Effect of catalyst ink composition on the performance of carbon aerogel based Fe-N-C catalyst for the oxygen reduction reaction

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Motivation & Approach

- In high temperature polymer electrolyte membrane fuel cells (**HT-PEMFC**) the Pt-based electrodes need high loadings up to 1 mg_{Pt} cm^{-2} per electrode due to **phosphate poisoning** of the platinum catalyst, leading to high material costs [1]
- **Fe-N-C** catalysts are promising **inexpensive** and **phosphate tolerant** Pt-free alternatives (Fig. 1) for oxygen reduction reaction (ORR) → reduction of material costs for HT-PEMFC
- Fe-N-Cs show lower volumetric activity compared to Pt/C → Thicker catalyst layers required, leading to higher mass transport limitations (performance decrease) [1]

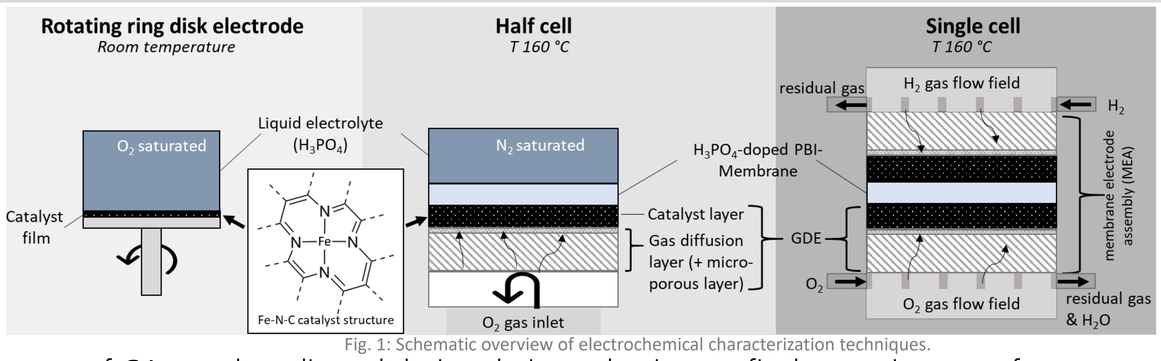


Fig. 1: Schematic overview of electrochemical characterization techniques.

- **Carbon aerogels** (CA) can serve to improve mass transport properties. The pore structure of CAs can be adjusted during their production, to fit the requirements for incorporation of catalytic active Fe-N_x-sites.[2] Optimized Fe-N-CAs should provide high accessibility of reactants to the catalyst to positively affect the performance.

Synthesis

CA → Impregnation (1 wt.% Fe-Precursor, 80 wt.% N-Precursor, 19 wt.% CA-Support oxidized) → 1. Pyrolysis (N_2, 900 °C, 1 h) → Acid leaching (2 M H_2SO_4, 90 °C, 16 h) → 2. Pyrolysis (N_2, 900 °C, 1 h) → Fe-N-CA

Table 1: Physical properties of CA-1			
Micropore-volume / $cm^3\ g^{-1}$	Mesopore-volume / $cm^3\ g^{-1}$	Specific surface / $m^2\ g^{-1}$	Electric conductivity @ 1 kN / $S\ m^{-1}$
0.13	1.05	652	369

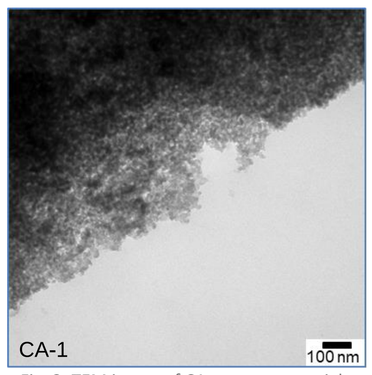


Fig. 2: TEM image of CA support material.

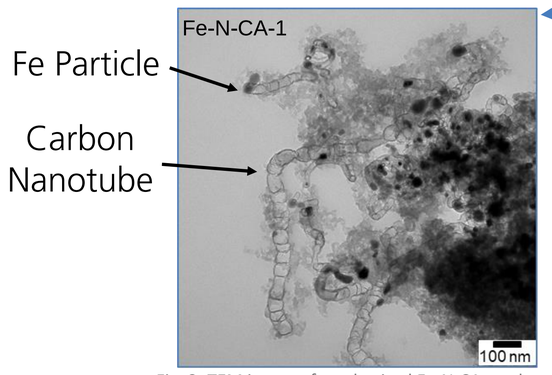


Fig. 3: TEM image of synthesized Fe-N-CA catalyst.

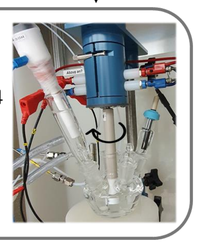
- Comparison of TEM of CA and Fe-N-CA
- Formation of unwanted Fe particles and carbon nanotubes (Fig. 3)
  - No electrochemical activity
- Carbon support: higher surface needed [3]
  - Precursors more accessible
  - Incorporation of more N-functionalities to form more Fe-N_x-sites
- CA surface > 1000 $m^2\ g^{-1}$ possible

Rotating Ring Disk Electrode (RRDE)

Nafion™ + Solvent + Fe-N-CA → RRDE-ink → Physical characterization (TEM, DLS)

