Multimodal Single-Entity Electrochemical Fluoride Sensor for Fuel Cell Membrane Degradation Diagnostics

Raul Lopez, Justin Fuentes, Adrian Gonzalez-Camps, Tinsley Benhaddouch, Ajeet Kaushik, Christopher Lloyd Metler, Shekhar Bhansali, and Dongmei Dong

1Department of Electrical and Computer Engineering, Florida International University, Miami, Florida, United States of America
2Department of Electrical and Computer Engineering, Florida Polytechnic University, Lakeland, Florida, United States of America
3Department of Environmental Engineering, Florida Polytechnic University, Lakeland, Florida, United States of America
4Department of Marine Biology, Florida International University, Miami, Florida, United States of America

To the best of our knowledge, very few works have been done for the continuous real-time monitoring of Proton Exchange Membrane Fuel Cells (PEMFCs) membrane degradation based on fluoride-specific electrochemical microsensors. PEMFCs are eco-smart energy sources for efficient transportation but experience variable degradation rates that wear the Membrane Electrode Assembly (MEA), a critical component of the fuel cell’s functionality. Current market options lack specific diagnostics and a legitimate indication of when exactly the membrane needs to be replaced. As such, this work focused on manufacturing a sensor for measuring MEA degradation in real-time by selectively monitoring fluoride concentration in effluent water, a signature PEMFCs degradation status, through functionalized LaF$_3$: (Au nanoparticle) thin films (~60 nm). The sensor’s exceptional specificity/sensitivity has been achieved in real-time at a sub 10 ppb level, optimized through spin-coating deposition and post-annealing process. Its multimodal readout has been achieved and studied through the characterizations of open circuit potential, cyclic voltammetry, chronoamperometry, and differential pulse voltammetry revealing a consistent linear decrease of 15.7 mA cm$^{-2}$ at 0 ppb to 10.2 mA cm$^{-2}$, while also maintaining its low-cost, small size, and robustness.

© 2022 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI:10.1149/2754-2726/ac8aa8]

Manuscript submitted August 4, 2022; revised manuscript received August 12, 2022. Published September 5, 2022.

There has been an increasing demand for renewable energy technology in almost every sector, and with the dawn of electric vehicles, an especially large demand in the transportation industry.1 Proton Exchange Membrane Fuel Cells (PEMFCs) address this demand through oxygen and hydrogen electrochemical reactions by supplying a renewable, zero-emission fuel source alternative to the traditional combustion engine. One of the limiting factors to the performance of the PEMFC is the Nafion® membrane, which is subjected to a radical attack that causes irreparable electro-mechanical damage in degradation.2 These radicals result from oxygen reduction at high potentials when the oxygen molecules bind with the platinum catalyst and migrate to the membrane.3 The radical attack causes polymer chain scission and irreversible reaction. It results in the global and local thinning of the ionomer, followed by producing fluorinated and sulfated degradation materials into reactant outlet streams. Synchronous fluorinated and sulfated degradation products will be accumulated into reactant outlet streams. Radical attack diminishes the performance and stability of membrane electrode assembly (MEA). The chemical degradation will increase the flow rate of the relevant fluorinated degradation products. The concentrations are enhanced at elevated temperatures and lower humidity conditions. The byproduct fluoride and sulfate anions emission rates can be drawn as the signature of the PEMFC degradations.

To accurately depict the membrane’s degradation, the fluoride ions of the effluent water released from the Nafion® membrane can be selected as Nafion®-based PEMFCs degradation signature. Capturing fluoride ions and translating their concentration as an electrical signal can be obtained through highly fluoride-selective sensing membranes. Creating highly sensitive electrodes can be achieved through functionalization and optimization of the sensing area; its diagnostic application in the fuel cell electrical vehicle sector is to be able to effectively predict the remaining lifespan of the fuel cell membrane as supposed to the current, potentially wasteful, means of getting the membrane changed of a vehicle. However, at present, vehicle companies suggest drivers replace their PEMFC membrane after a certain mileage and driving hours have been achieved,4 which can be wasteful as potentially healthy membranes can be replaced- or even dangerous if a PEMFC membrane has had more damage than what is projected due to operations at extreme environmental conditions.

