

Electronic Supplementary Information

Electrocatalysis of oxygen reduction on heteroatom-doped nanocarbons and transition metal-nitrogen-carbon catalysts for alkaline membrane fuel cells

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Table S1. Performance of metal-free electrocatalysts at the cathode of AEMFC.

| Catalyst | Cathode loading (mg cm ⁻²) | Cathode Pt loading (mg _{Pt} cm ⁻²) | Anode Pt loading (mg _{Pt} cm ⁻²) | T (°C) | Membrane | Ionomer (wt% or ionomer-to-carbon ratio, I/C) | Cathode gas flow (ml min ⁻¹) | Anode gas flow (ml min ⁻¹) | P_{max} (mW cm ⁻²) | P_{max} for Pt/C (mW cm ⁻²) | i at 0.6 V (mA cm ⁻²) | i at 0.6 V for Pt/C (mA cm ⁻²) | OCV (V) | Ref |
|---------------|--|---|---|--------|----------------------------|---|--|--|----------------------------------|---|-----------------------------------|--|---------|-----|
| NCNTs | 0.2 | 0.2 mg _{Pt} cm ⁻² | 0.5 mg _{Pt} cm ⁻² | 80 | FumaTech FAA | no ionomer | 300 | 300 | 25.5 | 19.1 | 37.5 | 27.5 | - | 137 |
| aligned NCNTs | 5 | 0.5 mg _{Pt} cm ⁻² | 0.5 mg _{Pt} cm ⁻² | 50 | FumaTech FAA | OH-type FAA (30 wt%) | 1000 | 500 | 37.3 | 61.7 | 32* | 77* | 0.87 | 138 |
| gCN-CNF | 2 | 0.1 mg cm ⁻² of 40% Pt/C | 0.5 mg cm ⁻² of 40% Pt/C | 50 | AEM from anonymous company | Tokuyama AS-4 | unknown | unknown | 171 | 222 | 248 | 308 | - | 139 |
| CNT/HDC | 2 | 0.5 mg cm ⁻² of 20% Pt/C | 0.5 mg cm ⁻² of 40% Pt/C | 50 | in-house pore-filling AEM | Acta I2 (20 wt%) | 1200 | 200 | 280* | 525* | 368 | 800* | - | 140 |
| NG | 2 | unknown | unknown | 60 | Neosepta AHA | Fumion FAA-3 (10 wt%) | 200 | 200 | 2.6 | 20* | 2* | 32* | - | 141 |
| NpGr-72 | 2.5 | 0.8 mg cm ⁻² of 40% Pt/C | 0.8 mg cm ⁻² of 40% Pt/C | 50 | Fumapem FAA-3 | Fumion (I/C=0.5) | 100 sccm | 50 sccm | 27 | 67 | 36* | 100* | 0.82 | 142 |
| N-S/Gr-1000 | 2 | unknown | 0.5 mg _{Pt} cm ⁻² | RT | Fumapem | Fumion FAA-3 | 200 | 200 | 19.8 | 67** | 22* | 100* | - | 143 |
| N-SWCNH N-800 | 3 | 0.8 mg cm ⁻² of 40% Pt/C | 0.5 mg cm ⁻² of 40% Pt/C | 50 | Fumapem FAA | Fumion (I/C=0.8, for Pt/C, I/C=0.4) | 100 sccm | 50 sccm | 30 | 60 | 40* | 100* | 0.75 | 144 |
| NHC | 1.0 | 1.0 mg cm ⁻² of 20% Pt/C | 1.0 mg cm ⁻² of 20% Pt/C | 70 | Fumapem FAA-3 | Fumion FAA-3 | 200 sccm | 200 sccm | 228 | 260 | 325* | 360* | - | 91 |
| NPOMC-L2 | 0.5 | 0.5 mg cm ⁻² of 20% Pt/C | 0.5 mg cm ⁻² of 20% Pt/C | 60 | lab-made alkaline AEM | unknown | 100 sccm | 100 sccm | 90* | 128* | 125* | 190* | - | 145 |
| N-S-MPC | 1-5 | 0.5 mg cm ⁻² of 40% Pt/C | 0.3-0.5 mg cm ⁻² of 40% Pt/C | RT | Tokuyama A201 | Tokuyama AS-4 (I/C = 1:3) | 70 | 100 | 21.7 | 37.7 | 36* | 60* | 0.93 | 146 |
| NC FU | 1 | unknown | 0.4 mg _{Pt} cm ⁻² | 60 | Nowoflon ET ETFE film | ETFE-g-poly(VBTMA+Cl-) AEI (I/C=1:4) | 1 slpm | 1 slpm | 703 | 1160 | 110* | unknown | 0.95 | 147 |

