An Anion-Exchange Membrane Fuel Cell Containing Only Abundant and Affordable Materials

Biemolt, J.; Douglin, J.C.; Singh, R.K.; Davydova, E.S.; Yan, N.; Rothenberg, G.; Dekel, D.R.

DOI
10.1002/ente.202000909

Publication date
2021

Document Version
Final published version

Published in
Energy Technology

License
CC BY-NC

Link to publication

Citation for published version (APA):
Biemolt, J., Douglin, J. C., Singh, R. K., Davydova, E. S., Yan, N., Rothenberg, G., & Dekel, D. R. (2021). An Anion-Exchange Membrane Fuel Cell Containing Only Abundant and Affordable Materials. Energy Technology, 9(4), [2000909].
https://doi.org/10.1002/ente.202000909
An Anion-Exchange Membrane Fuel Cell Containing Only Abundant and Affordable Materials

Jasper Biemolt, John C. Douglin, Ramesh K. Singh, Elena S. Davydova, Ning Yan,* Gadi Rothenberg,* and Dario R. Dekel*

Herein, a unique anion-exchange membrane fuel cell (AEMFC) containing only affordable and abundant materials is presented: NiFe hydrogen oxidation reaction (HOR) and nitrogen-doped carbon oxygen reduction reaction (ORR) electrocatalysts. AEMFCs are an attractive alternative to proton-exchange membrane fuel cells. They can run under alkaline conditions, allowing the use of platinum group metal (PGM)-free electrocatalysts. Yet, the same alkaline conditions incur an overpotential loss in ORR and also slow the HOR. This can be solved by using PGM electrodes, but then the original advantage disappears. In contrast, the fuel cell is free of both PGMs and critical raw materials (CRMs). Electrochemical studies confirmed that the catalysts are highly active in both HOR and ORR in an alkaline electrolyte. The morphology, composition, and chemical states of the electrocatalysts are characterized by different techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and electron energy loss spectroscopy (EELS). Then, the electrocatalysts’ performance is tested in a fuel cell device. The cell gives a maximum power density of 56 mW cm$^{-2}$ and a limiting current density of 220 mA cm$^{-2}$. These results are among the best CRM-free anion-exchange membrane fuel cells reported to date.

Sustainable chemistry and sustainable energy are popular buzz-words, yet they require viable technological concepts to become reality. As such, anion-exchange membrane fuel cells (AEMFCs) have attracted much attention lately due to their potential for avoiding platinum group metal electrocatalysts.\cite{1,2,3,4} Achieving this platinum group metal (PGM)-free goal, however, is extremely challenging. From all studies showing AEMFC performance data, only 6% are based on platinum-free electrocatalysts and very few of those are completely PGM-free.\cite{5,6} The first to report such cell performance were Lu et al.\cite{7} who showed in 2008 a Ni–Cr anode and Ag cathode AEMFC with a promising peak power density of 50 mW cm$^{-2}$. Five years later, two more studies achieved peak power densities of 76 and 40 mW cm$^{-2}$, using AEMFCs based on Ni/Ag and NiW/CoPPY-based (anode/cathode) electrocatalysts, respectively.\cite{8,9} Since then, the only report of an AEMFC based on PGM-free electrocatalysts used NiCo/C and Co$_3$O$_4$/C, with a peak power density of 22 mW cm$^{-2}$.\cite{10} While these pioneering studies showed the feasibility of PGM-free electrocatalysts, most still use critical raw materials (CRMs) such as cobalt, chromium, and tungsten.\cite{11,12}

Any large-scale and sustainable deployment of AEMFCs should minimize the use of both PGMs and CRMs.\cite{13} With this in mind, we focused our research on CRM-free electrocatalysts, aiming at demonstrating their feasibility in AEMFC performance tests. The Technion group showed previously that Ni$_3$Fe-based electrocatalysts are highly active for the hydrogen oxidation reaction (HOR) in alkaline conditions.\cite{14} and that Ni$_3$Fe/C HOR electrocatalysts are stable in alkaline media.\cite{15} Elsewhere, the UvA group demonstrated the utility of metal-free nitrogen-doped carbon catalysts for the oxygen reduction reaction (ORR) electrodes. In this communication, we combine a similar Ni$_3$Fe HOR catalyst and the ORR catalyst in a complete fuel cell, presenting an affordable and abundant electrocatalyst system for AEMFCs. For the HOR catalyst, we built on our studies of Ni$_3$Fe/C, which showed a negligible dissolution up to 0.7 V_{RHE}.\cite{15} This catalyst maintained its HOR activity after 1000 cycles to 0.3

