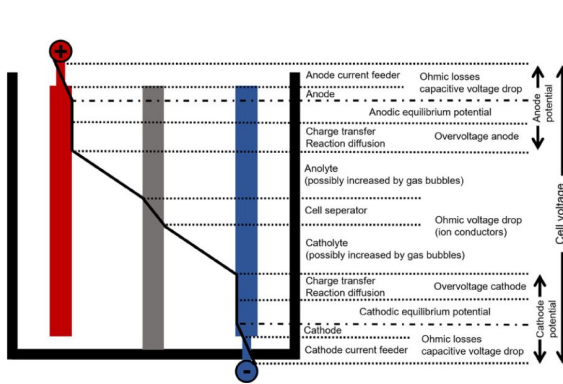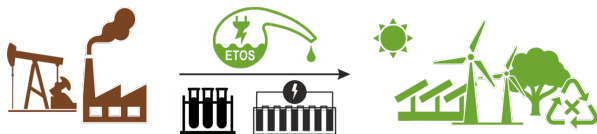

[Seidel, ..Waldvogel, MRS Energ. Sus.'20]

[Na et al., Nat. Comm.'19]

German Cluster4Future: Electrifying Technical Organic Synthesis

- First and largest platform to transfer electroorganic synthesis from lab to industry!
- Goal of cluster:
  - Enable the chemical industry to electrify
  - Replace chemical by electrochemical processes for fine chemicals production!
  - Establish engineering tools and models in the field!
- Huge industry interest
  22 projects, $>$ 15 industry partners, 9 years!
  Lead: S. Waldvogel, U. Krewer
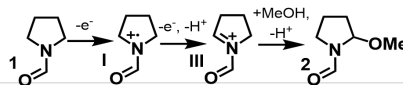
# Not Trivial - How to Embed Electrosynthesis in Full Process

b)

O₂

Katholyt ⊳
Anolyt ⊳

Elektrolysezelle   Extraktion   Kristallisation

Lösungsmittel

Produkt
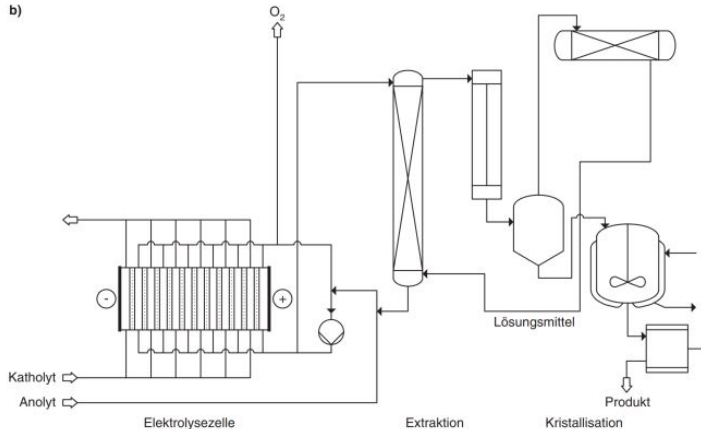
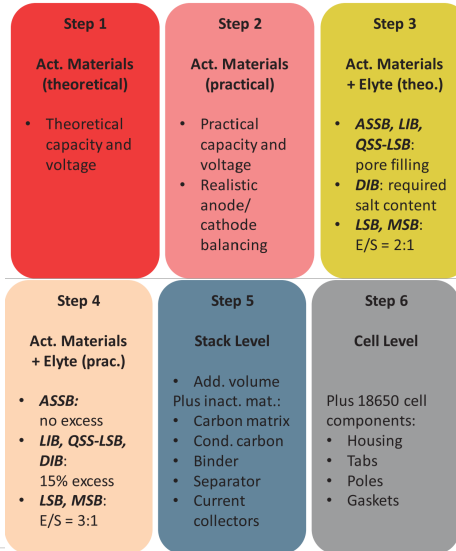[Schmidt, Elektrochem. Verfahrenstechnik, 2003]

- Electroorganic processes are not so trivial to embed in chemical reaction network.
- Downstream processes required with product separation from electrolyte.
- Replacing chemical by electrochemical synthesis processes requires holistic analysis and design!
- So far only little system-level research!
- Attractive playground for process systems engineering!
  e.g. superstructure optimisation