* estimated from the Figures

** calculated from other data provided

Table S2. Performance of M-N-C catalysts at the cathode of AEMFC.

| Catalyst | Cathode loading (mg cm ⁻²) | Cathode Pt loading | Anode loading | T (°C) | Membrane | Ionomer (wt% or ionomer-to-carbon ratio, I/C) | Cathode gas flow (ml min ⁻¹) | Anode gas flow (ml min ⁻¹) | P_{max} (mW cm ⁻²) | P_{max} for Pt/C (mW cm ⁻²) | i at 0.6 V (mA cm ⁻²) | i at 0.6 V for Pt/C (mA cm ⁻²) | OCV (V) | Ref |
|--|--|--|--|--------|--|---|--|--|----------------------------------|---|-----------------------------------|--|-------------------------|-----|
| Hypermec 4020 | 0.8 | 0.45 mg _{Pt} cm ⁻² | 0.45 mg _{Pt} cm ⁻² | 50 | commercial membrane | Acta I2 (I/C= 0.3:1) | 2000 (air) | 1000 | 205 | 400* | 275* | 440* | - | 148 |
| GP4-GPM | 3 | 0.5 mg _{Pt} cm ⁻² | unknown | 60 | aminated poly(LDEP-co-VBC) | PVBC | unknown | unknown | 260 | 260 | unknown | unknown | - | 149 |
| CoFeN/C | 4 | 0.4 mg _{Pt} cm ⁻² | 0.4 mg _{Pt} cm ⁻² | 50 | Tokuyama A201 | Tokuyama AS-4 | 400 | 200 | 177 | 196 | 160* | 160* | 0.97 | 94 |
| M-N-C (M= Fe, Co) | 4 | 0.5 mg _{Pt} cm ⁻² | 0.5 mg _{Pt} cm ⁻² | 60 | Tokuyama A201 | Tokuyama AS-4 | 400 | 400 | 75 (Fe) 68 (Co) | 80 | 105* (Fe) 90* (Co) | 110* | 1.04 (Fe), 0.99 (Co) | 93 |
| MPc/C (M=Fe, Co, Ni, Mn) | 2 | - | - | 50 | Tokuyama A901 | Tokuyama AS-4 (I/C= 1:4) | 200 sccm | 200 sccm | 85-105 | - | 90-160* | - | - | 150 |
| MPc/C (M=Co,Cu, Zn,Ni) | 3 | unknown | 0.5 mg cm ⁻² of 40% Pt/C | RT | Tokuyama A901 | Nafion (I/C=1:3) | 70 | 100 | 6.0-12.6 | 37.7 | 6-20* | 60* | 0.73-0.90 | 151 |
| CoFeN _x /C | 2.5 | 2.5 mg cm ⁻² of 40% Pt/C | 0.4 mg cm ⁻² | 60 | Tokuyama A201 | Tokuyama AS-4 (20 wt%) | 200 sccm | 100 sccm | 37 | 170* | 57* | 260* | - | 152 |
| FePc/C | 1 | 0.4 mg _{Pt} cm ⁻² | 0.4 mg _{Pt} cm ⁻² | 55 | Tokuyama A201 | Tokuyama AS-4 (I/C = 0.6) | 200 sccm | 100 sccm | 120 | 310* | 190* | 400* | - | 153 |
| BPox-NFe | 2.0 | - | unknown | 50 | α QAPS | α QAPS-S8 (20 wt%) | 250 | 250 | 107 | - | 55* | - | 0.83 | 154 |
| Fe-pyPANI-K | 1-3 | 0.5 mg cm ⁻² of 20% Pt/C | 0.5 mg cm ⁻² of 40% Pt/C | 50 | A901, Tokuyama | Tokuyama AS-4 | unknown | unknown | 157 | 189** | 139 | 230* | - | 155 |
| Fe-M-LA/C-700 | 4 | unknown | 0.4 mg cm ⁻² of 40% Pt/C | 60 | Tokuyama A201 | Tokuyama AS-4 | 250 | 200 | 137 | 157 | 180* | 260* | 0.94 | 156 |
| CoO-rGON | 0.75 | 0.75 mg cm ⁻² of Pt/C | 1.5 mg cm ⁻² of Pt/C | 60 | Tokuyama A201 | Tokuyama AS-4 (30 wt%) | 500 | 250 | 248 | 387 | 320 | 430 | - | 157 |
| Fe-Fe ₂ O ₃ /NGr | 3 | 0.35 mg _{Pt} cm ⁻² | 0.35 mg _{Pt} cm ⁻² | 60 | FumaTech FAA | unknown | 200 sccm | 200 sccm | 54.4 | 70 | 40* | 60* | 0.73 | 99 |
| Fe/Co-NpGr | 2.5 | 0.8 mg _{Pt} cm ⁻² | 0.8 mg _{Pt} cm ⁻² | 50 | FumaTech FAA | Fumion (I/C=1:2) | 100 sccm | 50 sccm | 35 | 60.3 | 54.4 | 82.1 | 0.85 | 158 |
| AT-Fe/N/C | 4 | - | 0.4 mg _{Pt} cm ⁻² | 60 | home-made α QAPS-S ₈ AEM | unknown | 250 sccm | 250 sccm | 164 | - | 200* | - | 1.0 | 159 |
| MPc/MWN CNT | 0.6 | 0.6 mg cm ⁻² of 46% Pt/C | 0.4 mg cm ⁻² of 46% Pt/C | 45 | Tokuyama A201, 28 μ m | Tokuyama AS-4 | 400 sccm | 200 sccm | 60 (Fe) 100 (Co) | 120 | 70* (Fe) 145* (Co) | 195* | - | 95 |