J. Biemolt, Dr. N. Yan, Prof. G. Rothenberg
Van ’t Hoff Institute for Molecular Sciences
University of Amsterdam
Science Park 904, XH Amsterdam 1098, The Netherlands
E-mail: n.yan@uva.nl; g.rothenberg@uva.nl

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/ente.202000909.

© 2021 The Authors. Energy Technology published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

DOI: 10.1002/ente.202000909
V_{RHE}, comparing favorably with Ni_{3}Mo/C and Ni_{3}Cu/C.\textsuperscript{[16,17]} We therefore opted for developing nickel-rich NiFe bimetallic HOR electrocatalysts. A nominal Ni_{7}Fe stoichiometry was chosen to increase the nickel content in the bimetallic nanoparticle, aiming for high HOR activity while still keeping some iron in the particles for chemical and electrochemical stability. The Ni_{7}Fe/C anodes were prepared by first mixing the salts of Ni and Fe in a nominal 7:1 molar ratio, followed by wet chemical reduction with sodium borohydride.\textsuperscript{[14,15]} This yields a uniform dispersion of Ni_{7}Fe/C of size \(\approx 10–15\) nm.

As the ORR catalyst, we used nitrogen-doped carbon,\textsuperscript{[18]} a family of materials known for their excellent ORR activity in alkaline conditions.\textsuperscript{[19–22]} This material is easily made on a multi-gram scale and can be tailored to specific operating conditions.\textsuperscript{[23,24]} Briefly, the material was prepared by first forming a magnesium–nitrotriacetic acid metal–organic framework. This was then carbonized, acid washed to remove any MgO and form hierarchical pores, and recarbonized (see Supporting Information for detailed experimental procedures).

The Ni/Fe atomic ratio, measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), was \(\approx 8.5\), confirming the nickel-rich content. Figure 1 shows the physical and chemical characterizations of the Ni_{7}Fe/C and N-doped carbon electrocatalysts. The scanning transmission electron microscope high-angle annular dark-field imaging (STEM-HAADF) image and the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental maps of Ni_{7}Fe/C for Ni, Fe, O, and C are shown in Figure 1a–e. The particle size of the NiFe alloy is \(\approx 10–15\) nm, with a fine mixing of the metals. From the single nanoparticle HAADF images, we estimate a uniform oxide layer coating of \(\approx 3.6\) nm. The oxide content is slightly higher than that reported for Ni_{3}Fe nanoparticles.\textsuperscript{[14,15]} Several studies state that the presence of metal–metal oxide phase is important for alkaline HOR catalysis.\textsuperscript{[25–27]} The core/shell structure shown in the HAADF images also reflects the surface segregation, suggesting that detailed surface analysis (e.g., by X-ray photoelectron spectroscopy [XPS]; see later) is useful. Additional morphological data are shown in Figure S1 and S2, Supporting Information. These observations are supported by cross-analysis using electron energy loss spectroscopy (EELS; see maps and spectra in Figure S3, Supporting Information). The peak at high energy loss regions at 531 eV, doublet at 708/721 eV, and the doublet at 853/872 eV correspond to O, Fe L\textsubscript{2,3}, and Ni L\textsubscript{2,3}, respectively, due to inner electron transition and suggests that Fe and Ni nanoparticles are at least partially oxidized.\textsuperscript{[28]}