Ion-sensitive capacitive electrochemical sensors have been promising microsensors due to their efficient functionality, low cost, small size, robustness, and applications for continuous real-time monitoring. Leveraging on the development and evolution of sensor technologies, we have developed microsensors providing the possibilities for integrating at the cathode and anode exhaust for monitoring the PEMFC degrading status. Degradation with a certain signature can be captured and represented multimodally through various electrochemical models. The leading degradation signature for Nafion®-based PEMFCs is the emission of fluoride anions (F$^-$) which is output along with the effluent water.5 The F$^-$ concentration has been drawn as a signature to depict the membrane’s degradation accurately. Capturing fluoride and translating its concentration as an electrical signal has been obtained through highly fluoride-selective membranes. We will use fluoride emission as a diagnostic model in this work. Highly fluoride-sensitive membranes (LaF$_3$) will be introduced into a thin layer of sensing membrane for microsensors. The functionalization of the sensing membrane varies the selectivity/sensitivity of microsensors. It gives a complementary approach to existing PEMFC characterization and diagnostics techniques. Currently, there are other tools for sensing fluoride anions in a solution, but almost none are viable as an integrated solution for detecting the fluoride emission rate (FER) in PEMFCs. These other tools are more delicate, costly, and less sensitive. Most are also of larger dimensions and with poor portability. The Hanna Instruments fluoride combination ion selective electrode (FISE) [Model# HH4110] is employed to establish a baseline and a sensitivity reference point to validate the sensing performance in this work. FISE effectively detects fluoride ions to 20 ppb and requires setup, maintenance, and specific storage parameters, making it a less viable integrated diagnostics option for PEMFCs. The long-term goal is to develop microsensors for continuous real-time monitoring of the...
byproducts and thus membrane loss of PEMFC. The relevance of the F\(^{-}\) and PEMFC degradation has been studied based on the anion concentration measurement to quantify the PEMFC degradation rate. The anions separated from degrading ionomer are focused on fluorinated groups. Signatures are drawn as FER. FER is commonly used to calculate PEMFC membrane loss. The loss can be quantified with FERs considering the initial weight % of the fluoride in the ionomer. Membrane thickness loss is studied with the loss value (g cm\(^{-2}\)) and ionomer density. It can be estimated by the summation of FERs measured over time.\(^6\)

\[
\text{FER} = \frac{\text{measured (ppm)} \times \text{amount collected (ml)}}{\text{duration of collection (h)} \times \text{active area (cm}^2\text{)}}
\]

\[
\text{ionomer mass loss (g/cm}^2\text{)} = \frac{0.6 \times \text{weight % of F}^- \text{in Ionomer}}{\text{ionomer mass loss}}
\]

\[
\text{ionomer thickness loss (cm)} = \text{fluoride emission} \times 1.96, \text{Ionomer density}
\]

In this work, led by the unifying goal of detecting F\(^{-}\), the sensor development process evolved conceptually and physically throughout the investigation. LaF\(_3\) was chosen to comprise the membrane, given the electrochemical interaction between the chosen electrolyte, analyte, and the F\(^{-}\) sensor. The compound is optimized with the preferred orientation (002), as it can provide increased surface sites and available pathways for conductive charge transfer.\(^7\) It leads to the likelihood for F\(^{-}\) in the analyte to bind at the interface and form a double-layer capacitive response. The investigation focuses on gold screen printed electrodes (SPE), considering the conductivity and ability to be manipulated as pleased for electrochemical responses. The gold working electrode functionality has called for adjustments to subsequent fabrication procedures, such as solution application and annealing. Within the actual experimentation process, chemical ratios and parameters were fine-tuned for electrochemical sensing response. Multimodal readout single entity electrochemical sensor has been investigated based on OCP, CV, CA, and DPA response. The sensing output is consistent and reproducible. Linearized calibration curves with up to 99% coefficient are obtained at ppb and ppm ranges, respectively. The detection of the limit can reach the sub-10 ppb level. The correlation of sensor development and fuel cell energy storage provides a specific efficient diagnostics tool for probing the degradation for fundamental research and real-world applications.