| | | | | | | | | | | | | | | |
|---------------------|-----|---------------------------------------|---------------------------------------|----|----------------|------------------------------------|----------|----------|-------|----------|----------|----------|--------|-----|
| (M=Co, Fe) | | | | | | | | | | | | | | |
| CNT/PC | 2 | unknown | 0.5 mg _{Pt} cm ⁻² | 80 | homemade AEM | Acta I2 (30 wt%) | 1200 | 400 | 380 | 525* | 498 | 825* | - | 160 |
| Co/N/MWC NT | 0.6 | 0.6 mg cm ⁻² of 46 % Pt/C | 0.4 mg cm ⁻² of 46% Pt/C | 50 | Tokuyama A201 | Tokuyama AS-4 | 200 sccm | 100 sccm | 115 | 112*-120 | 150* | 155-200* | 0.945 | 96 |
| CoNC-900 | 2 | unknown | 0.8 mg cm ⁻² of 40% Pt/C | 50 | Fumapem FAA | Fumion (10 wt%) | 100 sccm | 50 sccm | 60 | 64 | 80 | 80 | 0.92 | 161 |
| FeNCNH | 4 | 0.8 mg cm ⁻² of 40% Pt/C | 0.5 mg cm ⁻² of 40% Pt/C | 50 | Fumapem FAA | Fumion (I/C=0.8; for Pt/C I/C=0.4) | 100 sccm | 50 sccm | 35 | 60* | 30 | 100* | 0.83 | 162 |
| M/N/CDC (M= Fe, Co) | 1.5 | 1.5 mg cm ⁻² of 46% Pt/C | 1 mg _{Pt} cm ⁻² | 50 | Tokuyama A201 | Tokuyama AS-4 | 0.8 nlpm | 0.4 nlpm | 78-80 | 90 | 125-130* | 150* | 1.02** | 100 |
| Fe-HNCS | 4 | 0.5 mg _{Pt} cm ⁻² | 0.5 mg _{Pt} cm ⁻² | 60 | Tokuyama A201 | Tokuyama AS-4 | 400 | 400 | 68 | 80 | 95* | 110* | 0.96 | 163 |
| Fe-N-CC | 0.2 | 0.2 mg cm ⁻² of 20% Pt/C | 0.4 mg _{Pt} cm ⁻² | 50 | Tokuyama A201 | Tokuyama AS-4 (20 wt%) | 1000 | 500 | 120* | 107* | 150* | 140* | 0.96 | 164 |
| CS_FePc_450 | 1 | 1 mg cm ⁻² of 40% Pt/C | 0.5 mg cm ⁻² of 40% Pt/C | 50 | A901, Tokuyama | Tokuyama AS-4 | unknown | unknown | 160* | 206* | 255* | 340* | - | 165 |
| BIDC3 | 4 | unknown | 0.3 mg cm ⁻² of 40% Pt/C | 60 | Tokuyama A201 | Tokuyama AS-4 (35 wt%) | unknown | unknown | 47* | 160* | 50 | 220* | 0.97 | 166 |
| m-FePhen-C | 1-4 | 1 mg cm ⁻² of 40% Pt/C | 0.5 mg cm ⁻² of 40% Pt/C | 50 | A901, Tokuyama | Tokuyama AS-4 | unknown | unknown | 272 | 206 | 400* | 320* | - | 167 |
| Fe-NMG | 3.5 | 0.2 mg _{Pt} cm ⁻² | 0.2 mg _{Pt} cm ⁻² | 70 | Tokuyama A201 | Tokuyama AS-4 (35 wt%) | 200 | 250 | 218 | 200 | 325* | 310* | - | 168 |

