Dual-transition metal and nitrogen co-doped silicon oxycarbide-based catalysts for oxygen reduction at the high temperature PEM fuel cell cathode

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DLR

Introduction

- The modern lifestyle and progressive economic growth - ever-increasing, global energy consumption, speeding up the climate change.
- The global dependency on fossil fuel has disadvantages (carbon and pollutant emissions), CO_2, NO_x, SO_x, particulate matter.
- Research on clean, efficient, and more sustainable energy technologies. **Fuel cells** have been recognized as possible energy conversion devices for mobile and stationary applications.

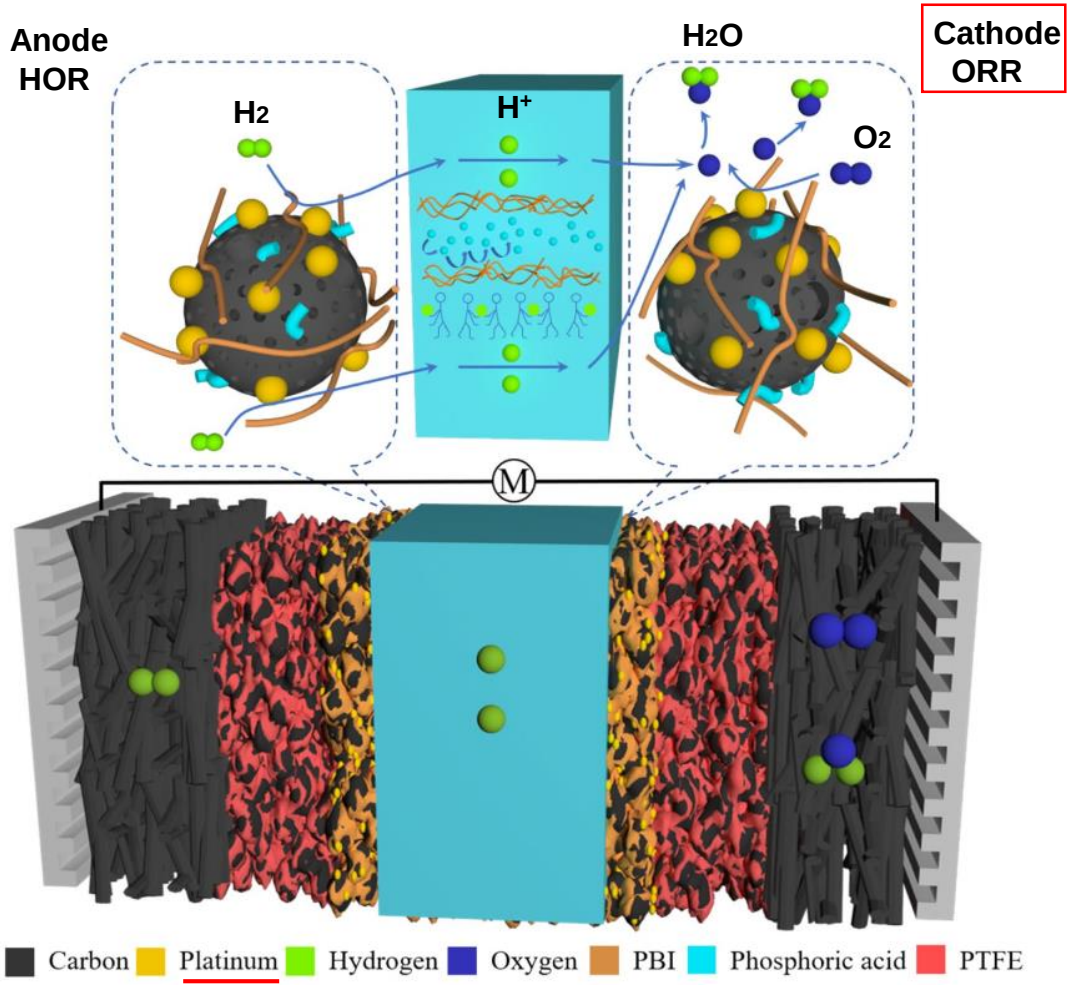
DLR (German Aerospace Center)

- More than 9000 employees work in 54 institutes and facilities
- 30 sites across Germany
- DLR Institute of Engineering Thermodynamics - Location Oldenburg

High-temperature polymer electrolyte membrane fuel cell (HT-PEM) workgroup

DOI: 10.1039/d3ta06895a DOI: 10.1002/adma.202302207

High temperature PEM fuel cell (HT-PEMFC)



Scheme 1. Schematic representation of the structure of HT-PEMFCs. The relative sizes and distances are not to scale, and the catalyst layer, binder, filler, MPL, and carbon fibers possess significantly different porosities and sizes. DOI: 10.1007/s41918-023-00180-y

HT-PEMFC is environmentally friendly energy conversion device suitable for heavy-duty transport, stationary, and aviation applications.

Hot HT-PEMFC topic: the development of efficient Pt-group-metal (PGM)-free **oxygen reduction reaction** (**ORR**) catalyst for the fuel cell cathode.

ORR pathways:

4 electrons (e.g. Pt/C)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

2 electrons (peroxide production)

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

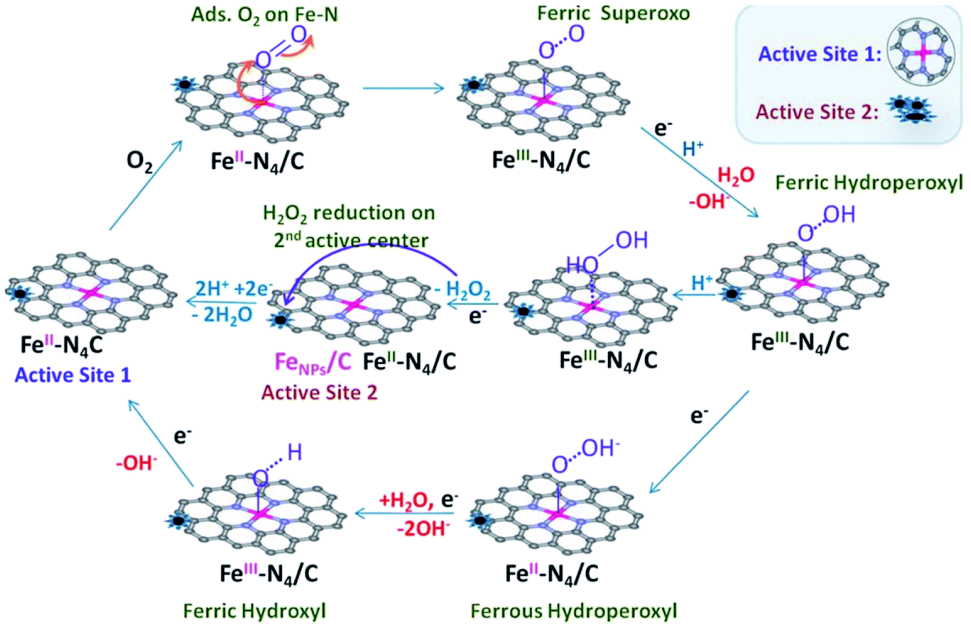
M-N-C cathode catalyst materials

- Most promising materials have been developed based on the transition metal and nitrogen co-doped nanocarbon materials (M-N-C).

- **Nanocarbon materials**: graphene, multi-walled carbon nanotubes (MWCNT), carbide-derived carbons (CDC), polymer-derived carbon (PDC) etc.
  - **high surface area, high durability, good electrical conductivity**

- **Transition metal (TM) and nitrogen co-doping:**

  a) transition metal (e.g. Fe, Co, Mn) ion coordinated to nitrogen sites (**Me-Nx**)
  b) active N species
  c) transition metal nanoparticles
  - **provide active sites for ORR**



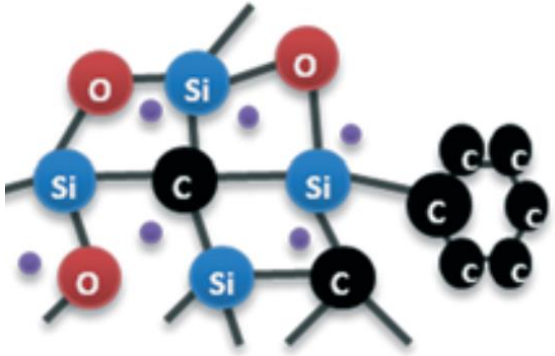
DOI: 10.1021/jp500781v

Dual metal M-N-C catalysts

The main aim:
Preparation of **dual metal** M-N-C materials for HT-PEMFC cathode (M-N-C type)

1. Catalyst support/carbon backbone:
   Silicon oxycarbide (SiOC) based materials

2. Dual atom metal combinations (supported by literature):
   1. Fe/Co
   2. Fe/Mn
   3. Fe/Cu



Previous collaborations with University of Bremen.