Figure 1f shows the SEM image of the N-doped carbon. The flakes are a few microns in diameter, with a macroporous network that enables a fast mass transfer. TEM reveals mesopores within the structure, further expanding the network. The material has a high specific surface area of 1320 m\textsuperscript{2} g\textsuperscript{−1} and ample pore volume (3.10 cm\textsuperscript{3} g\textsuperscript{−1} in total, of which 80% comes from mesopores). Its nitrogen content is 4.6 wt%, of which 36% pyridinic, 51% graphitic, and 14% oxidized. A detailed study of the morphology and surface composition of this material is published elsewhere.\textsuperscript{[18,24]}

The X-ray diffraction (XRD) pattern of Ni_{7}Fe/C, shown in Figure S4a, Supporting Information, suggests an amorphous phase (similar patterns were reported for Ni_{3}Fe/C prepared by the same synthesis protocol).\textsuperscript{[15]} We see a dominant peak at \(2\theta = 45.34\degree\), which is higher than the counterpart of the pure Ni (JCPDS #00-004-0850), Fe (JCPDS #00-006-0696), and Ni-Fe (JCPDS #00-037-0474) phases. This also suggests lattice contraction, in contrast to Ni_{3}Fe/C, where lattice expansion was observed.\textsuperscript{[14,15]}

---

**Figure 1.** Catalyst characterization: a) HAADF image of Ni_{7}Fe/C; b–e) STEM-EDS maps of Ni_{7}Fe/C; f) scanning electron microscopy (SEM) of the N-doped carbon; and g) transmission electron microscopy (TEM) of the N-doped carbon.
The Ni2p XPS spectrum of Ni$_2$Fe/C is shown in Figure S4b, Supporting Information (the full survey spectrum is shown Figure S5 and Tables S1 and S2, Supporting Information). We see that the Ni:Fe surface atom ratio equals 15.3. The peak at 853.72 eV is at a binding energy close to Ni$^{2+}$. As the Ni 2p$_{3/2}$ peak position in Ni–Fe alloy is nearly identical to that of Ni$^{2+}$, this peak relates to a Ni–Fe alloying component.$^{[29]}$ NiO is usually phase, with and higher than the previous reports.\(^ {2}\) at a current of 2000 rpm, and ORR: 0.1 V. The electrochemical cell was assembled by pressing a Ni(OH)$_2$ anode electrocatalyst gas diffusion electrode cathode (see photo and schematic in Figure 3, as well as electrode preparation photos in Figure S7, Supporting Information). Figure 3c shows the resulting polarization curve of the cell. This cell shows promising performance with a maximum power density of 56 mW cm$^{-2}$ at a current density of 138 mA cm$^{-2}$. In particular, the cell achieved a limiting current density higher than 200 mA cm$^{-2}$. This remarkable current density value is the highest reported to date (in fact, it is double the limiting current densities reported for AEMFCs using CRM-containing electrocatalysts in both the anode and the cathode; see Table S3, Supporting Information).

Finally, we tested the two electrocatalysts in an AEMFC setup. A 5 cm$^2$ electrochemical cell was assembled by pressing a Ni$_2$Fe/C electrocatalyst-coated membrane anode onto an N-doped carbon electrocatalyst gas diffusion electrode cathode (see photo and schematic in Figure 3, as well as electrode preparation photos in Figure S7, Supporting Information). Figure 3c shows the resulting polarization curve of the cell. This cell shows promising performance with a maximum power density of 56 mW cm$^{-2}$ at a current density of 138 mA cm$^{-2}$. In particular, the cell achieved a limiting current density higher than 200 mA cm$^{-2}$. This remarkable current density value is the highest reported to date (in fact, it is double the limiting current densities reported for AEMFCs using CRM-containing electrocatalysts in both the anode and the cathode; see Table S3, Supporting Information).