**Materials and Experimental Procedures**

The fluoride-specific sensors’ fabrication process comprises four main steps: deep eutectic solvent (DES)/LaF\(_3\)(Au nanoparticles NPs) solution preparation, spin-coating, and post-annealing. Au NPs were added to the DES prior to application to ceramic substrates. Au NPs of 30 nm diameters were added to the LaF\(_3\) DES due to their high specific areas.

**Deep eutectic solvent (DES)/LaF\(_3\)(Au nanoparticles) precursor solution preparation.**—Deep eutectic solvent (DES) is used to dissolve lanthanum fluoride powder for even application to substrates. The addition of Au nanoparticles (NP) to the DES/LaF\(_3\) solution prior to application to the substrate. Mix 2 ml (2.194 g) of ethylene glycol [(CH\(_2\)OH)\(_2\), 99.0%, Sigma Aldrich] and 2.747 g of choline chloride [HOC\(_3\)H\(_2\)(CH\(_3\))\(_2\)Cl, 99.0%, Sigma Aldrich]. Stir the solution at a speed of 500 rpm for 90 min at a temperature of 85 °C. After 90 min of constant stirring, 4.476 ml of a semi-transparent and slightly viscous solution should be obtained. Add 0.5621 g of LaF\(_3\) [LaF\(_3\), 99.99%, Sigma Aldrich] to the solution to achieve a 0.6 mol ratio of LaF\(_3\) to ethylene glycol and choline chloride solution. Stir at 60 °C at a speed of 1000 rpm for 1 h. After 1 h, add one drop of Tx-101 surfactant [Sigma Aldrich] and stir for an additional 15 min. Allow the solution to cool to room temperature, and then filter the solution with 1 ml of diluted water and filter paper. Finally, add 0.746 ml of Au NP solution [30 nm diameter Au NP in citrate buffer, Sigma-Aldrich] to the DES/LaF\(_3\) solution and stir until evenly mixed.

**Spin coating.**—Five coatings of the DES/LaF\(_3\) or DES/LaF\(_3\)(Au NP) precursor solution were applied to the substrate via spin coating. After placing the gold SPE substrate onto the spin coater chuck, cover the substrate entirely with DES/LaF\(_3\)(Au NP) solution using a disposable pipette. Spin coat in two steps using the following parameters: (i) using 1000 RPM speed, the ramp of 500 rpm s\(^{-1}\), duration of 10 s, (ii) using 1500 RPM speed, the ramp of 500 RPM s\(^{-1}\), duration of the 30 s. Carefully remove the substrate from the spin coater, remove the tape with tweezers, and anneal for 30 min at 120 °C. Once the sample cools, repeat the same spin coating and 30-minute annealing process. After the second 30-minute annealing, spin coat the sample a third time.

**Post annealing.**—After spin coating the sample three times and performing two 30-minute annealing cycles, the sample is ready for post-annealing. Anneal the sample using the parameters as specified in Table I.

The annealing process was shaped throughout our investigation. The purpose of reaching high temperatures through annealing was to obtain the preferred orientation (002) of LaF\(_3\), and the selection is gradually enhanced with temperature.\(^8\) Thus, the maximum temperatures of 1000 °C for LaF\(_3\) coated on gold SPE during annealing were explored.

**Ferri-ferro solution preparation.**—200 ml of phosphate-buffered saline (pH 7.4) [Cl\(_3\)H\(_2\)K\(_2\)Na, Gibco], 1.6463 g of potassium ferricyanide powder [K\(_4\)[Fe(CN)\(_6\)], Sigma-Aldrich], and 2.11 g of potassium ferrocyanide powder [K\(_3\)[Fe(CN)\(_6\)], Sigma-Aldrich] were mixed in a beaker. The final solution obtained was bright yellow and transparent.