SiOC-based M-N-C were found to be suitable for Fuel cell cathode catalyst application.

Issue 3, 2019
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From the journal:
Catalysis Science & Technology

Polymer-derived Co/Ni-SiOC(N) ceramic electrocatalysts for oxygen reduction reaction in fuel cells†

Check for updates

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DOI: 10.1039/c8cy02207k

Catalyst preparation

1. Polymer-derived carbon (PDC) precursor materials (**University of Bremen**):
    1. Powders of *poly(methyl phenyl silsesquioxane), poly(methylsilsesquioxane), graphite, azodicarboxamide, and (3-Aminopropyl)triethoxysilane, imidazole, metal acetylacetonates* dispersed in xylene.
    2. Pyrolysed, ball-milled, sieved → PDC precusor materials:

       PDC, MnFe-PDC, CoFe-PDC, CuFe-PDC

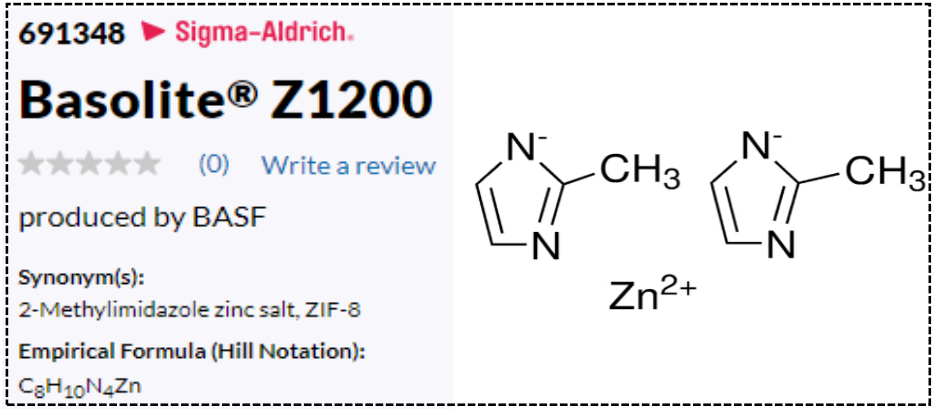
2. Functionalisation with N-source ZIF-8 (Basolite® Z1200) (**DLR**):
    1. Mixed 50/50 wt% of PDC/ZIF-8 in methanol, drying.
    2. Pyrolysed at 950 °C → N-SiOC catalyst materials:

       MnFe-N-SiOC, CoFe-N-SiOC, CuFe-N-SiOC

    **3. Acid leaching:*

    2M sulfuric acid for 16 h at 90 °C followed by second pyrolysis:

    MnFe-SiOC-Acid, CoFe-SiOC-Acid, CuFe-SiOC-Acid



Physical characterisation of ZIF-8 modified PDC materials

Scanning electron microscopy (SEM)

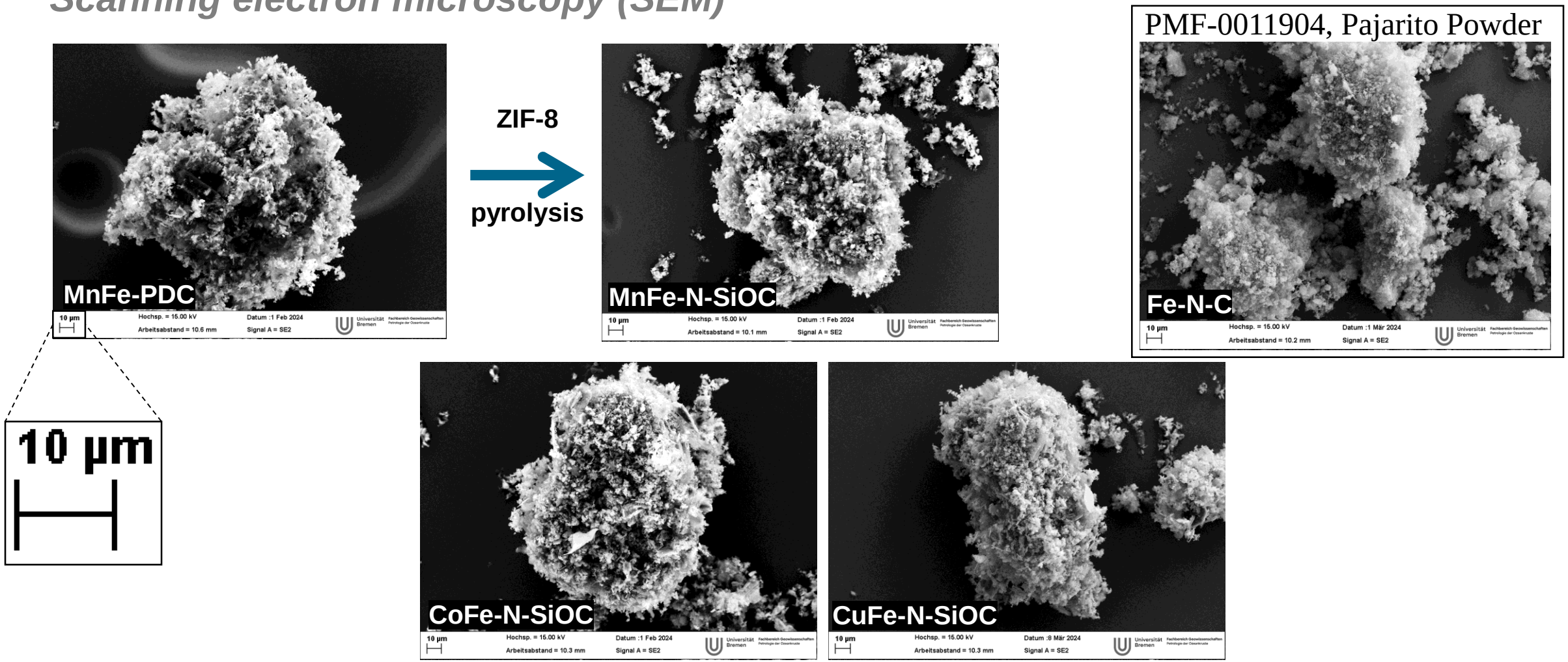


Fig. 1. SEM images of different materials. The FeMn-based material is shown before (-PDC) and after modification with ZIF-8 via pyrolysis at 950 °C (-N-SiOC). The commercial Fe-N-C is also shown for comparison.

Physical characterisation of ZIF-8 modified PDC materials

Energy-dispersive X-ray spectroscopy (EDS)

	PDC	CoFe-PDC	CoFe-N-SiOC	MnFe-PDC	MnFe-N-SiOC	CuFe-PDC	CuFe-N-SiOC
C	73.7 ± 1.9	77.1 ± 3.5	75.5 ± 0.9	76.9 ± 1.0	78.4 ± 1.5	74.6 ± 7.4	76.8 ± 2.4
N	2.70 ± 0.13	3.38 ± 0.13	**6.30 ± 0.42**	3.61 ± 0.28	**6.71 ± 1.03**	2.77 ± 1.26	**7.34 ± 0.71**
O	18.3 ± 1.5	15.1 ± 2.4	13.3 ± 1.3	13.2 ± 0.7	10.3 ± 0.8	16.5 ± 4.8	12.1 ± 1.2
Si	5.36 ± 0.67	4.04 ± 0.77	4.14 ± 0.62	5.65 ± 0.89	3.85 ± 0.35	4.78 ± 1.19	2.81 ± 1.49
Fe	-	0.21 ± 0.08	0.23 ± 0.05	0.35 ± 0.07	0.26 ± 0.04	0.25 ± 0.06	0.21 ± 0.06
Mn	-	-	-	0.29 ± 0.06	0.20 ± 0.06	-	-
Co	-	0.20 ± 0.06	0.20 ± 0.07	-	-	-	-
Cu	-	-	-	-	-	0.26 ± 0.12	0.38 ± 0.13
Zn	-	-	**0.29 ± 0.10**	-	**0.28 ± 0.15**	-	**0.28 ± 0.14**

Table 1. Elemental composition (at%) of different materials. After the modification of precursor material (-PDC) with ZIF-8 via pyrolysis at 950 °C (-N-SiOC), the introduction of Zn and increase in N amount is observed.