We have built a completely PGM-free and CRM-free anion-exchange membrane fuel cell using Ni$_2$Fe/C and N-doped carbon electrocatalysts. The cell achieved a maximum power density of 56 mW cm$^{-2}$ at a current density of 138 mA cm$^{-2}$, which are among the highest values reported to date for CRM-free electrocatalyst systems. We believe that CRM-free fuel cells are the only viable option for a large-scale, long-term, and sustainable energy transition. However, such a transition also requires solutions
using known concepts and techniques, limiting the need for new production lines and methods. Our electrocatalysts fit these criteria, with straightforward and scalable preparation protocols (all detailed experimental procedures are included in the Supporting Information). As such, we hope that the publication of these results will inspire others in developing sustainable and long-term solutions for the energy transition challenge problems facing our future.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was partially funded by the Nancy & Stephen Grand Technion Energy Program (GTEP); the EU Horizon 2020 research and innovation program (grant no. 721065), and the Planning & Budgeting Committee/Israel Council for Higher Education (CHE) and Fuel Choice Initiative (Prime Minister Office of ISRAEL), within the framework of “Israel National Research Centre for Electrochemical Propulsion (INREP)”. J.B., G.R., and N.Y. thank the Netherlands Organization for Scientific Research (NWO) NWO-GDST Advanced Materials program (project no. 729.001.022) for financial support.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

Keywords
clean energy, critical raw material-free, hydrogen, platinum group metal-free, sustainable sourcing

Figure 3. a) Photo and b) schematic of the AEMFC setup. c) Polarization curve of the AEMFC with Ni/Fe/C anode and N-doped carbon cathode catalysts. T_{cell} = 95 °C, RH of 100%, flow rates of 0.01 L min^{-1} of H_{2} (2 barg) and 0.2 L min^{-1} of O_{2} (no back pressure) for anode and cathode, respectively.