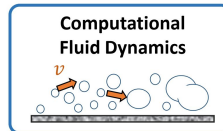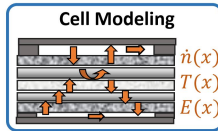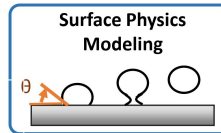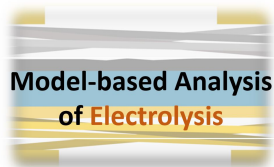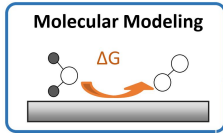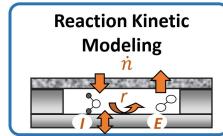# Debottlenecking also needed for Li-Ion & Next-Generation Batteries
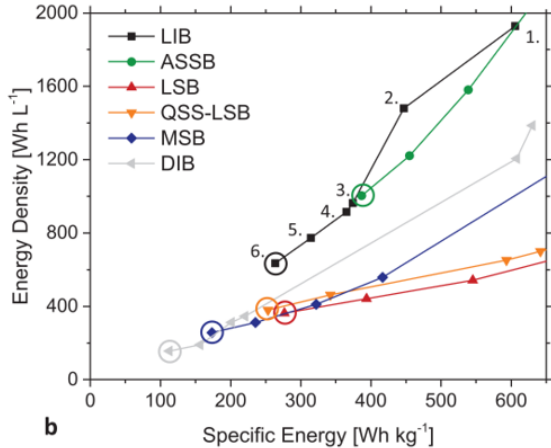
LIB: Li-ion; ASSB: All Solid State; Q: Quasi solid state;
LSB: Li-S; MSB: Mg-S; DIB: dual ion

[Betz et al., Adv. Energy Mat. 2019, 9]

Step 1	Step 2	Step 3
Act. Materials (theoretical)	**Act. Materials (practical)**	**Act. Materials + Elyte (theo.)**
• Theoretical capacity and voltage	• Practical capacity and voltage • Realistic anode/cathode balancing	• *ASSB, LIB, QSS-LSB:* pore filling • *DIB:* required salt content • *LSB, MSB:* E/S = 2:1

Step 4	Step 5	Step 6
Act. Materials + Elyte (prac.)	**Stack Level**	**Cell Level**
• *ASSB:* no excess • *LIB, QSS-LSB, DIB:* 15% excess • *LSB, MSB:* E/S = 3:1	• Add. volume Plus inact. mat.: • Carbon matrix • Cond. carbon • Binder • Separator • Current collectors	Plus 18650 cell components: • Housing • Tabs • Poles • Gaskets

Modeling for Understanding Electrochemical Processes

Reaction Kinetic Modeling
$\dot{n}$
r
i E

Molecular Modeling
ΔG

Model-based Analysis of Electrolysis

Surface Physics Modeling
θ

Cell Modeling
$\dot{n}(x)$
$T(x)$
$E(x)$

Computational Fluid Dynamics
v

[Etzold, Krewer, Thiele, Dreissler, Klemm, Turek, Chem. Engg. J. 2021]

- Number and state of electrochemical models far behind that for chemical processes.
- CFD and molecular modeling widespread!
- Kinetic modeling rare! Only few reliable kinetics!
  Missing brick to predict performance!

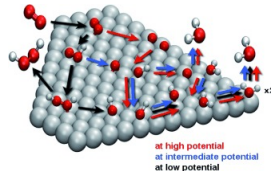# Reaction Kinetic Modeling as Key to Understand & Improve Electrodes

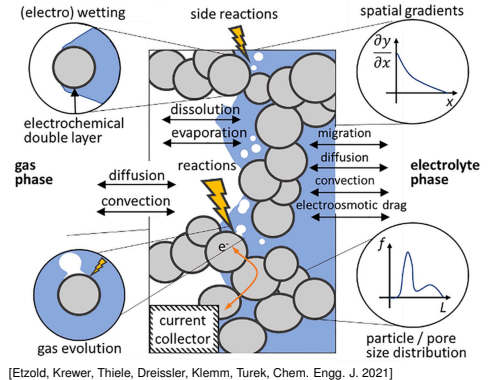## Microkinetics: analysis of reactions in/at electrode
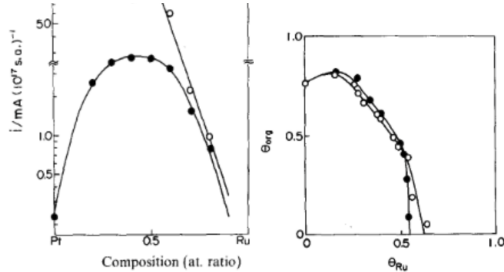
top: adsorbate competition for methanol oxidation at Pt/Ru

[Watanabe, Motoo, Electroanal. Chem. 1974]

right: DFT reveils O_2 reduction pathway as f(potential)

[Keith, Jacob, Angewandte Chemie 2010]

at high potential
at intermediate potential
at low potential

Macrokinetics: reveal transport impact

(electro) wetting
side reactions
spatial gradients
$\frac{\partial y}{\partial x}$

electrochemical double layer
dissolution
evaporation
migration
diffusion

gas phase
reactions
electrolyte phase

diffusion
convection
convection
electroosmotic drag

e−
gas evolution
current collector
particle / pore size distribution
f

[Etzold, Krewer, Thiele, Dreissler, Klemm, Turek, Chem. Engg. J. 2021]

