Influence of the Electrolyte on the Performance of bifunctional Gas Diffusion Electrodes for Zinc Air Batteries

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Introduction

Motivation

- **Zinc-Air-Batteries (ZAB) -** a solution for **midterm energy storage systems** due to their cost structure, safety and abundance of materials**.**
- State-of-the-art **gas-diffusion electrodes (GDE)** challenge the economic feasibility due to the sluggish oxygen reactions ($\eta_{RTE} \approx 60\%$)
- Oxygen evolution (OER) and oxygen reduction reaction (ORR) show quite different needs for pore size and electrolyte concentration → Optimization needed

Hypothesis

Oxygen reduction reaction benefits from lower KOH concentrations, oxygen evolution benefits from higher concentrations

Objective

Identify optimal electrolyte concentration

Dry-pressing electrodes

Advantages

- Flexible, small scale GDE production
- Easy to learn
- Solvent free
- Upscaling: rolling process

Manufacturing Step	Parameters		
Milling	Catalyst Support	Catalyst	PTFE
	70wt.%	20wt.%	10wt.%
Doctor Blading	Diameter	Thickness	
	50mm	1mm	
Pressing (+Mesh)	Force	Mesh	
	7 MPa (1.4t)	d = 250-500µm	
Heat Treatment	Melting PTFE		
	1h @ 340°C		

Effect of KOH concentration

$$O_2 + 2\,H_2O + 4\,e^- \rightleftharpoons 4\,OH^-$$

OER: OH^- concentration ↑ → Reaction rate ↑

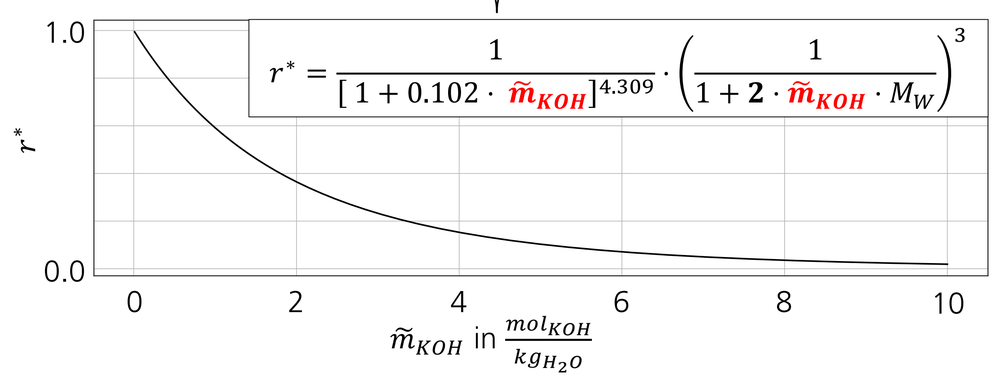
ORR: OH^- concentration ↑ → O_2 Solubility ↓→ Reaction rate ↓

$$r = k_0 \boldsymbol{x_{O_2}} \boldsymbol{x_W^2} \cdot \exp\left[-\frac{(1-\alpha)F}{RT}\,\eta\right]$$

ORR Kinetics (1)

$$x_{O_2}^{eq.} = \frac{K_{O_2,H_2O}^{eq.} \cdot M_W \cdot p_{O_2}}{\left[1 + \kappa \cdot \boldsymbol{\tilde{m}_{el}^{y}}\right]^{h} \cdot \left(1 + \sum_{i \neq W} M_W \boldsymbol{\tilde{m}_{el}}\right)}$$

O_2 Solubility (2)