Physical characterisation of ZIF-8 modified PDC materials

High-resolution transmission electron microscopy (HR-TEM)

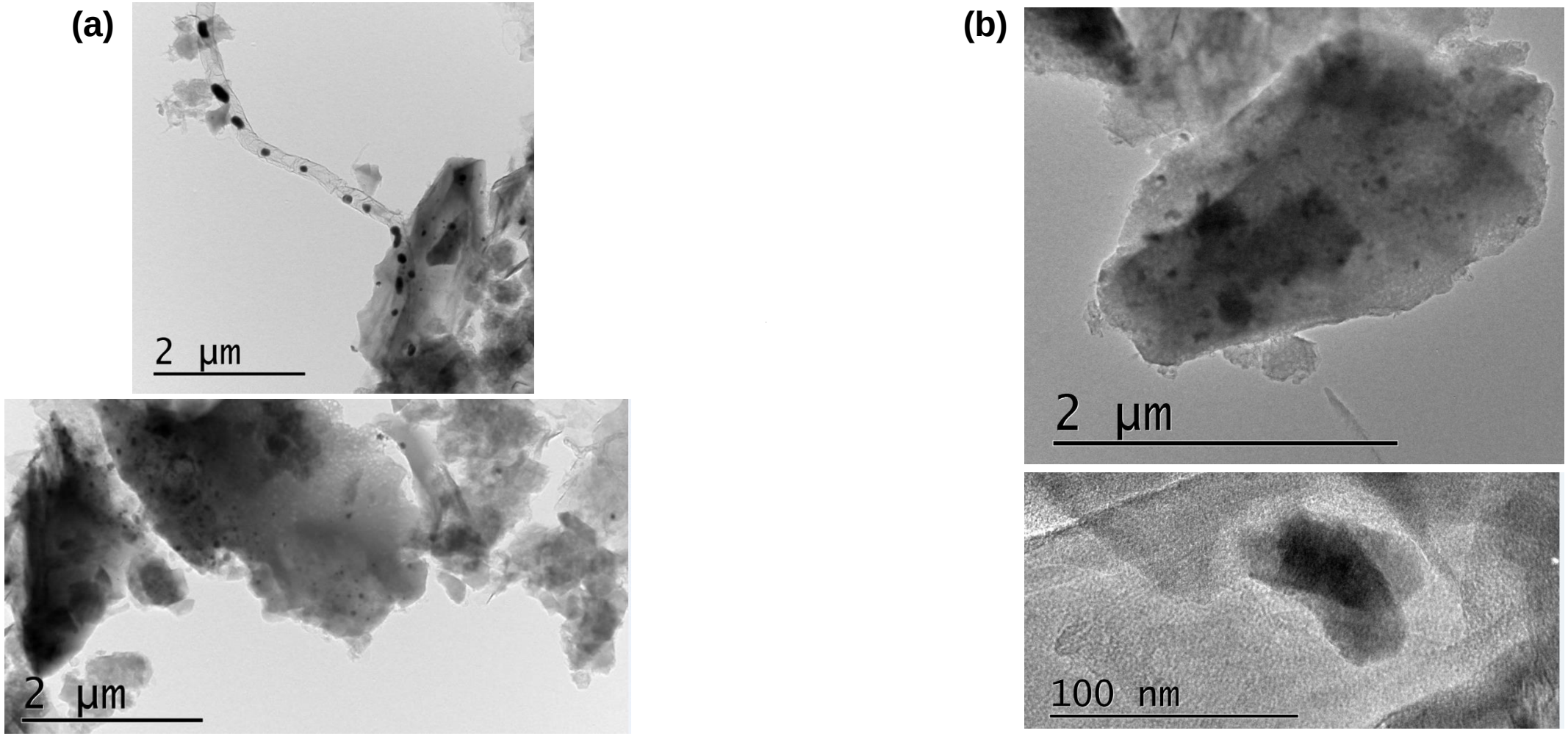


Fig. 2. HR-TEM images of different materials after ZIF-8 modification, (a) CuFe-N-SiOC, (b) MnFe-N-SiOC.

Physical characterisation of ZIF-8 modified PDC materials

X-ray photoelectron spectroscopy (XPS)

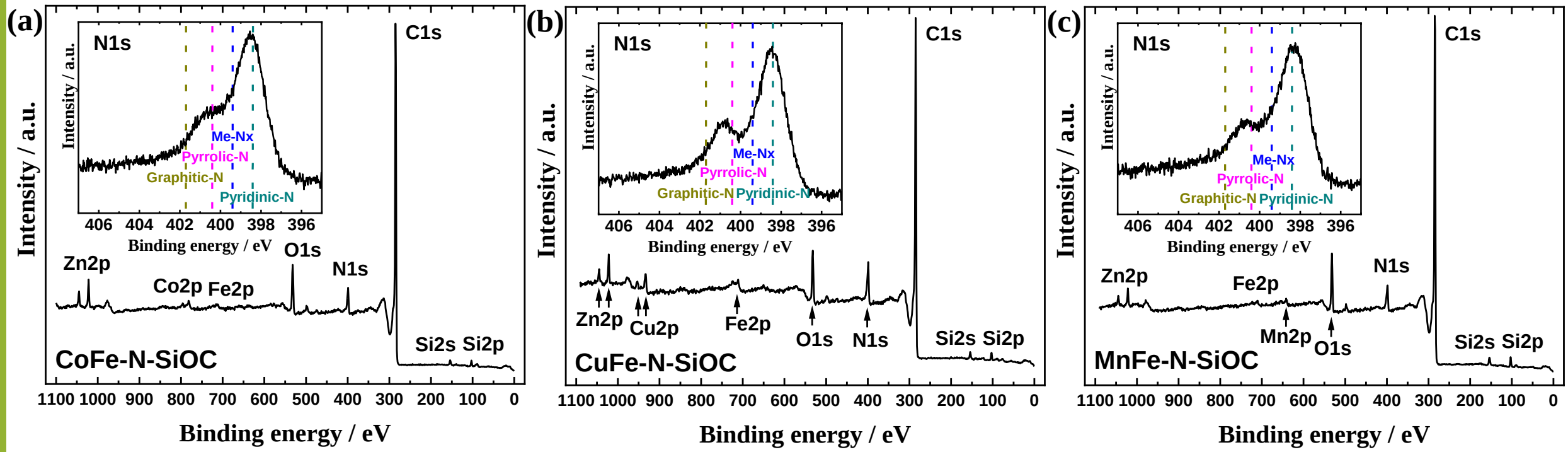


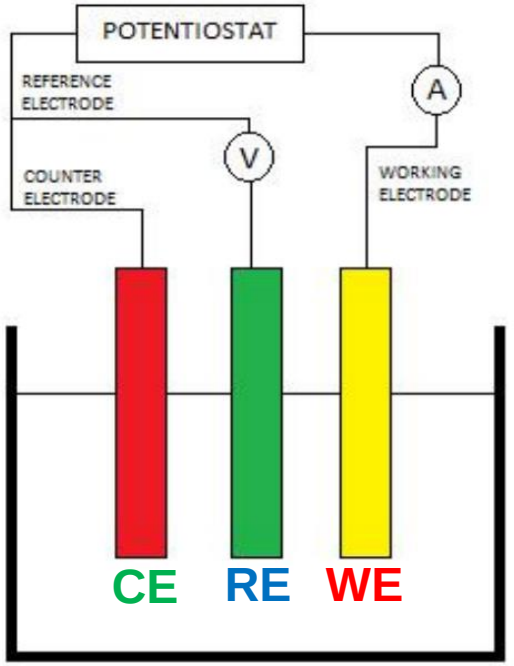
Fig. 3. XPS survey spectra of different catalyst materials after the modification with ZIF-8 via pyrolysis at 950 °C (-N-SiOC). The insets show the high-resolution spectrum in the N1s region for the corresponding material.