Kinetic Model Equations and Parameterisation Options

Kinetic model formulation: $A \rightarrow A^{\ddagger} \rightarrow A^{+} + e^{-}$

- Electrochemical rate equation (chemical steps: $\eta = 0$):

$$r = \underbrace{k \exp\left(-\frac{\Delta G^{0,\ddagger}}{RT}\right)}_{k_f} c_A (1-\theta) \exp\left(\frac{\alpha F \eta}{RT}\right)$$

- Energy may depend on surface coverage: $\Delta G^{0,\ddagger} = f(\theta)$
- Usually only one e^{-} transferable per step.
- Suggestion of candidate for multistep mechanism using literature, experiments, or theory (DFT/MD).

Parameter identification strategies (e.g. k, $\Delta G^{\ddagger}(\theta)$)

- Option 1: estimate by reproducing experiments; uses real electrodes
- Option 2: from DFT/MD; only for ideal surfaces; limited accurracy

[O' Haire]
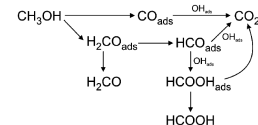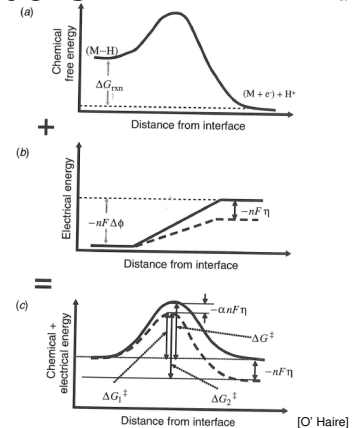
Option 2: Identification from Dynamic vs. Steady State Experiment

[Krewer, Vidakovic-Koch, Rihko-Struckmann, ChemPhysChem 2012; Krewer, Kamat, Sundmacher, JEAC 2007; Krewer, Röder, Harinath, Braatz, Bedürftig, Findeisen, JES 2018]

Identification from steady state experiments?

- At steady state, current I correlates with reaction rates r_i:
  $I = \sum_i z_i F r_i$ with z_i: no. of e^- in r_i

- Separate analysis of single processes (r_i, transport) severely hampered;

- Tafel slope analysis error-prone or inconclusive (see right: CO2R).

Dynamic analysis for model/parameter identification!

- EIS: sinus. input; CV: ramp; chronoamp./potentiometry: step

- Fast and slow processes react with different response times.

- Models contain dynamics via charge (Q) and species (n) balances
  $\frac{dQ}{dt} = C_{dl}\frac{dE}{dt} = I - \sum_i z_i F r_i$
  $\frac{dn_j}{dt} = \dot{n}_j + \sum_i \nu_{ij} r_i$

- Dynamic model allows separation and analysis of single processes.
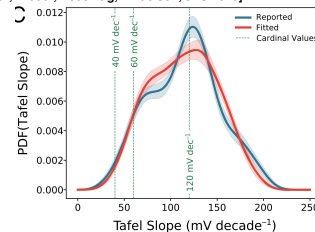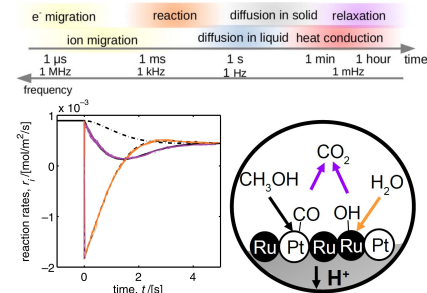
[Limaye et al., Nat.Comm. 2021]

Content

O_2 → * → H_2O ①
*H_2O
② $H^+ + e^-$
*OH
③ $H^+ + e^-$
*O
④ H_2O
*OH_2O
⑤ $H^+ + e^-$
*OOH
⑥ $H^+ + e^-$
*OO
⑦
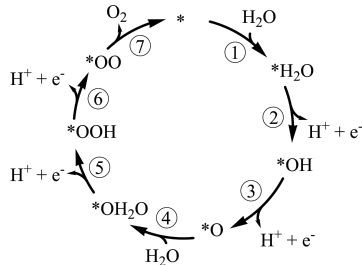
[Geppert, Röse, (...), Krewer, J. Am. Chem. Soc. 2022]