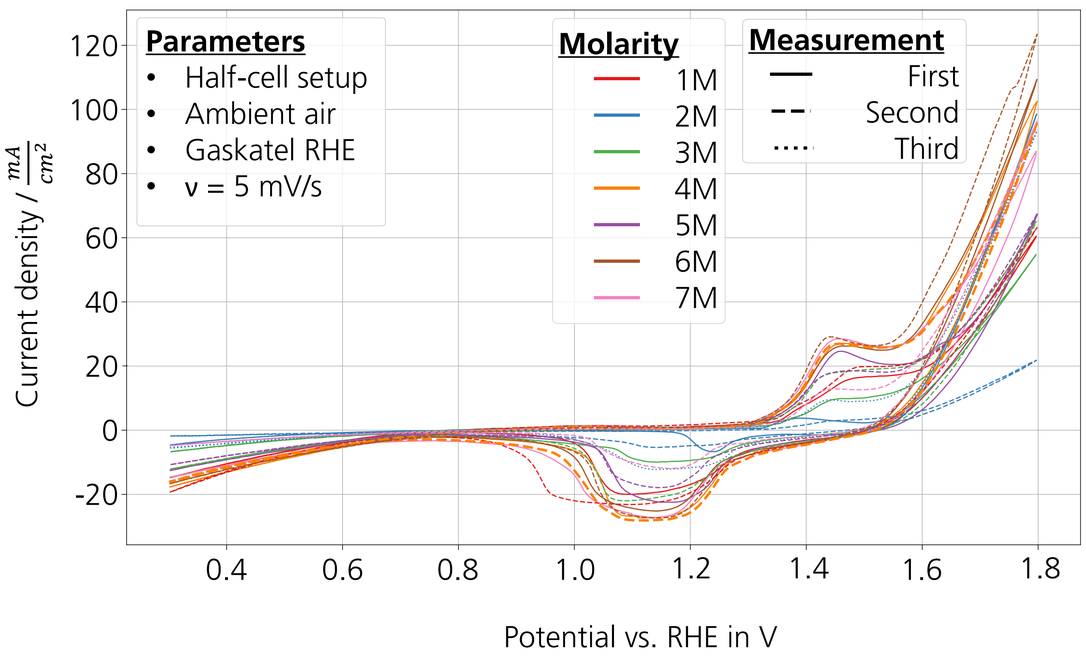


Experimental

90 wt.% Ni
10 wt.% PTFE
→ **Catalyst** NiFeOOH

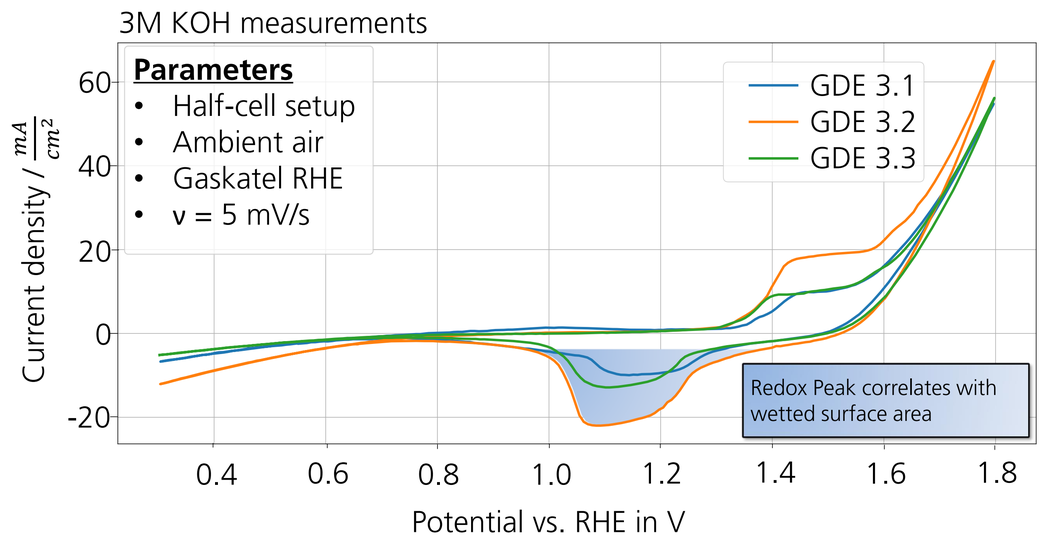
GDE

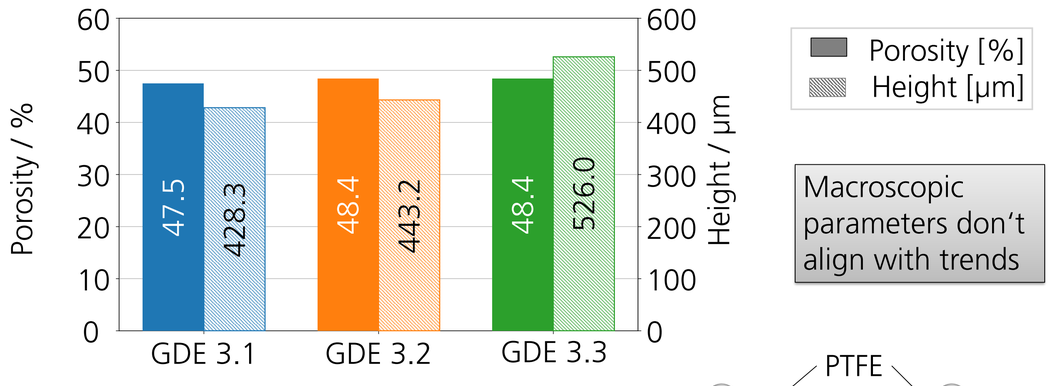
Porosity	Thickness	Pore size
≈ 48%	≈ 500µm	≈10µm



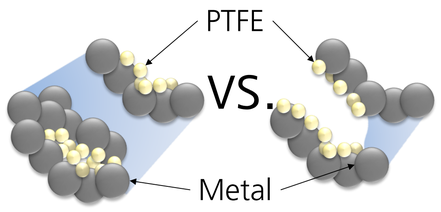
Lacking reproducibility!
Only overall trends match expectations

Wettability issues





Wettability differs:
PTFE pore wall fraction not controlled, only mass fraction



References

(1) Rohe, M., et al. (2019). "Processes and Their Limitations in Oxygen Depolarized Cathodes: A Dynamic Model-Based Analysis."
(2) Desmond Tromans. "Modeling oxygen solubility in water and electrolyte solutions". In: Industrial & engineering chemistry research 39.3 (2000), pp. 805–812.

Summary

- The theory predicts an opposite influence of KOH concentration on ORR and OER.
- Electrolyte study only roughly confirms the trends
- Non-reproducible internal wettability of the electrodes has an influence on the order of magnitude of the electrolyte concentration.

➢ Manufacturing method unsuitable for studying subtle differences
➢ Currently new manufacturing method under development

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