RRDE

RRDE Setup
- 0.5 M H_3PO_4
- room temperature



- Setting up reference system for characterization of novel Fe-N-CA catalysts
  - Polarization curves: commercial Fe-N-C (PMF) as reference material for evaluating **catalyst activity** (Fig. 4) compared to synthesized Fe-N-CA.
    - ➢ Comparable mass activity at 0.8 V of PMF: 3.46 ± 0.4 A g^{-1} to literature PMF: 2.49 A g^{-1} [1] and BP-Fe-N-C: 8.6 A g^{-1} [4]
  - Stress test: investigation of **catalyst stability**, square-waved load cycling at 0.6 and 1.0 V, hold each 3 s for 10.000 cycles under O_2 [5]
  - Aim: Selecting the Fe-N-CA with highest activity and stability for GDE fabrication
- Adaption of ink composition for Fe-N-CA needed to decrease **discrepancies** between RRDE activity and real electrode performance
  - Investigation of different ink compositions
  - Influence of variation of solvent and Nafion™-ratio,-type on viscosity, pH value, particle agglomeration and impact on activity
  - Optimized ink should help to estimate the catalyst activity more meaningful

First electrochemical investigation:
Activity of Pt/C compared to Fe-N-C catalyst

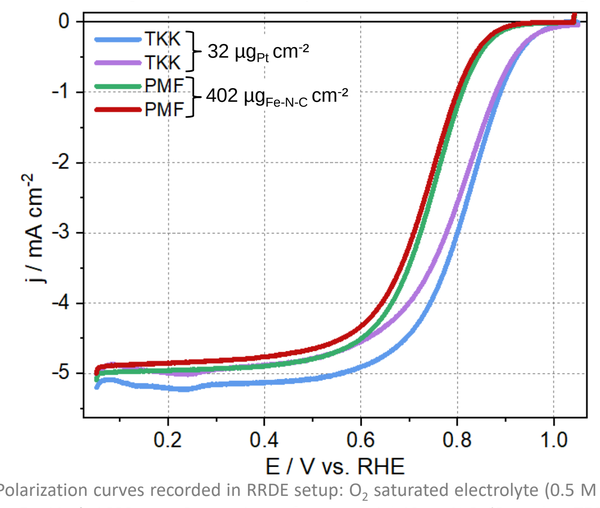


Fig. 4: Polarization curves recorded in RRDE setup: O_2 saturated electrolyte (0.5 M H_3PO_4), scan rate 5 mV s^{-1}, 1600 rpm. Comparison of commercial 40 wt.% Pt/C catalyst TEC10E40E (Tanaka) to commercial Fe-N-C catalyst PMF-0011904 (Pajarito Powder).

Outlook

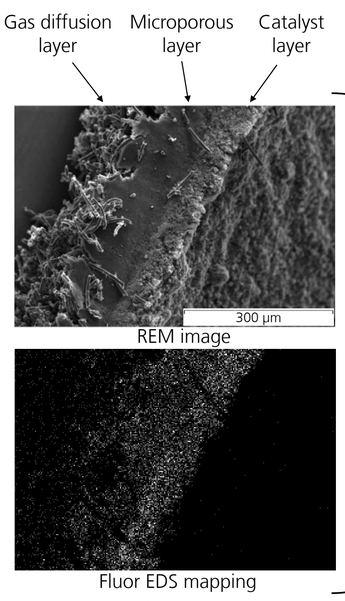


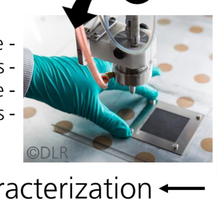
Fig 5. SEM/EDX investigation of ultrasonic spray coated GDE.

Next steps

Binder + Solvent (+ Additive) + Fe-N-CA → Ultrasonic GDE-ink → Phys. char.

Doctor Blade GDE-ink (Binder + Solvent (+ Additive) + Fe-N-CA) → Phys. char.

Temperature hot plate - Catalyst layer thickness - Flow rate - Drying process -



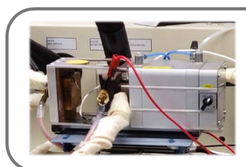
- Catalyst layer thickness
- Blade speed
- Drying process (hot plate)

GDE fabrication → GDE

Physical characterization
e.g. Hg-Porosimetry, contact angel, ICP MS, µ-CT, SEM/EDS

GDE + Membrane (hot-pressed) + Pt/C Anode → MEA

GDE Half Cell
- conc. H_3PO_4
- T 160 °C



Single Cell
- H_3PO_4-doped (PBI) Membrane
- T 160 °C

Underlined steps are part of optimization process

- Optimization of CA to obtain novel Fe-N-CA
- Ink composition variation for GDEs
  - Literature shows that **performance** of low temperature PEMFC is **affected by Fe-N-CA ink compositions** [2]
  - Binder: PTFE and PBI, from 10 – 50 wt.% in the catalyst layer
  - Additives: Nafion and Triton X-100, other
  - Goal: reduction of ink sedimentation during coating, optimized coating viscosity for ultrasonic spraying and doctor blade
- GDE fabrication optimization
  - Improvement of morphology and wettability
  - **Reduction of mass transport limitations**
  - Enhancement of GDE performance
  - Single cell tests for most promising GDEs
- Overall goal: GDE with max. 40 % performance decrease after 100 h single cell operation

Acknowledgements:

The authors acknowledge the Electron and Light Microscopy Service Unit of the School of Mathematics and Science of the Carl von Ossietzky University for the use of the imaging facilities.

This research was conducted within the DLR project "LaBreNA".

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DLR Deutsches Zentrum für Luft- und Raumfahrt
German Aerospace Center