H₂O Electrolysis: Understanding Oxygen Evolution

[Escalera-Lopez (Krewer) et al. ACS Catal. 2021]
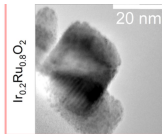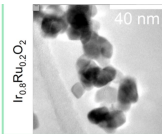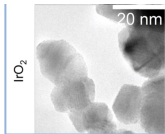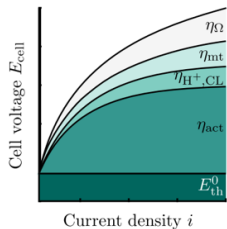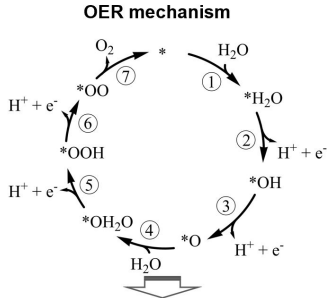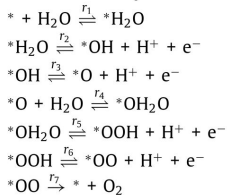

[Schmidt et al 2020 J. Electrochem. Soc. 167 114511]

- Oxygen evolution (OER; $2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$) as largest loss process in PEM water electrolysis.

- How to extract information from experimental cyclovoltammograms (CV; current response to potential ramps) of catalyst particles?

- Characteristic peaks for IrO_2 and RuO_2 differ

- Mixtures show peaks of both metals.

- Goal: reproduce with kinetic model and evaluate information!
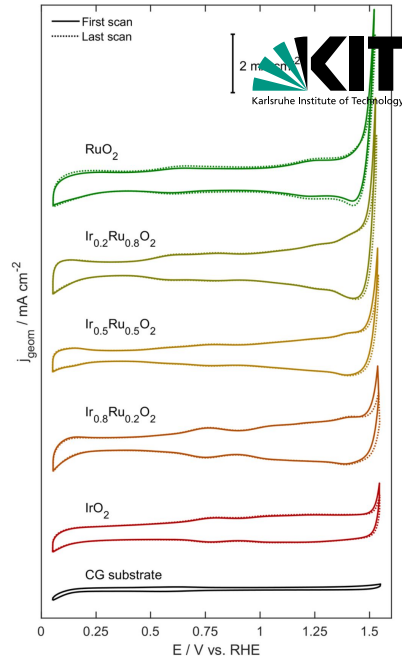
Microkinetic Model for CV Simulation of O_2 Evolution

OER mechanism

Reaction equations

$* + H_2O \overset{r_1}{\rightleftharpoons} {}^*H_2O$

${}^*H_2O \overset{r_2}{\rightleftharpoons} {}^*OH + H^+ + e^-$

${}^*OH \overset{r_3}{\rightleftharpoons} {}^*O + H^+ + e^-$

${}^*O + H_2O \overset{r_4}{\rightleftharpoons} {}^*OH_2O$

${}^*OH_2O \overset{r_5}{\rightleftharpoons} {}^*OOH + H^+ + e^-$

${}^*OOH \overset{r_6}{\rightleftharpoons} {}^*OO + H^+ + e^-$

${}^*OO \overset{r_7}{\rightarrow} * + O_2$

Dynamic input

$$E(t) = E_0 + t\frac{dE}{dt} - j(t)AR$$

Set of rate equations

$$r_{\pm i} = \prod_j \left(a_j^{\nu_{\pm ij}} \cdot \theta_j^{\nu_{\pm ij}}\right) f_{\pm i}(\theta)\, k_0 \exp\left(\frac{-\Delta G_{a,i} \mp \beta \Delta G_{r,i} \pm \beta |\nu_{ie^+}| eE}{k_B T}\right)$$

Hill de Boer (van der Waals) adsorption

$$f_{\pm i}(\theta) = \exp\left(\beta\left[\prod_j \left(\frac{\Delta G_{int,j}}{k_B T}\theta_j\right)^{\nu_{\pm ij}} - \prod_j \left(\frac{\Delta G_{int,j}}{k_B T}\theta_j\right)^{\nu_{\mp ij}} + \prod_j \frac{\theta_j^{\nu_{\pm ij}}}{\theta_j^{\nu_{\mp ij}}} - \prod_j \frac{\theta_j^{\nu_{\mp ij}}}{\theta_j^{\nu_{\pm ij}}}\right]\right)$$

Surface coverage balance

$$\frac{d\theta_j}{dt} = \sum_i \nu_{ij} \cdot (r_{+i} - r_{-i})$$

Dynamic change in current

$$\frac{dq}{dt} = C_{dl} \cdot \frac{dE}{dt} = j(t) - F\rho \sum_i \nu_{ie^+} \cdot (r_{+i} - r_{-i})$$

- Mechanism comprises seven intermediates
- 4 electrochemical, 3 chemical (sorption)
- Single reaction rates enter dynamic species and charge balance
- Parameter to be identified from CV: Energies ΔG, site density ρ