**Electrochemical characterization.**—Electrochemical Characterization of the sensor samples was conducted utilizing 3-electrode open circuit potential (OCP), cyclic voltammetry (CV), chronoamperometry (CA), and differential pulse voltammetry (DPV) scan. The scans were all performed with a CH Electrochemical Analyzer (Model number: CHI1200B) in a K\(_3\)[Fe(CN)\(_6\)]/K\(_4\)[Fe(CN)\(_6\)]/Phosphate-buffered saline analyte solution, commonly referred to as “Ferri-Ferro.” All scans utilized the functionalized electrode as the working electrode, a commercial Ag/AgCl reference electrode [Model CHI111, CH Instruments, Inc.], and a commercial Platinum wire counter electrode [Model CHI115, CH Instruments, Inc.]. Wearing latex gloves, the beaker,
reference electrode, and counter electrode were all rinsed with DI water and dried with a nitrogen gun. The beaker was filled with 50 ml of Ferri-Ferro analyte solution, and the Platinum wire counter and Ag/AgCl reference electrodes were attached to the corresponding wires of the Electrochemical Analyzer. The gold SPE provides a 0.0314 cm² active area with a 2 mm diameter. The functionalized electrode was attached to the appropriate wire of the Electrochemical Analyzer with the alligator clip. The functionalized electrode was handled with tweezers by the uncoated top area and attached to the electrochemical analyzer wire by the uncoated sensor area. All three electrodes were immersed in the Ferri-Ferro.

Open circuit potential (OCP).—Run time was set to 1000 s to allow for complete stabilization. NaF standard was added to achieve 5 ppm, 10 ppm, 15 ppm, and 20 ppm concentrations of F⁻ ions in the Ferri-Ferro analyte solution. Each addition of F⁻ ions was performed in the 30 s after the previous scan to allow time for the analyte to reach equilibrium. As F⁻ ions were added, a decrease in OCP was recorded. Once every addition was completed, the test was aborted 30 s immediately after the final addition to allow for automatic scaling.

Cyclic voltammetry (CV).—Following the same preparation procedures, sample intervals were set to record every 0.1 s. A control CV scan was performed in the Ferri-Ferro analyte with no fluoride ions. The following scans were performed in Ferri-Ferro with different concentrations of added F⁻ ions. F⁻ standard solution was added to achieve 10 ppb to 200 ppm concentrations of F⁻ ions in the Ferri-Ferro analyte. Each addition of NaF was performed in the 30 s after the previous scan to allow time for the analyte to reach equilibrium. As F⁻ ions were added, a decrease in current density was recorded.

Chronoamperometry (CA).—Following the same preparation procedures, the first CA of each sample was performed after having optimized the CV potential window. Using the CHI software, the parameters of # of steps (2), pulse width (80), sample interval (0.0025), quiet time (2), sensitivity (0.01), and initial charge (positive) were held constant for every test. The initial/low/high voltage parameters changed between samples, represented by the anodic and cathodic peaks of the respective CV graph, between samples. With each addition of F⁻, the CA was run directly after the CV finished. Thus, CA tests experienced the exact same concentrations of F⁻ per scan as their corresponding CV test; doing so eliminated the potential for extraneous variables to hinder the CV-CA relationship.

Differential pulse voltammetry (DPV).—Following the same preparation procedures described, set the experimental parameters, which are as follows: Initial E(V) = −0.3. Final E(V) = 0.9. Incr E (V) = 0.01. Amplitude (V) = 0.05. Pulse Width (sec) = 0.01. Sample Width (sec) = 0.01. Sample Width (sec) = 0.005. Pulse Period (sec) = 0.1 Quiet Time (sec) = 2. Sensitivity (A/V) = 0.001. With parameters set, prepare F⁻ standard solution to achieve 10 ppb to 200 ppm concentrations of F⁻ ions. The experiment started recording the control data without adding the F⁻ standard. Following the control, add F⁻ to achieve various concentrations and repeat steps to record data.

Results and Discussion

Electrochemical sensor development for fuel cell membrane diagnostics.—Figure 1 visualizes the development process of F⁻ electrochemical sensors from precursor solution preparation, spin coating to post-annealing, and anion detection. The detailed parameters are specified in the experimental section. The fabricated electrochemical sensor targets the specific Naion-based PEMFC degradation. The chemical and mechanical degradation causes the membrane breakdown and F⁻ release. Variations in ionic concentration result in a change in the electrochemical signal. The passivation layer ion-sensitive membrane (ISM) functions as the sensing area and determines the specificity and selectivity of the sensor. The site binding model has been proposed at the interface of the sensor layer and the fuel cell effluent water in Fig. 1.
double layer exists at the interface. It refers to a Stern inner layer and a diffuse layer. The inner layer comprises the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP). The microsensor development brings opportunities for integration with fuel cell vehicles for real-time specific diagnostics.