RRDE half-cell testing
(Rotating ring-disk electrode)

Metrohm

DLR

LSV recorded at 1600 rpm



DOI: 10.1088/1757-899X/340/1/012017

WE1: ORR current
WE2: Peroxide oxidation current

From WE1/WE2 difference – peroxide yield and electron transfer number per O_2 molecule

WE1: M-N-C catalyst on GC
WE2: Pt ring
RE: MMS (converted to RHE)
CE: Pt wire
Electrolyte: 0.5 M H_3PO_4, 23 °C

https://www.metrohm.com/en/products/a/ut_r/aut_rrde_s.html

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RRDE half-cell testing for ORR in 0.5 M H_3PO_4 at 23 °C

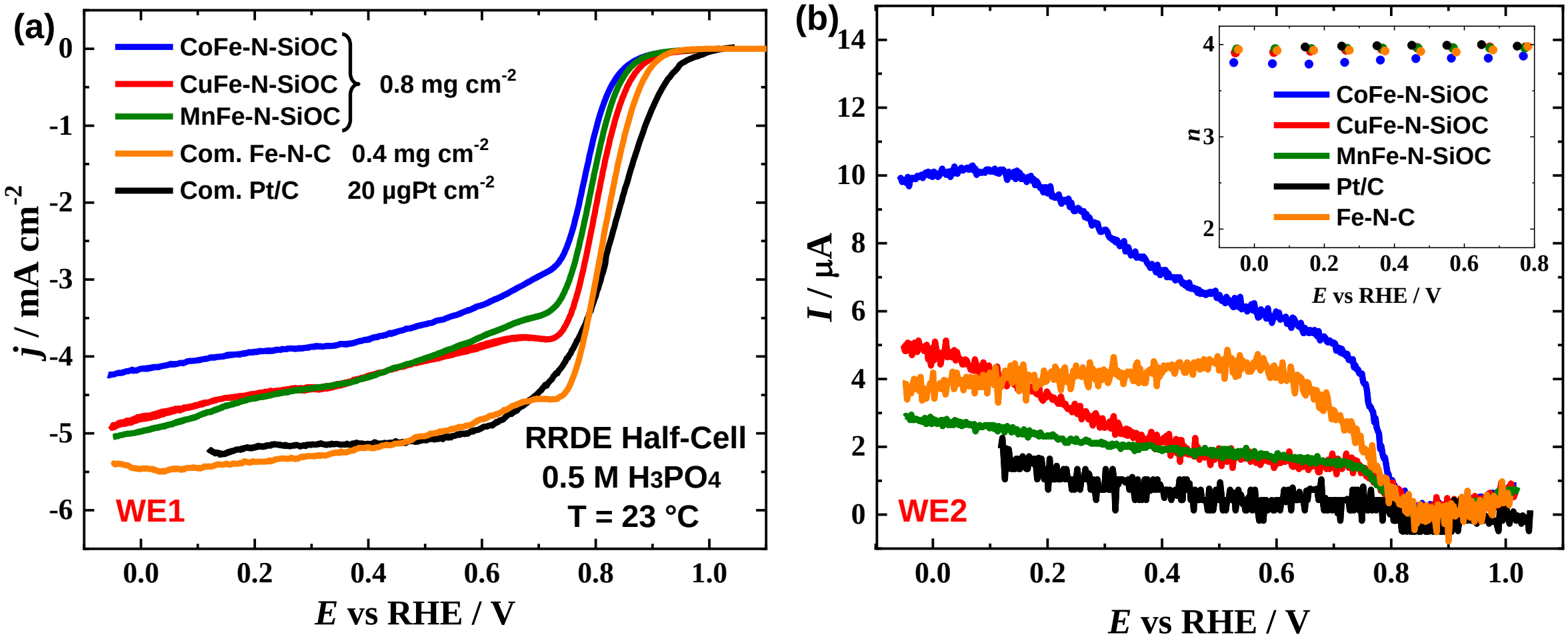


Fig. 4. (a) Disc current density, (b) ring current and electron transfer numbers (*n*) for different catalyst coated GC-disk/Pt-ring electrodes recorded at 1600 rpm in O_2-saturated phosphoric acid solution.

RRDE half-cell testing for ORR in 0.5 M H_3PO_4 at 23 °C

Catalyst	$E_{1/2}$	$MA_{0.75V}$	$MA_{0.80V}$
CoFe-N-SiOC	770 ± 3	3.41 ± 0.14	1.25 ± 0.10
MnFe-N-SiOC	774 ± 2	3.63 ± 0.08	1.80 ± 0.07
CuFe-N-SiOC	781 ± 6	3.67 ± 0.37	2.20 ± 0.14
Fe-N-C	808 ± 2	11.03 ± 0.14	7.56 ± 0.15
Pt/C (20wt. Pt)	824 ± 3	29.73 ± 2.33	37.35 ± 2.91

Table 2. Half-wave potential ($E_{1/2}$, unit mV vs. RHE) and mass activity (MA, unit A $g_{Catalyst}^{-1}$) values at 0.75 V and 0.80 V for ORR derived from the disc currents of RRDE measurements performed at 1600 rpm.

Acid leaching (2 M H_2SO_4) influence on RRDE results

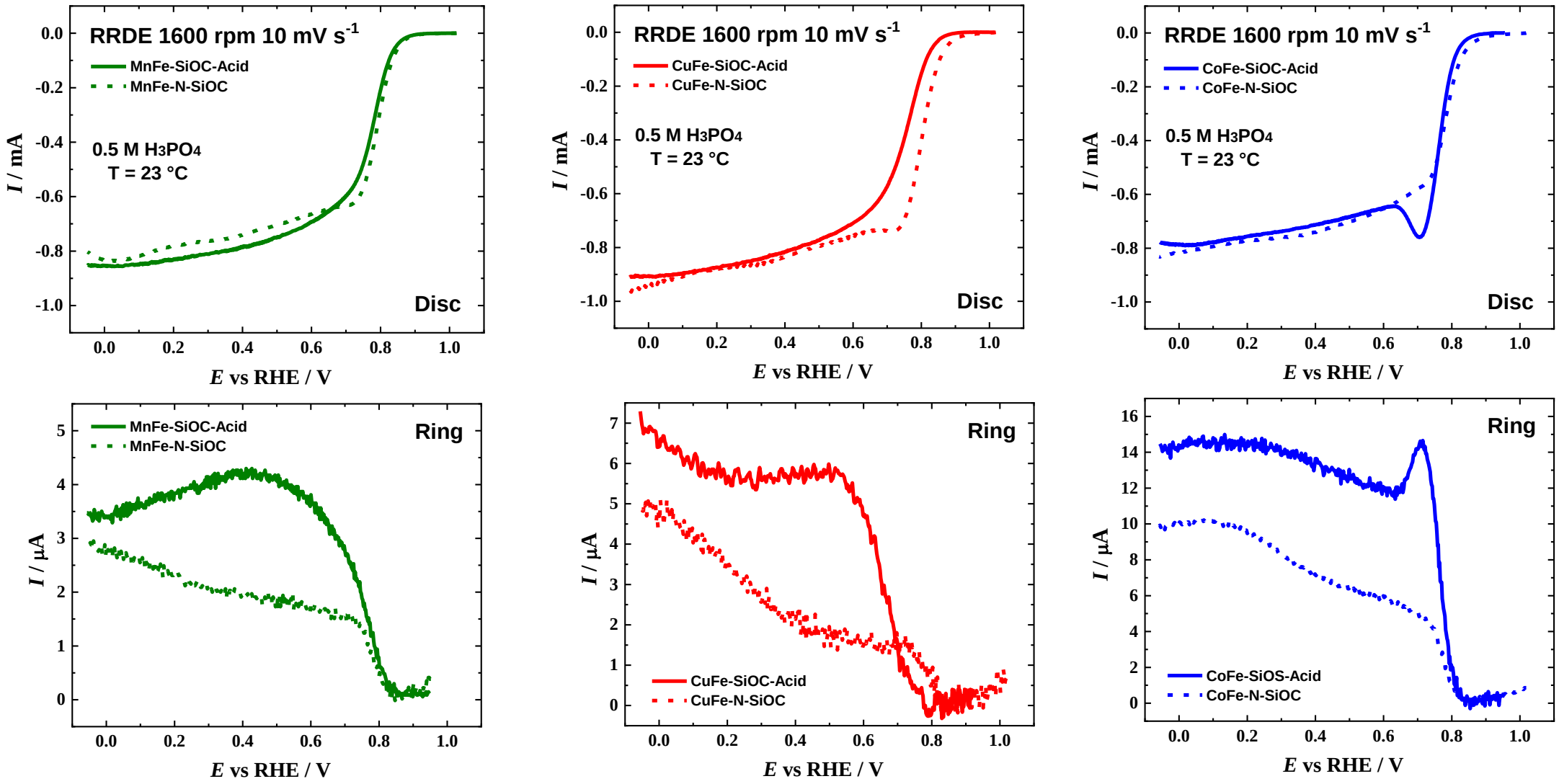


Fig. 5. Acid leaching route is in 2 M sulfuric acid for 16 h at 90 °C + second pyrolysis (*Not beneficial for peroxide yield*)