H₂O Electrolysis: O₂ Kinetic Identification for IrO₂
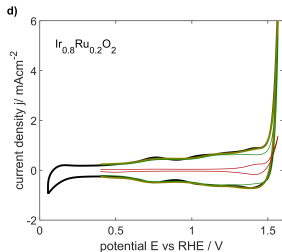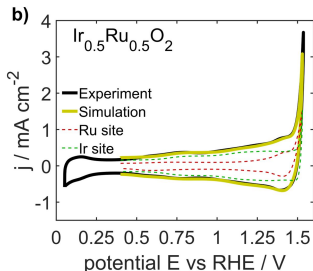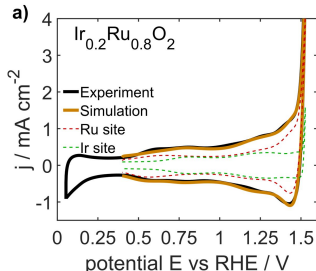
[Geppert, Röse, Pauer, Krewer, ChemElectroChem, 2022]
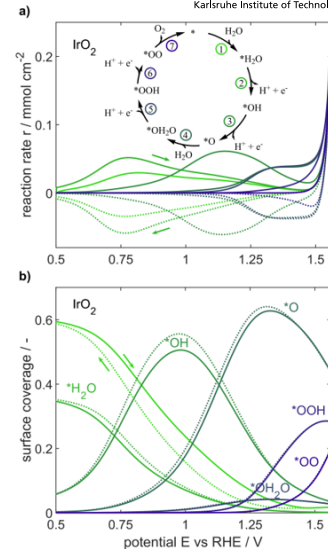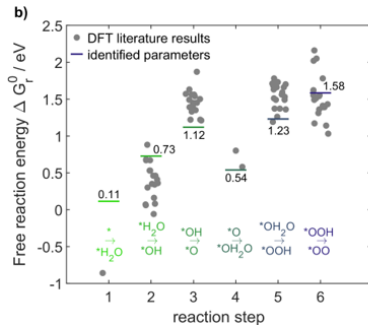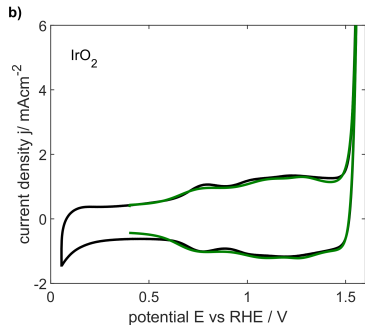
- Excellent reproduction of IrO₂ CV with kinetic model.
- Identified energy parameters of steps are close to DFT ones.
- Accumulating species show limitation at 1.6V:
  H₂O sorption (*O), O₂ desorption (*OO), OOH* deprotonation

H₂O Electrolysis: Kinetic Insights for Binary Catalysts
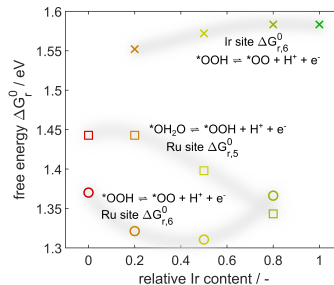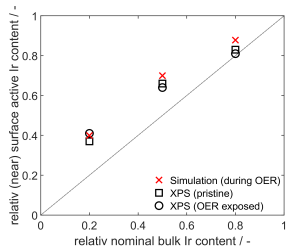
- Model reproduces CVs and identifies energies for different Ir:Ru mixtures.

- Individual sites of binary catalyst experience performance enhancement (lower energies).

- Model identifies and quantifies deviation from nominal surface composition: Ir↑ (Ru-dissolution).

Electroorganic Synthesis: Can We Identify Mechanisms & Kinetics?
Cooperation Atobe/Shida, U. Yokohama

Exp.: slight H_2 evolution; CV depends on ketone conc. and scan rate
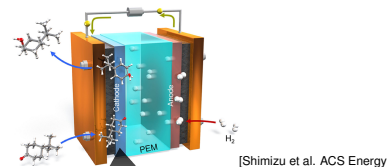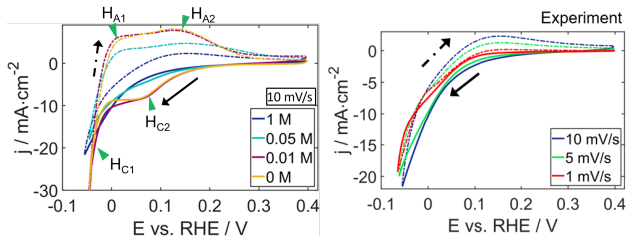
[Shimizu et al. ACS Energy Lett. 2023]
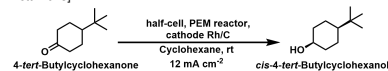
Sim.: Langmuir-Hinshelwood mech. more likely than Elay-Rideal (no H-ads)
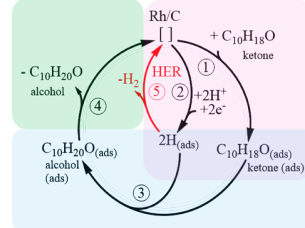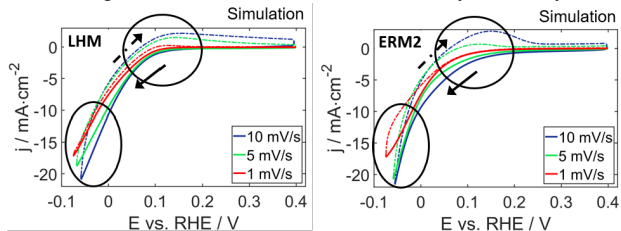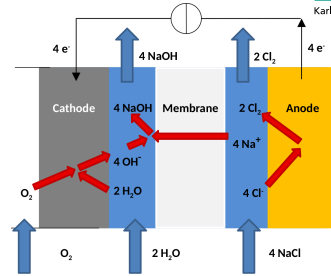