[1] B. P. Setzler, Z. Zhuang, J. A. Wittkopf, Y. Yan, Nat. Nanotechnol. 2016, 11, 1020.
[2] E. Agel, J. Bouet, J. F. Fauvarque, J. Power Sources 2001, 101, 267–274.
[3] J. R. Varcoe, P. Atanassov, D. R. Dekel, A. M. Herring, M. A. Hickner, P. A. Kohl, A. R. Kucernak, W. E. Mustain, K. Nijmeijer, K. Scott, T. Xu, L. Zhuang, Energy Environ. Sci. 2014, 7, 3135.
[4] S. Gottesfeld, D. R. Dekel, J. Page, C. Bae, Y. Yan, P. Zelenay, Y. S. Kim, J. Power Sources 2018, 375, 170–184.
[5] D. R. Dekel, J. Power Sources 2018, 375, 158.
[6] X. Peng, V. Kashyap, B. Ng, S. Kurungot, L. Wang, J. Varcoe, W. Mustain, Catalysts 2019, 9, 264.
[7] S. Lu, J. Pan, A. Huang, L. Zhuang, J. Lu, Proc. Natl. Acad. Sci. U. S. A. 2008, 105, 20611.
[8] Q. Hu, G. Li, J. Pan, L. Tan, J. Lu, L. Zhuang, Int. J. Hydrog. Energy 2013, 38, 16264.
[9] S. Gu, W. Sheng, R. Cai, S. M. Alia, S. Song, K. O. Jensen, Y. Yan, Chem. Commun. 2013, 49, 131.
[10] V. Men Truong, J. Richard Tolchard, J. Svendby, M. Manikandan, H. A. Miller, S. Sunde, H. Yang, D. R. Dekel, A. Oyarce Barnett, Energies 2020, 13, 582.
[11] A. Chapman, J. Arendorf, T. Castella, P. Thompson, P. Willis, L. T. Espinoza, S. Klug, E. Wichman, Study on Critical Raw Materials at EU Level – Final Report, European Commission, 2013.
[12] S. M. Fortier, N. T. Nassar, G. W. Lederer, J. Brainard, J. Gambogi, A. A. McCullough, Draft Critical Mineral List—Summary of Methodology and Background Information—U.S. Geological Survey Technical Input Document in Response to Secretarial Order No. 3359, U.S. Geological Survey, Reston, VA 2018.
[13] T. Asefa, X. Huang, Chem. – Eur. J. 2017, 23, 10703.
[14] E. Davydova, J. Zaffran, K. Dhaka, M. Toroker, D. Dekel, Catalysts 2018, 8, 454.
[15] E. S. Davydova, F. D. Speck, M. T. Y. Paul, D. R. Dekel, S. Cherevko, ACS Catal. 2019, 9, 6837.
[16] S. Kabir, K. Lemire, K. Aryushkova, A. Roy, M. Ongaard, D. Schlueter, A. Oshchepkov, A. Bonnefont, E. Savinova, D. C. Sabariraj, P. Mandal, E. J. Crumlin, I. V. Zhenyk, P. Atanassov, A. Serov, J. Mater. Chem. A 2017, 5, 24433.
[17] A. G. Oshchepkov, P. A. Simonov, O. V. Cherstiouk, R. R. Nazmutdinov, D. V. Glukhov, V. I. Zaikovskii, T. Yu. Kardash, R. I. Kvon, A. Bonnefont, A. N. Simonov, V. N. Parmon, E. R. Savinova, Top. Catal. 2015, 58, 1181.
[18] D. Eisenberg, W. Stroek, N. J. Geels, C. S. Sandu, A. Heller, N. Yan, G. Rothenberg, Chem. – Eur. J. 2016, 22, 501.
[19] J. Zhang, Z. Zhao, Z. Xia, L. Dai, Nat. Nanotechnol. 2015, 10, 444.
[20] H. Jiang, J. Gu, X. Zheng, M. Liu, X. Qiu, L. Wang, W. Li, Z. Chen, X. Ji, J. Li, Energy Environ. Sci. 2019, 12, 322.
[21] J. Tang, J. Liu, C. Li, Y. Li, M. O. Tade, S. Dai, Y. Yamauchi, Angew. Chem., Int. Ed. 2015, 54, 588.
[22] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Science 2016, 351, 361.
[23] J. Biemolt, G. Rothenberg, N. Yan, Inorg. Chem. Front. 2020, 7, 177.
[24] D. Eisenberg, P. Prinsen, N. J. Geels, W. Stroek, N. Yan, B. Hua, J.-L. Luo, G. Rothenberg, RSC Adv. 2016, 6, 80398.
[25] F. Yang, X. Bao, P. Li, X. Wang, G. Cheng, S. Chen, W. Luo, Angew. Chem., Int. Ed. 2019, 58, 14179.
[26] Y. Yang, X. Sun, G. Han, X. Liu, X. Zhang, Y. Sun, M. Zhang, Z. Cao, Y. Sun, Angew. Chem., Int. Ed. 2019, 58, 10644.
[27] A. G. Oshchepkov, A. Bonnefont, V. A. Saveleva, V. Papaefthimiou, S. Zafeiratos, S. N. Pronkin, V. N. Parmon, E. R. Savinova, Top. Catal. 2016, 59, 1319.
[28] R. H. Manso, P. Acharya, S. Deng, C. C. Crane, B. Reinhart, S. Lee, X. Tong, D. Nykypanchuk, J. Zhu, Y. Zhu, L. F. Greenlee, J. Chen, Nanoscale 2019, 11, 8170.
[29] Y. Nagai, M. Senda, T. Toshima, Jpn. J. Appl. Phys. 1987, 26, L1131.
[30] L. Marchetti, F. Miserque, S. Perrin, M. Pijolat, Surf. Interface Anal. 2015, 47, 632.
[31] J. Legrand, S. Gota, M.-J. Guittet, C. Petit, Langmuir 2002, 18, 4131.
[32] Y. Shen, L. Liu, Y. Wang, H. Kim, Fuel Process. Technol. 2011, 92, 1368.
[33] Z. Zhuang, S. A. Giles, J. Zheng, G. R. Jenness, S. Caratzoulas, D. G. Vlachos, Y. Yan, Nat. Commun. 2016, 7, 10141.
[34] A. Roy, M. R. Talarposhti, S. J. Normile, I. V. Zenyuk, V. De Andrade, K. Artushkova, A. Serov, P. Atanassov, Sustain. Energy Fuels 2018, 2, 2268.
[35] W. Sheng, A. P. Bivens, M. Myint, Z. Zhuang, R. V. Forest, Q. Fang, J. G. Chen, Y. Yan, Energy Environ. Sci. 2014, 7, 1719.