* estimated from the Figures

** calculated from other data provided

Table S3. Performance of metal-free electrocatalysts at the cathode of AEM-DMFC

| Catalyst | Cathode loading (mg cm ⁻²) | Anode loading (mg _{Pt} cm ⁻²) | T (°C) | Membrane | Anode (ml min ⁻¹) | Cathode (ml min ⁻¹) | P_{\max} (mW cm ⁻²) | P_{\max} (Pt/C) (mW cm ⁻²) | OCV (V) | Ref |
|------------------------|--|--|--------|------------------------|-------------------------------|---------------------------------|-----------------------------------|--|---------|-----|
| N-FWCNT | 2.2 | 3 | 50 | FAA3 (FumaTech) | 2 (1 M MeOH) | 200 (O ₂) | 0.75 | 0.70 | 0.5 | 34 |
| N-FWCNT | 2.2 | 3 | 50 | FAA3 (FumaTech) | 2 (1 M MeOH) | 200 (Air) | 0.73 | 0.18 | | 179 |
| N-MWCNT N-FLG-MWCNT | 2.2 | 3 | 40 | FAA3 (FumaTech) | 2 (1 M MeOH) | 200 (O ₂) | 0.92 | 0.72 | 0.64 | 180 |
| C-PY-900 | 4 | 1, Pd/C | 50 | Nafion ionomer/AEM | 1 (1 M MeOH-6 M KOH) | 20 (O ₂) | 39* | 22* | 0.83* | 182 |
| N-CNT | 4 | 1 | 25 | Nafion/Na ⁺ | 5 (2 M MeOH-6 M NaOH) | 70 (O ₂) | 8* | - | 0.38* | 181 |
| CB-NF | 3 | 3 | 60 | xQAPS | 5 (2 M MeOH-2 M KOH) | 100 (O ₂) | 15 | 13 | 0.8 | 183 |
| BP-18F | 3 | 3 | 60 | xQAPS | 5 (2 M MeOH-2 M KOH) | 100 (O ₂) | 15.6 | 9.44 | 0.7* | 184 |