Langmuir Hinshelwood Mechanism (LHM)

Content
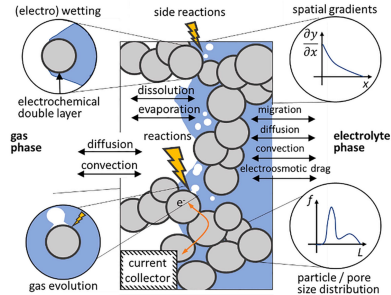
Cl$_2$ Production: What Limits Performance in O$_2$ Depletion Cathode (ODC)?

[Roehe, Kubannek, Krewer, ChemSusChem, 2019]

porous ODC — liquid area
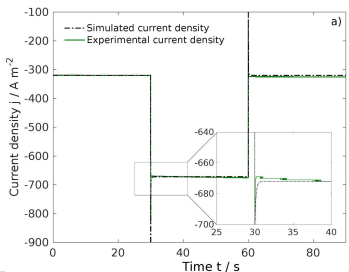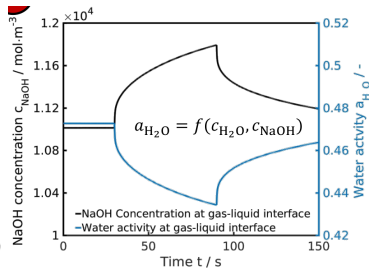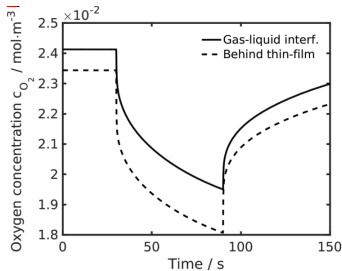
O$_2$ · O$_2$-dissolution → · OH$^-$ (Na$^+$) · O$_2$ · H$_2$O
O$_2$ · · O$_2$ + 2 H$_2$O + 4 e$^-$ → 4 OH$^-$ · O$_2$ · Na$^+$
H$_2$O ← · H$_2$O-evaporation ← · H$_2$O · OH$^-$

gas bulk · gas phase · flooded agglomerates · liquid diffusion layer · electrolyte bulk

thin-film

z →
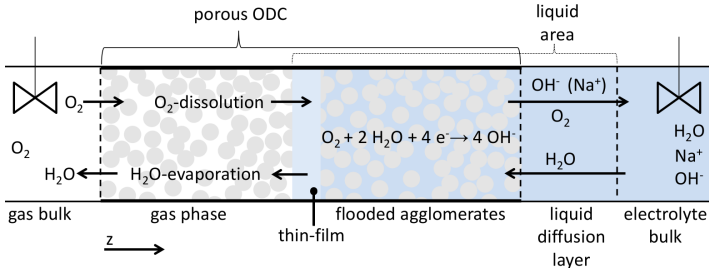
- Cl$_2$ may be efficiently produced with O$_2$ counter electrode
- Partly aq. NaOH-flooded Ag gas diffusion electrode (GDE), reactants O$_2$ and H$_2$O fed from opposite sides.
- Limitation by slow transport of O$_2$ frequently assumed.
- How can we identify the limitation? Use macrokinetic model!
  1-d model: diffusion, convection, g/l phase change, reaction

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- Model analysis reveals underlying mechanism:
- Surprisingly slow O_2 dynamics (min vs. ms);
- Cause: limitation due to slow transport of NaOH decreases oxygen solubility.
- Model explains: Setup with forced NaOH transport removes transport limitation.

What Limits Processes in CO$_2$ Reduction on Flat Ag?

[Dorner, Röse, Krewer, ChemElectroChem, 2023]

- Ag rotating disc electrode, CO$_2$ saturated 0.1M KHCO$_3$

- CO2R: $CO_2 + H_2O + 2e^- \longrightarrow CO + 2OH^-$, carbonation, HER: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$, diffusion, migration

- (Partial) current density and plateau strongly influenced by dynamic operation (scan rate) for 50 rpm.