Open circuit potential continuous monitoring.—Figure 2 shows the open circuit potential of a LaF3 coated electrode in response to the serial addition of fluoride standard to Ferri-Ferro. The starting potential \( E^0 \), was recorded to be 191.6 mV. Each increment in F-concentration led to a linear decrease of approx. 1.05 mV in potential. The mean linear change in potential \(-1.025 \text{ mV/5 ppm} \) in tandem with \( E^0 \) can be further extrapolated to obtain this fluoride sensor’s equivalent equation. The Nernst equation was manipulated to characterize the potentiometric behavior of the fluoride sensor.  

\[
E = E^0 + \frac{RT}{F} \ln(Q)
\]

is the general form of the Nernst equation. \( F \) is the ionic charge of the stock added to the analyte. Since the sample is responsive to fluoride, the ionic charge is \(-1 \), leading to an inversion in sensing behavior. \( Q \) is the sensing quotient manipulated to follow the concentration, \( C \). The natural log is multiplied by \( 2.303 \), which is the conversion factor to \( \log \). After manipulating the Nernst equation, 

\[
E = E^0 - \frac{2.303RT}{F} \log(C)
\]

is obtained. In the case of this sample, \( \frac{2.303RT}{F} \) is 10.5 mV. The sensitivity of this sample can be abstracted to a 10.25 mV per log(C) increase. 

\[
E = 191.6 \text{ mV} - (10.5 \text{ mV}) \log(C)
\]

closely represents the potential results obtained. This potentiometric response can be abstracted as overall sensitivity to the ion. The figure demonstrates that LaF3 leads to stabilization in OCP after a fast response time. One factor that leads to this is the stronger chemo-physi adsorption of the analyte to the membrane. Once F\(^-\) is introduced to the analyte, the ions immediately adsorb onto the LaF3 membrane. Since F\(^-\) has a negative charge, the membrane interface becomes negatively charged and thus repels the negatively charged \([\text{Fe(CN)}_6]^{4-}\). The figure also outlines that the electrical characteristics of the sensor are reproducible.

Electrochemical cyclic voltammetric calibration.—The electrochemical technique CV measures current response as a function of linearly cycled potential sweeps, revealing the reaction’s reduction-oxidation properties in the chemical cell. As voltage positively increases, the electrolyte solution \( K_\text{Fe(CN)}_6/\text{K}_4\text{Fe(CN)}_6 \) reaches the oxidation potential, the current rapidly increases, maximizes at the anodic peak, & then decreases as the oxidant depletes. A mirror trend is visible as the reduction process occurs, showing a cathodic peak of comparable magnitude in an opposite current direction. Once the scan is completed, a conventional CV pattern typical for a battery like an ion diffusion controlled behavior forms, enabling the recognition of the difference in current response within the cell. The presence of membrane-degraded fluorinated emissions is imitated by adding increasing F\(^-\) concentrations at ppb and ppm ranges. The functionalized LaF3 membrane coated at the working electrode selectively interacts with added F\(^-\) ions; due to the structure of LaF3’s preferred orientation 002, molecular channels house the introduced F\(^-\), creating a negative charge repelling the following anions in the electrolyte, i.e., \([\text{Fe(CN)}_6]^{3-}\), \([\text{Fe(CN)}_6]^{4-}\). As F\(^-\) accumulates at the interface, a double layer capacitive response forms, blocking redox interaction and preventing charge transfer of \([\text{Fe(CN)}_6]^{3-}\) and \([\text{Fe(CN)}_6]^{4-}\). Thus, the sharp decrease in anodic and cathodic peaks visible in Fig. 3 from 9.74 mA cm\(^{-2}\) at 0 ppb to 7 mA cm\(^{-2}\) at 200 ppm is attributed to an inverse relationship between current amplitude and F\(^-\) concentration. Illustrating the calibration curve of a functionalized gold SPE, Fig. 3c reveals a coefficient of determination value \( R^2 \) of 0.99 concerning anodic peak current. Since the value of \( R^2 \) nears 1, the sensing performance through CV proves reliable F\(^-\) detection up to 10 ppb level. The sensor with coats of mere LaF3 has indicated a decrease in peak current density. As a result, the determination of F\(^-\) in waste-water of fuel cells is obtained with an efficient electrochemical response.