Acid leaching (2 M H_2SO_4) influence on RRDE results

Catalyst	$E_{1/2}$	$MA_{0.75V}$	$MA_{0.80V}$
CoFe-SiOC	770 ± 3	3.41 ± 0.14	1.25 ± 0.10
CoFe-SiOC-Acid	772 ± 2	↑ 3.74 ± 0.18	23% ↓ 0.96 ± 0.09
MnFe-SiOC	774 ± 2	3.63 ± 0.08	1.80 ± 0.07
MnFe-SiOC-Acid	↓ 757 ± 6	↓ 2.99 ± 0.17	30% ↓ 1.26 ± 0.11
CuFe-SiOC	781 ± 6	3.67 ± 0.37	2.20 ± 0.14
CuFe-SiOC-Acid	↓ 726 ± 8	↓ 2.26 ± 0.23	58% ↓ 0.91 ± 0.09

Table 3. Half-wave potential ($E_{1/2}$, unit mV vs. RHE) and mass activity (MA, unit A $g_{Catalyst}^{-1}$) values at 0.75 V and 0.80 V for ORR derived from the disc currents of RRDE measurements performed at 1600 rpm.

RDE half-cell stability testing for ORR in 0.5 M H_3PO_4 at 23 °C

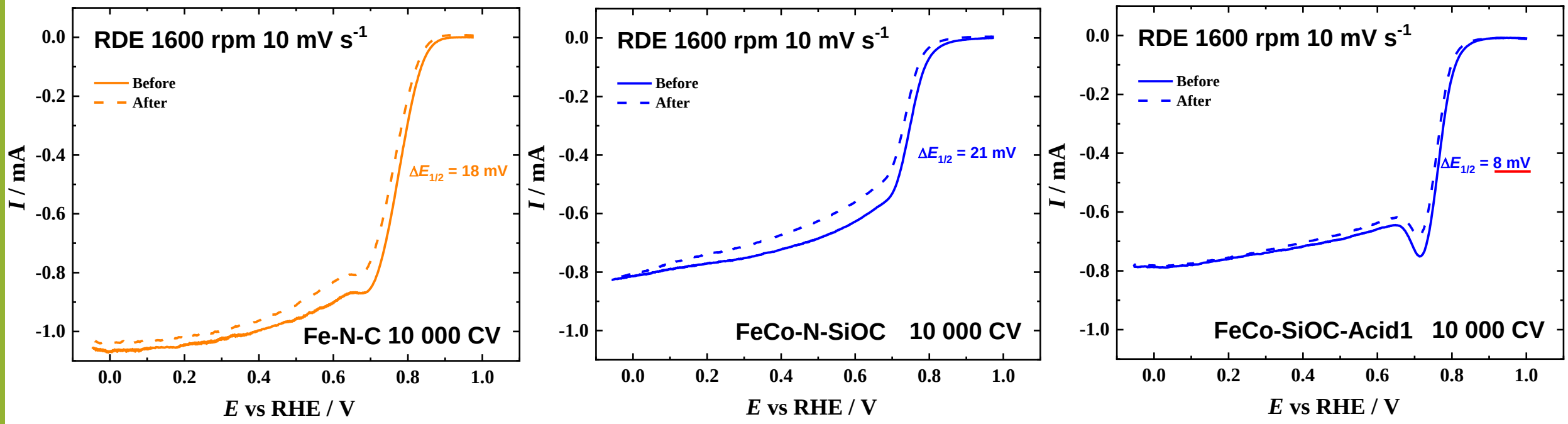
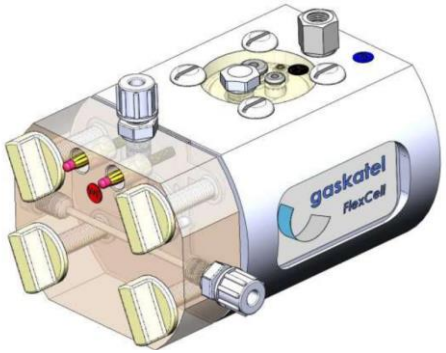


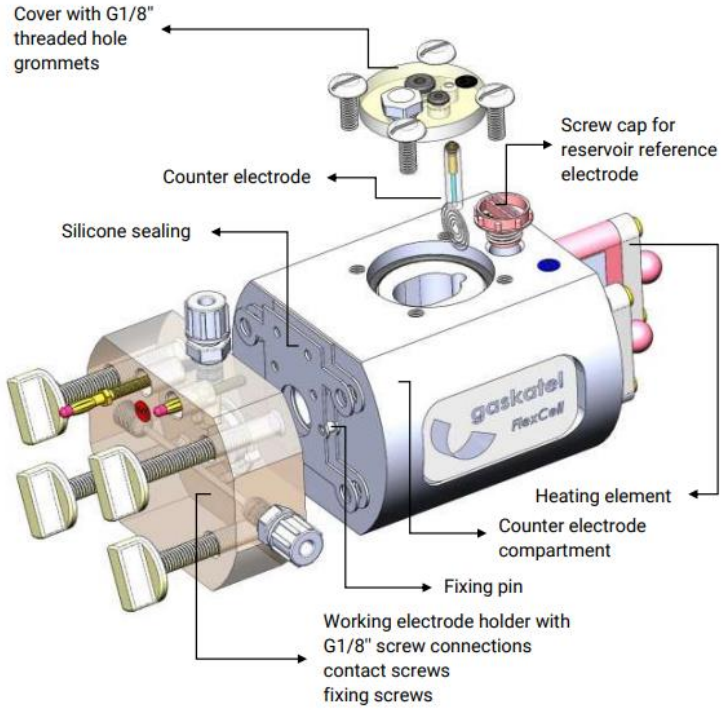
Fig. 6. RDE voltammetry curves recorded at 1600 rpm before and after stability testing for 10 000 cyclic voltammetry (CV) cycles in O_2- saturated 0.5 M H_3PO_4 solution. Commercial Fe-N-C (PMF-0011904, Pajarito Powder) is included for comparison.

(26 h CV test in 400 mV potential window)

GDE half-cell testing

(Gas diffusion electrode)

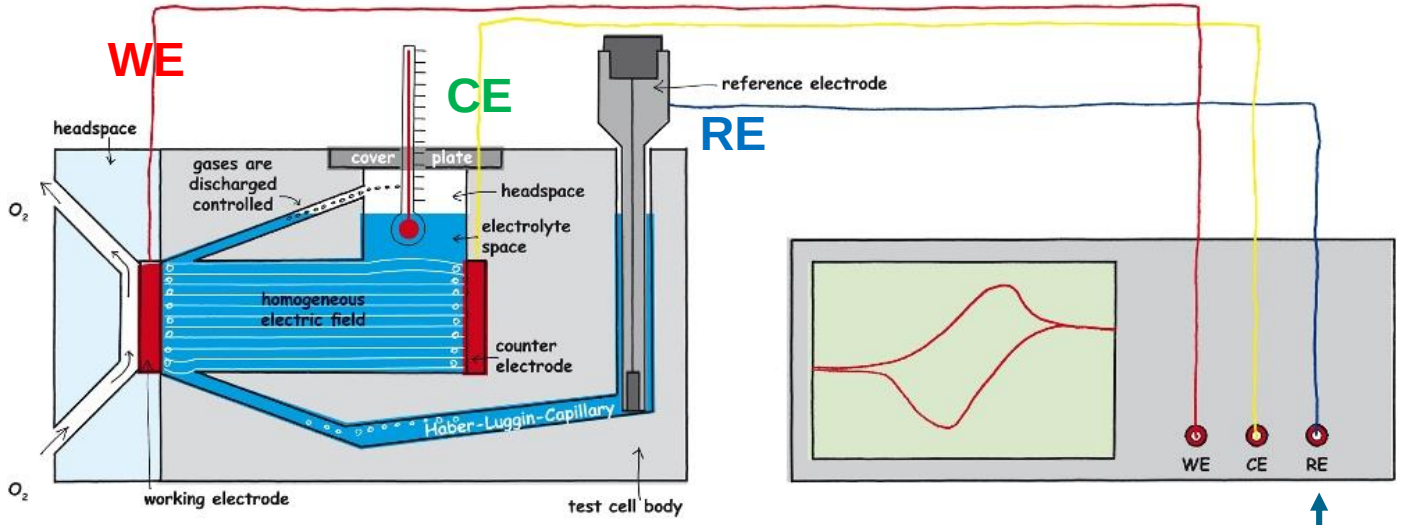




gaskatel

Test Cell FlexCell

Voltammetric Test Cell PTFE / PP



WE: M-N-C catalyst, 3 mg cm^{-2} (coated on commercial GDL)