- Performance limited by CO$_2$ transport and carbonation! $CO_2 + 2OH^- \longleftrightarrow CO_3^{2-} + H_2O$

- Side reactions and transport impact widespread! $f(E, I)$!
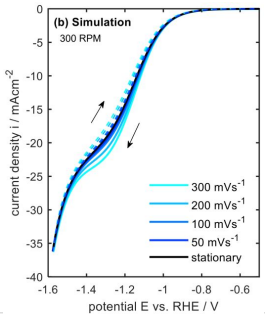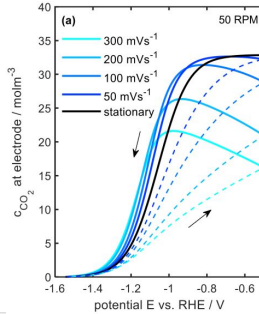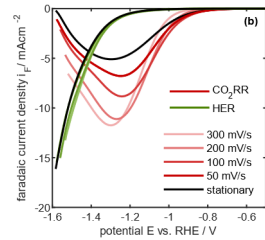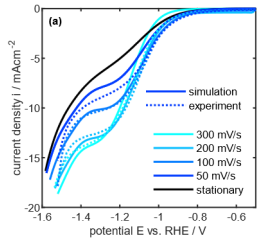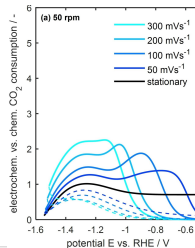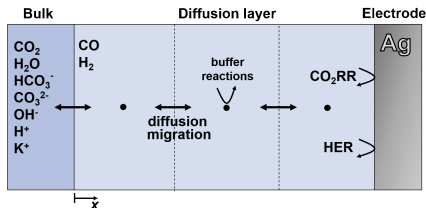
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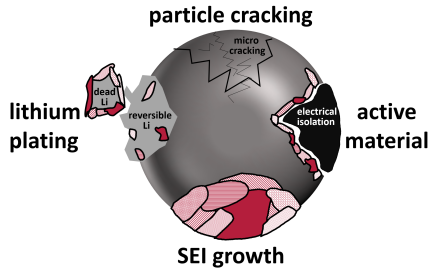
H₂O Electrolysis: Tracking Catalyst Degradation

[Geppert, Röse, (...), Krewer, J. Am. Chem. Soc. 2022]
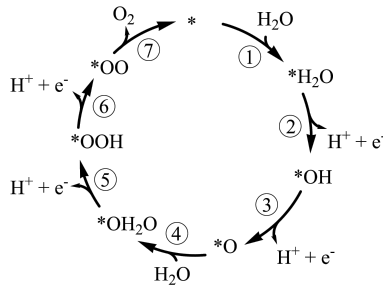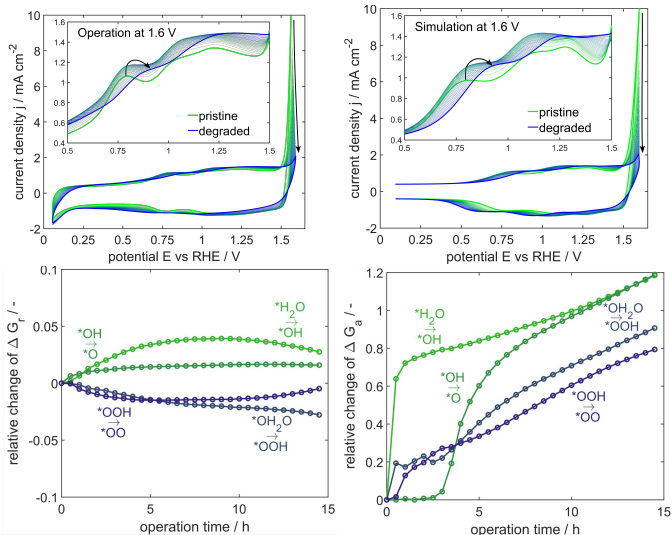
- All O_2 evolution catalysts: Long-term operation leads to activity losses.
- State estimation methods needed for optimal operation!
- Kinetic model can capture features.
- Model reveals aging-induced increase in activation energies.

Estimating (Degradation) State for Li-ion Batteries

- Remaining capacity of batteries decreases during operation
- Mechanical issues complement chemical degradation; most influential: growth of passivation layer (solid-electrolyte interphase, SEI)
- Dynamic measurements contain information on degradation processes!
- Dynamically parameterised models reveal electrode changes operando!