Moreover, we have investigated the electrochemical sensor response at ultra-low concentrations at 0, 10, 20, 30, 40, 50, and 60 ppb in Fig. 4a. Consistent characteristics further confirm the reliability and reproducibility of the developed microsensors for F\(^-\) detection. By extracting the CV peak current, a good linear relation has also been demonstrated in the sensor calibration curve in Fig. 4b.

Electrochemical differential pulse voltammetric calibration.—CA is an amperometric test that measures a cell’s current as a function of time and seeks to validate the CV response. It applies a constant square voltage, taken from the potential values at which oxidation and reduction happened in the CV over a set time. The potential step perturbation diffuses the active species to the working electrode’s surface concerning the Cottrell equation, 

\[
\frac{E}{\sqrt{t}} = \frac{4}{\sqrt{\pi N}} nFAD_{\text{ion}} \sqrt{t}
\]

generating a current \( I \), where \( F \) is Faraday’s Constant (96,485 C mol\(^{-1}\)), \( A \) is the working electrode’s area, \( D \) is the diffusion constant, \( n \) is the number of electrons being transferred, and \( C_0 \) is the analyte’s initial concentration. The CA ran for the 80 s for each concentration, initializing the first step to correspond with the forward scan peak potential (held at 0.131 V) and the second step corresponding to the CV reverse-scan peak potential (held at 0.275 V), allowing time for the current to stabilize. As evident in Fig. 5, as a constant voltage is applied to each step, the reaction begins to decay and slowly completes. Consistent with the CV test, we simulated fuel cell fluorinated effluent activity by introducing increasing F\(^-\) concentrations and running the CA test at each level using optimized constant parameters. The LaF3 membrane’s sensing capabilities function in CA correspondingly to CV, repelling and rejecting Fe(CN)\(_6\)\(^{3-}\) and Fe(CN)\(_6\)\(^{4-}\) after accumulation at the interface. Figure 5b linearizes this by plotting the integral of current, namely, charge versus time, showing a reduction of 2.7 mC at 0 ppb to 0.96 mC at 50 ppm. The charge signal decreases linearly in response to F\(^-\) concentration, suggesting sensitivity variations at ppb and ppm levels.

Electrochemical differential pulse voltammetric calibration.—Figure 6 Shows the differential pulse voltammetry (DPV) results of the sample with an increasing concentration of F\(^-\). DPV is a technique that minimizes the capacitive current associated with ion adsorption on the surface of the electrode. This is due to the differential nature of this characterization technique. DPVs operate by recording the difference in the current before and after applying a small step in potential. In between the time of recording the current pre-step and post-step, the rapid decaying nature of capacitive current leads to a significant decrease in capacitive current. Due to this, the diffusive nature of the sample, led by faradaic current, can
be more thoroughly investigated using DPV. Figure 6 shows a consistent decrease in response to the increase in F⁻ concentration. The peak shows two different linearized behaviors depending on the concentration range. Concentrations in the ppb range have a different linearized slope than the ppm range due to the concentration towards the ppb range approaching the limit of detection of the sensor. Consistent with the CV, the DPV shows a decreasing trend in response to the addition of F⁻ in which the current density magnitude decreases. This trend is due to the consistency of capacitive current and faradaic current. F⁻ is likely to cause a decrease in diffusive activity, leading to a decrease in faradaic current and a decrease in DPV peak current density.
The multimodal output of the developed electrochemical sensor has been successfully demonstrated with OCP, CV, CA, and DPA signals. Consistency in the electrical signal with the $\text{F}^-$ concentration increase has been shown. After all the electrochemical calibration measurements at various concentrations of $\text{F}^-$ ions, re-test experiments have been conducted to investigate the stability and repeatability of the sensor.
The electrochemical sensor has been tested in the absence of $F^-$ ions. The CV and DPV results are overlayed at the initial and final states, respectively. A highly overlapping behavior has been observed in Fig. 7, which confirms the excellent stability of the sensor.\textsuperscript{14}