RE: RHE

CE: Pt wire

Electrolyte: conc. H_3PO_4, 160 °C

(+ PBI membrane between M-N-C and electrolyte)

https://gaskatel.de/en/test-cells-for-the-electrochemistry/

GDE half-cell testing for ORR (conc. H_3PO_4 at 160 °C)

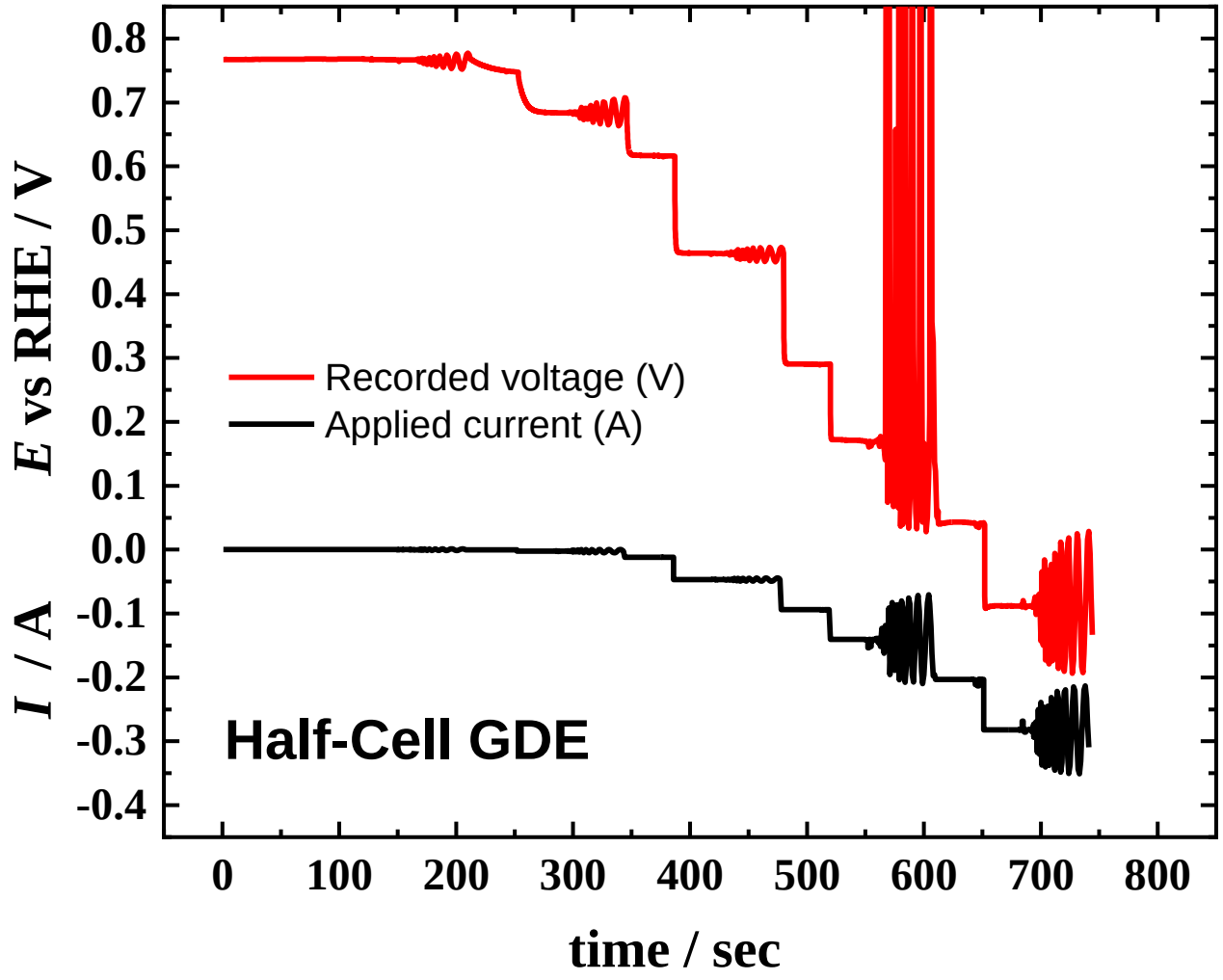


Fig. 7. Measurement consists of chronopotentiometry followed by impedance spectroscopy at certain current value steps (e.g. -0.3 mA, -2.35 mA, -11.8 mA... ...-280 mA). Resistance value is used for iR-drop compensation at certain current.

GDE half-cell testing for ORR (conc. H_3PO_4 at 160 °C)

(Single measurement with each catalyst material)

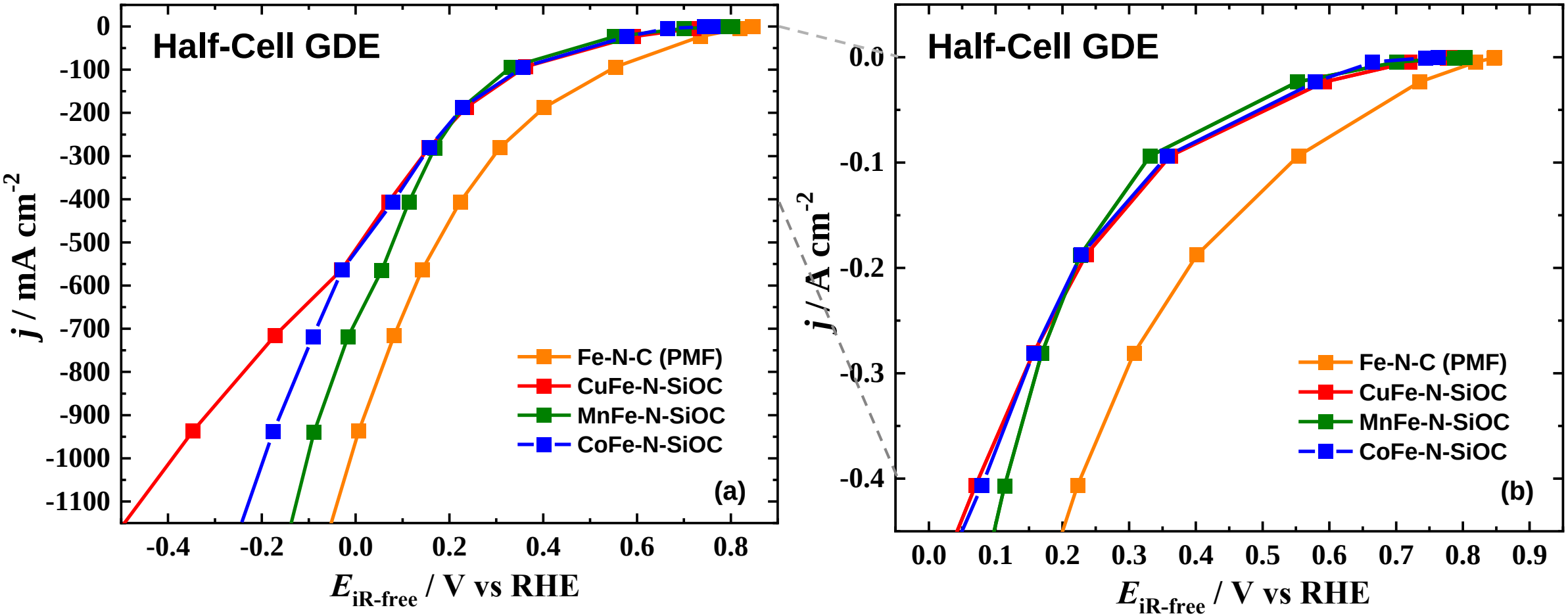


Fig. 8. GDE half-cell polarisation curves. Shown data points have been obtained via chronopotentiometry measurements corrected for iR-drop value using the impedance spectroscopy at corresponding current value.