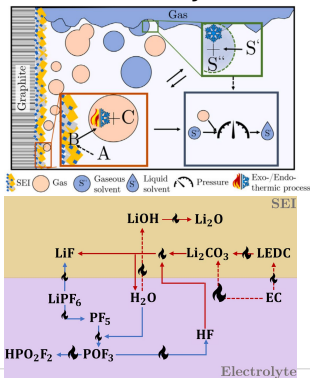Institute for Applied Materials - Electrochemical Technologies
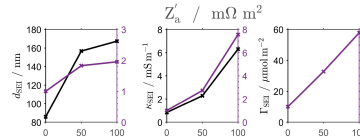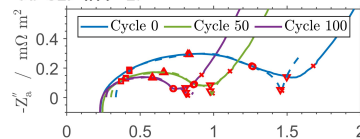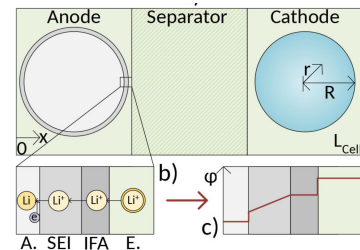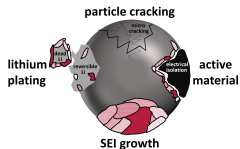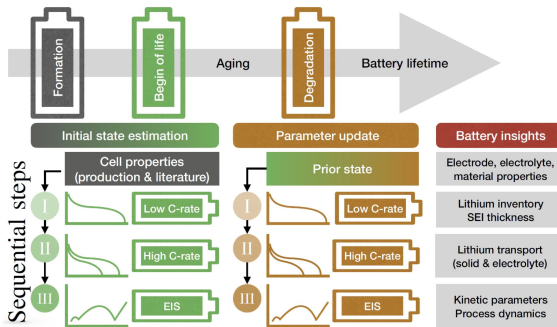
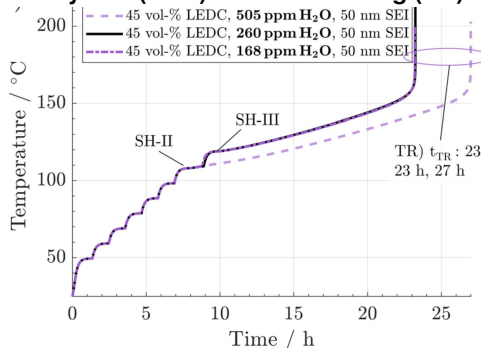# Hot New Topic: Safety Models to Prevent Thermal Runaway of Batteries

[Baakes, Luethe, Gerasimov, Laue, Balbuena, Krewer, J. Power Sources 2022; Baakes, Witt, Krewer, Chem. Science 2023]
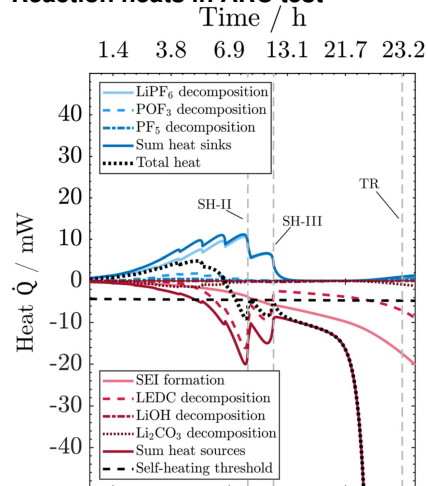

Thermal runaway model

Safety test (ARC) with self-heating (SH)

- 45 vol-% LEDC, **505 ppm H_2O**, 50 nm SEI
- 45 vol-% LEDC, **260 ppm H_2O**, 50 nm SEI
- 45 vol-% LEDC, **168 ppm H_2O**, 50 nm SEI

TR) t_{TR} : 23 23 h, 27 h

- Self-heating due to SEI decomposition.
- Complex interaction of negative and positive reaction heats.
- Sensitive to ageing & water!

Reaction heats in ARC test

# Model-assisted Analysis and Design of Electrochem. Processes

Electrochemical processes

- ... needed and versatile: energy storage, H_2 production, CO_2 valorisation, and a myriad of chemicals!
- Only few synthesis processes established so far! Quantitative R&D and models needed on all levels!

Kinetic models give essential insights for process optimisation!

- Reaction mechanism identification tricky; dynamics allows kinetics identification & parameterisation!
- Electrodes frequently suffer from complex interaction of reaction with transport and side reactions!
- Identified kinetic models enable estimating degradation state.

The upcoming age of electrochemical processes urgently needs (system) engineers!
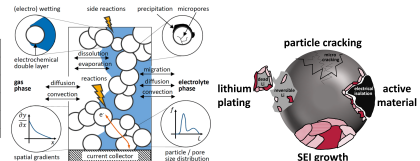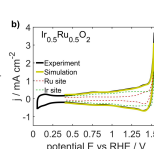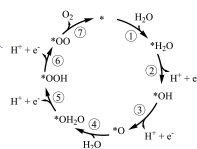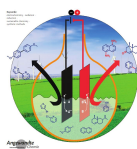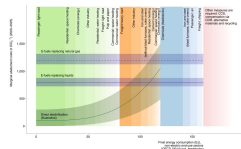
Acknowledgements

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Thank you for your attention!