*Estimated values from the figures

Table S4. Performance of M-N-C catalysts at the cathode of AEM-DMFC.

| Catalyst | Cathode loading (mg cm ⁻²) | Anode loading (mg _{Pt} cm ⁻²) | T (°C) | Membrane | Anode (ml min ⁻¹) | Cathode (ml min ⁻¹) | P_{\max} (mW cm ⁻²) | $P_{Pt\max}$ (mW cm ⁻²) | OCV (V) | Ref |
|--------------------------|--|--|--------|-----------------|-------------------------------|------------------------------------|-----------------------------------|-------------------------------------|--------------|------|
| Fe-N-C | 3 | 3 | 80 | Tokuyama | 1 (2 M MeOH-1 M NaOH) | 100 (O ₂) | 33 | 8 | 0.85 | 185 |
| Fe ₃ C/NG-800 | 3 | 2 | 60 | Nafion | 5 (2 M MeOH) | 100 (O ₂) | 31 | 45 | 0.75 | 186 |
| Fe ₃ C/NG-800 | 3 | 2 | 60 | AEM | 5 (2 M MeOH-1 M NaOH) | 100 (O ₂) | 19 | 15 | 0.87 | 186 |
| Co-N/C-700 | 3 | 3 | 80 | PAEK | 5 (2 M MeOH-2 M KOH) | 100 (O ₂) | 40.1 | 21 | 0.8 | 187 |
| NCPs | 3 | 3 | 60 | A201 Tokuyama | 2 (2 M MeOH) | 200 (O ₂) | 22.7 | 13.5 | 0.81 | 188 |
| Nano-P-ZIF-67 | 3 | 3 | 80 | PAEK* | 5 (2 M MeOH-2 M KOH) | 100 O ₂ | 45.5 | 20 | 0.35 | 189. |
| GNPCSS-800 | 4 | 3 | 80 | PAEK* | 2 M MeOH-2 M KOH | 100 O ₂ | 33 | 22.5 | 0.71 | 190 |
| Fe-AAPyr-G2 | 5.48 | 2.5 | 80 | ATMPP | 0.5 (2 M MeOH-2 M KOH) | 200 (O ₂) | 52 | 20 | 0.88 | 192 |
| Fe-N-CDC | 1.73 | 1.27 | 50 | FAA3 (FumaTech) | 0.2 (1 M MeOH-0.1 M KOH) | 200 (O ₂) | 6.85 | 4.70 | 0.3 | 195 |
| Co-N-CDC | 1.83 | 1.27 | 50 | FAA3 (FumaTech) | 0.2 (2 M MeOH-2 M KOH) | 200 (O ₂) | 6.21 | 4.70 | 0.27 | 195 |
| Hypermec K14 (Acta) | 3.5 | - | 60 | Tokuyama | 7 (10% EtOH-10% KOH) | 150 (O ₂) 150 (Air) | 102 85 | 90 65 | 0.79 0.79 | 197 |
| (Bg-CA-M)-Fe/N/C-800 | 2.56 | Pd/C 0.5 | | Tokuyama | 2 (2 M EtOH-1 M KOH) | 300 (O ₂) | 64 | -- | 0.88 | 198 |
| Fe-N/MPC1 | 2.5 | 1 | 90 | Nafion 117 | 1 (2 M MeOH) | 200 (O ₂) | 22.6 | 30.9 | 0.64 | 199 |

* poly(arylene ether ketone)