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GDE testing (acid leaching influence)

(Averaged measurement results with each catalyst material)

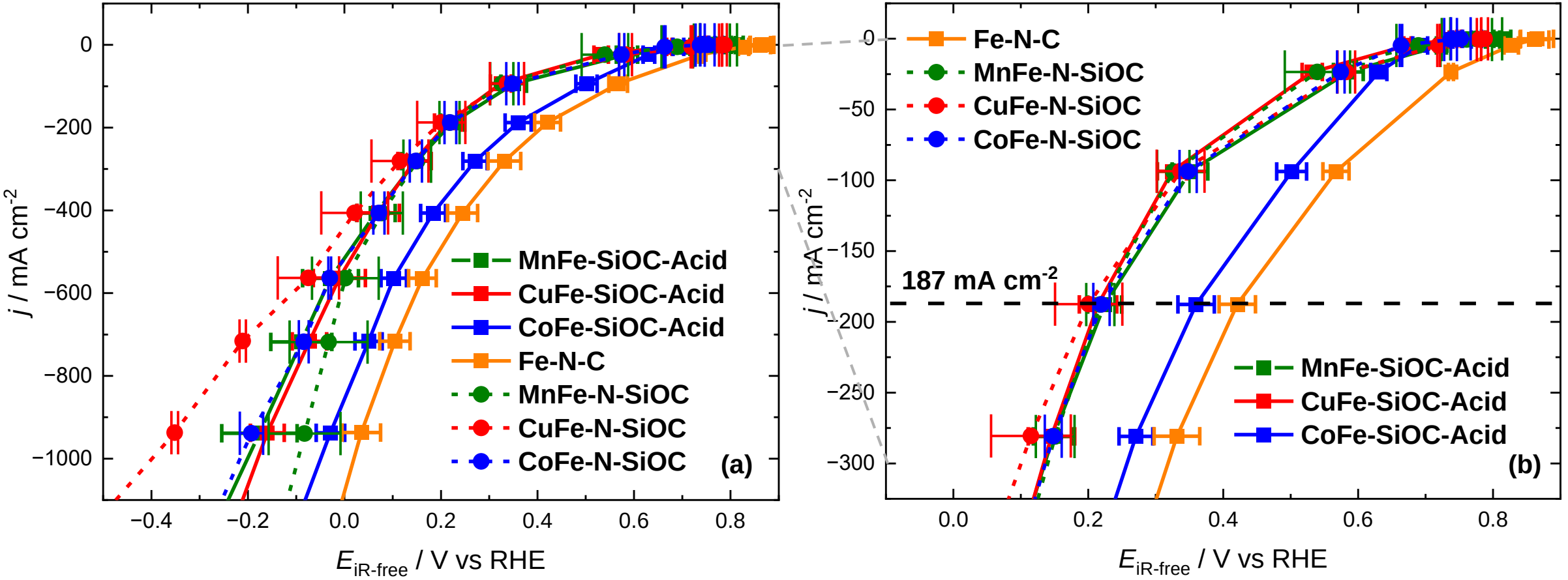

Fig. 9. GDE half-cell polarisation curves. Acid leaching route is in 2 M sulfuric acid for 16 h at 90 °C + second pyrolysis.

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GDE testing (acid leaching influence)

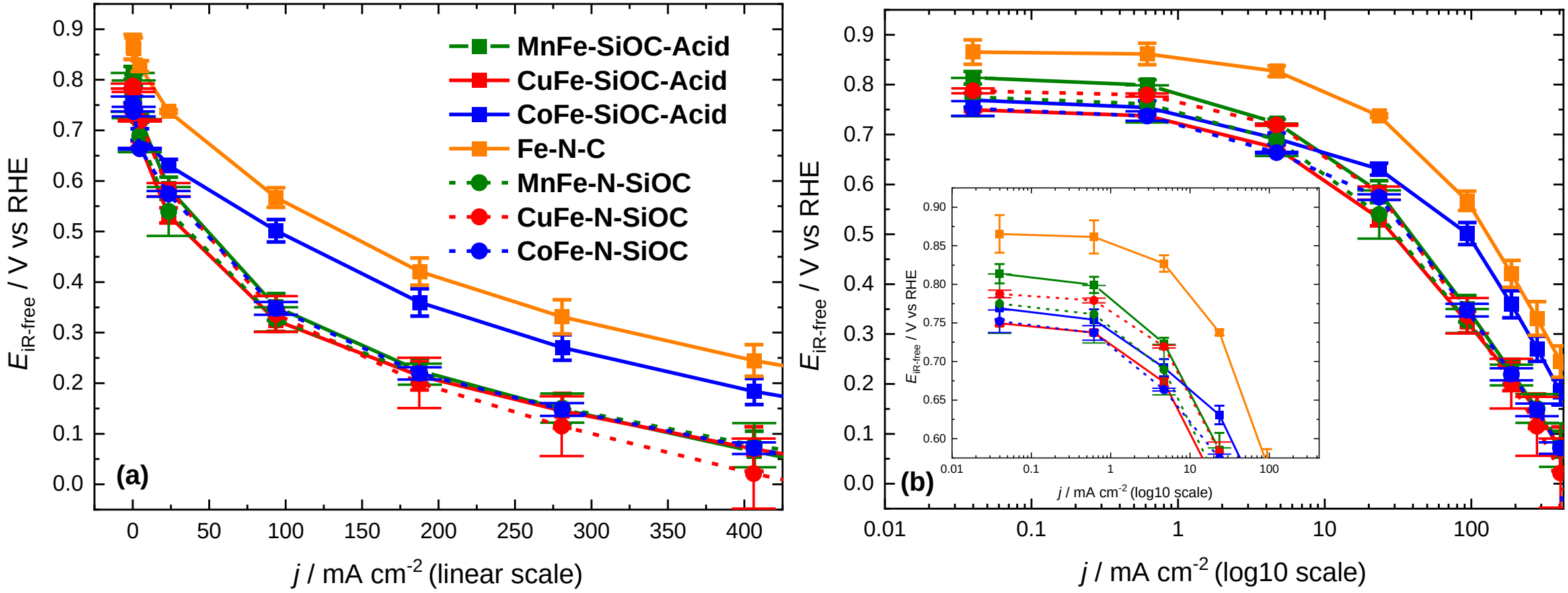

Fig. 10. Investigation of low current density region (ca. 0.9 - 0.6 V) using the logarithmic scale for current density.

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GDE testing and acid leaching influence

Catalyst	OCP	E_{187}
CoFe-N-SiOC	752 ± 15	219 ± 12
CoFe-SiOC-Acid	**17 mV** ↑ 769 ± 14	**64%** ↑ 360 ± 27
MnFe-N-SiOC	775 ± 38	218 ± 21
MnFe-SiOC-Acid	**39 mV** ↑ 814 ± 12	**~3%** ↑ 224 ± 25
CuFe-N-SiOC	788 ± 15	201 ± 50
CuFe-SiOC-Acid	**38 mV** ↓ 750 ± 13	**~6%** ↑ 214 ± 28
Fe-N-C	865 ± 24	421 ± 27

Table 4. Open circuit potential (OCP, unit mV vs. RHE) and potential value at 187 mA cm^{-2} (E_{187}, unit mV vs. RHE) for ORR derived from the GDE polarisation curves with different cathode catalyst materials.

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Conclusions

Dual transition metal containing SiOC materials

Functionalised with N using ZIF-8 and pyrolysis method

RRDE half-cell testing for ORR in 0.5 M H_3PO_4, 23 °C:

- CuFe and MnFe-containing materials more promising at RT ($E_{1/2}$, n value)
- CoFe material showed an increase in ORR activity and long-term stability after acid treatment
- Acid treatment not beneficial for CuFe and MnFe-containing materials

GDE half-cell testing for ORR with conc. H_3PO_4 at 160 °C:

- Acid treated and non-treated CuFe and MnFe-containing materials similar
  - *MnFe material showed considerable increase in OCP value after acid treatment*
- CoFe material showed a considerable increase in ORR activity after acid treatment

(Manuscript under preparation)

Aknowledgements

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Mr. Peter Wagner
Prof. Dr. Kaspar Andreas Friedrich

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PUTJD1170 Postdoctoral research grant (11.2023 – ...)

Thank you for your kind attention!

Questions?