**Conclusions**

After a thorough investigation of $F^-$ detection with multi-readout of the developed electrochemical sensor based on OCP, CV, CA, and DPV characterizations, a consistent sensing response at ppb and ppm levels has been achieved. The OCP data shows real-time continuous monitoring capability, revealing that LaF$_3$ causes enhanced voltage stabilization over time as $F^-$ is introduced into the system. Complementary to the potentiometric technique, the amperometric CV and CA validate the results by showing a consistent sensing response, revealing a linear decrease in peak current density and accumulated charges, respectively. The decrease in current density is due to capacitive behavior at the interface of LaF$_3$/Ferri-Ferro. It is also found the functionalization with LaF$_3$ films yields a significant linear decrease in the Faradaic current from 15.7 mA cm$^{-2}$ at 0 ppb to 10.2 mA cm$^{-2}$ at 200 ppm in the DPV technique. Compactly, a multimodal output sensor capable of paving the way for cost-efficient, real-time monitoring and diagnosing fuel cell membrane degradation will accelerate the mass deployment of PEMFC technology in an easier and safer approach. The implications of such progress will reshape the future automotive industry, lowering total greenhouse gas emissions and propelling the usage of eco-friendly vehicles worldwide.

**Acknowledgments**

DOE-M2FCT supports this work under AWD00000013872 (LBNL No. 7621351). DOE-NNSA also supports this work funded under the minority-serving institutional partnership program (MSIPP) Advanced Sensors Technologies for Applications in Electrical Engineering-Research and Innovation eXcellence Consortium (ASTERIX) under Award NA0003981.

**ORCID**

Tinsley Benhaddouch \(\text{https://orcid.org/0000-0002-0967-690X}\)
Dongmei Dong \(\text{https://orcid.org/0000-0002-0626-5611}\)

**References**

1. D. Grieshaber, R. MacKenzie, J. Vörös, and E. Reimhult, \textit{Infomat.}, 8, 1400 (2008).
2. J. Zhang, G. Jiang, T. Cumberland, P. Xu, Y. Wu, S. Delaai, A. Yu, and Z. Chen, \textit{Infomat.}, 1, 234 (2019).
3. O. Lynduk, S. Kalmina, and V. Buchyk, \textit{Polityka Energetyczna-Energy Policy Journal.}, 23, 141 (2020).
4. A. Spears, T. Rockward, R. Mukundan, and F. H. Garzon, \textit{ECS Trans.}, 98, 407 (2020).
5. A. Spears, T. Rockward, R. Mukundan, and FH Garzon, \textit{ECS Trans.}, 92, 467 (2019).
6. N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart, and J. L. Dempsey, \textit{J. Chem. Educ.}, 95, 197 (2018).
7. H. Cho, K. Kim, M. Meyyappan, and C. K. Baek, \textit{Sensors and Actuators B: Chem.}, 279, 183 (2019).
8. F. Yan, X. Ma, Q. Jin, Y. Tong, H. Tang, X. Lin, and J. Liu, \textit{Microchim. Acta}, 187, 1 (2020).
9. R. P. Ramasamy, Z. Ren, M. M. Mench, and J. M. Regan, \textit{Biotecnol. Bioengineering}, 101, 101 (2005).
10. A. J. Spears, T. Rockward, R. Mukundan, and F Garzon, \textit{J. Electrochem. Soc.}, 168, 064503 (2021).
11. M. H. Rahman, S. Ahmmed, S. Tabassum, and A. B. Ismail, \textit{AIP Adv.}, 11, 035010 (2021).
12. P. Manickam, S. K. Pasha, S. A. Snipes, and S. Bhansali, \textit{J. Electrochem Soc.}, 164, B54 (2016).
13. Honda, \textit{Honda Clarity Fuel Cell: Owner’s Manual} (American Honda Motor Company, Torrance, California) (2020).
14. P. Bergveld, \textit{Sensors and Actuators B: Chem.}, 88, 1 (2003).