Extra no. 1

PBI membranes for HT-PEMFCs

HT-PEFCs run at an operating temperature of about 160 °C with membrane electrode assemblies (MEAs), based on a polybenzimidazole-type polymer loaded with phosphoric acid (H_3PO_4) – e.g. *m*-PBI or *ab*-PBI (see Fig. 1). In the temperature range between 160 °C and 180 °C, the polymers loaded with H_3PO_4 display very high proton conductivity, relatively low gas permeability, and good mechanical stability.

The high operating temperature above 100 °C has several advantages over low-temperature polymer membrane fuel cells (LT-PEMFCs), which are limited to operating temperatures below 80 °C.

m-PBI, Poly[2,2'-(m-phenylen)- 5,5' bibenzimidazol]

ab-PBI, Poly[2,5-benzimidazol]

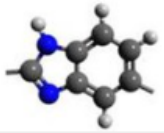

Fig. 1: Repeating units of two polybenzimidazole-type polymers

https://www.fz-juelich.de/en/iek/iek-14/research/pcl/spectroscopy/pbi-membranes

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Extra no. 2

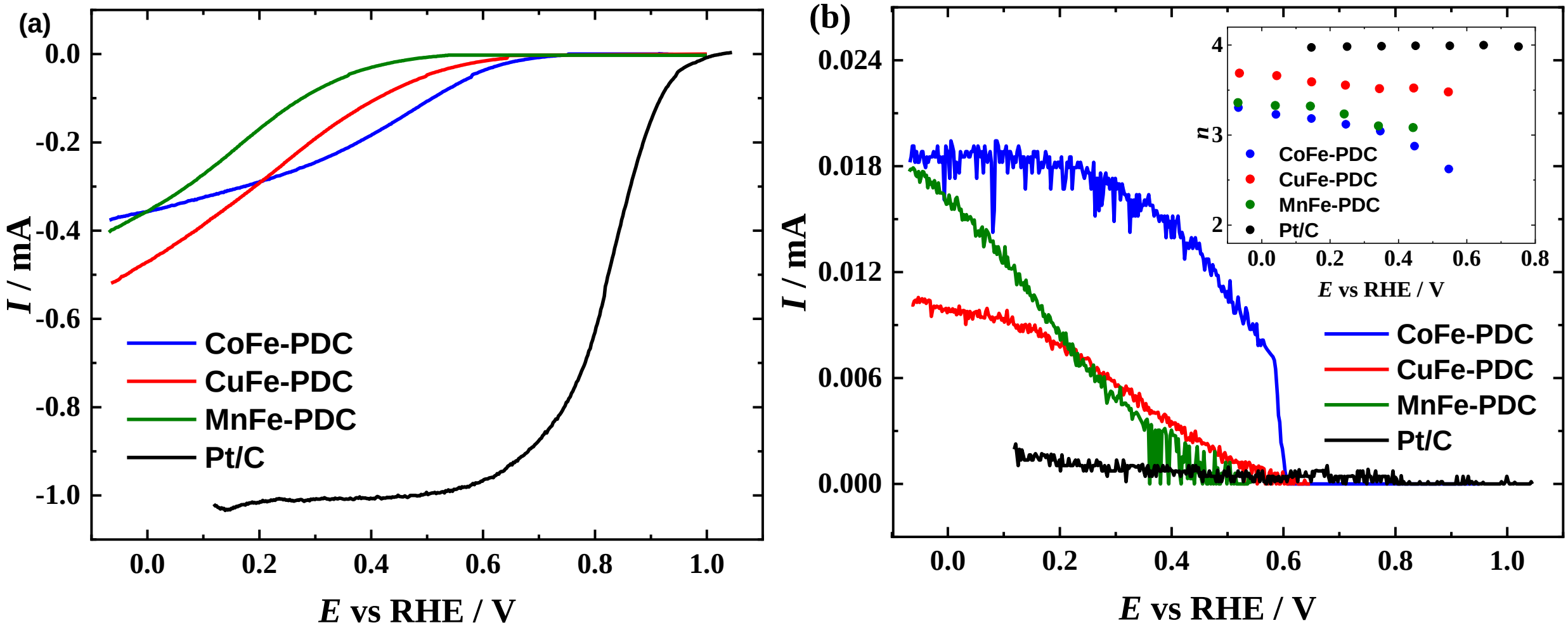

Fig. E1. (a) Disc current, (b) ring current and electron transfer numbers (*n*) for different catalyst coated GC-disk/Pt-ring electrodes recorded at 1600 rpm in O_2-saturated 0.5 M phosphoric acid solution.

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Extra no. 3

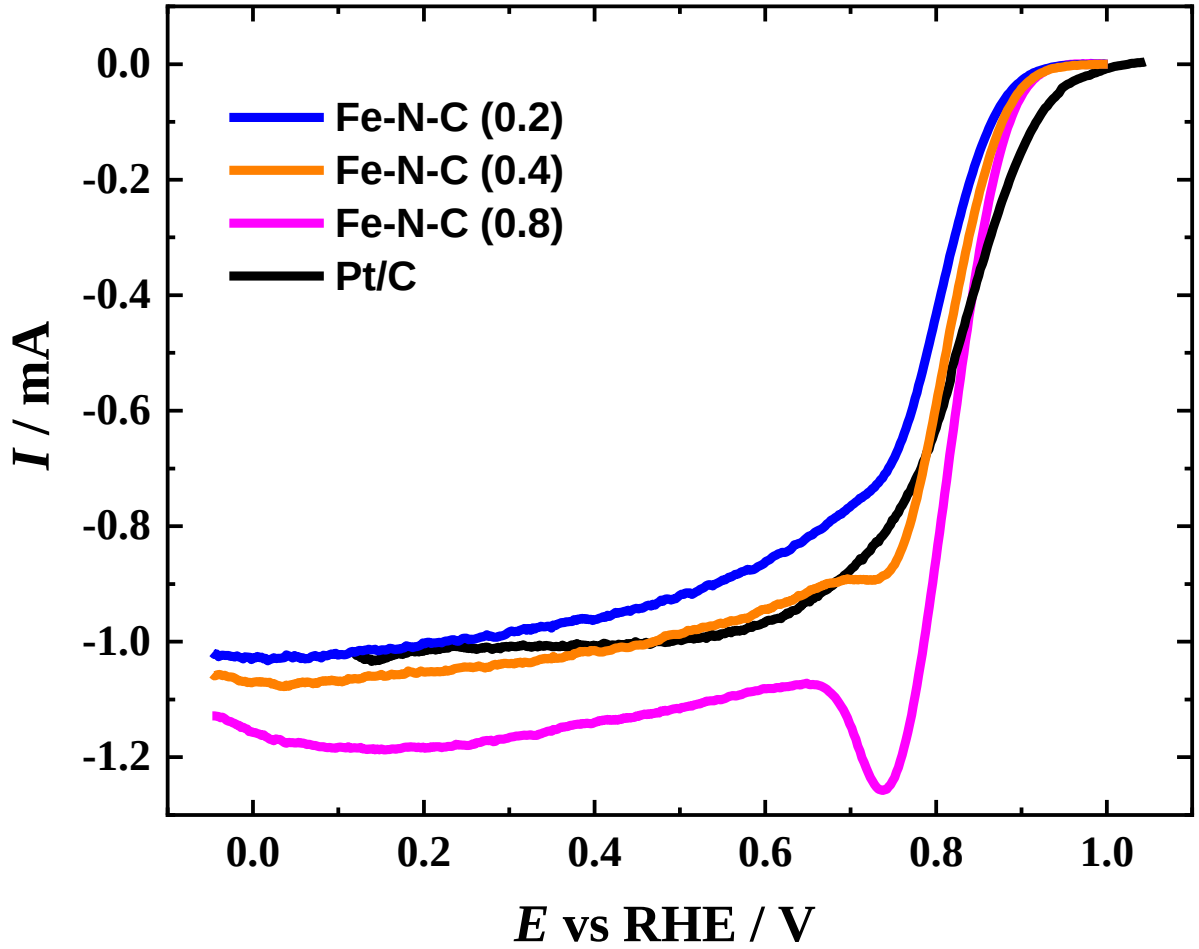

Fig. E2. RDE voltammetry curves for ORR recorded at 1600 rpm in O_2-saturated 0.5 M phosphoric acid solution with different loadings of commercial Fe-N-C catalyst (mg cm^{-2}) and Pt/C (20 μg_{Pt} cm^{-2}). Catalyst loading of 0.4 mg cm^{-2} (PMF-0011904, Pajarito Powder) was chosen for comparison in this work.

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