Operando Raman Micro-Spectroscopy of Polymer Electrolyte Fuel Cells

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Operando Raman micro-spectroscopy of the membrane electrode assembly (MEA) of a fully operating hydrogen/oxygen Nafion electrolyte fuel cell is described. Coarse depth profiling of the fuel cell system enabled appropriate positioning of the micro-spectroscopy laser focal point for MEA catalytic layer spectroscopy. An increase in the ionomer state-of-hydration, from oxygen reduction at the cathode, transitions ion exchange sites from the sulfonic acid to the dissociated sulfonate form. Visualization of density functional theory calculated normal mode eigenvectors assignments enabled assignments of Nafion side-chain vibrational bands in terms of the exchange site local symmetry: C1 and C3V modes correlate to the sulfonic acid and sulfonate forms respectively. The gradual transition of the MEA spectra from C1 to C3V modes, from the fuel cell open circuit voltage to the short circuit current respectively, demonstrate the utility of vibrational group mode assignments in terms of exchange site local symmetry.

Molecular modeling calculations.—Unrestricted DFT37 with the X3LYP38 functional was used for geometry optimizations and normal mode frequency calculations of (a) hydrated Nafion-[H], (b) dehydrated Nafion-[H]-, (c) 2-trifluoroethoxy-perfluoroethane-2-sulfonate (TPSd), (d) 2-trifluoroethoxy-perfluoroethane-2-sulfonic acid (TPSH), (e) triflate, (f) triflic acid, and (g) difluoromethyl ether (DTFME) (Fig. 2). The X3LYP is an extension to the B3LYP39 functional providing more accurate heats of formation. Jaguar 8.7 (Schrödinger Inc., Portland, OR) was used with the all-electron 6-311G** basis set (Pople triple-ζ basis set (*** and *++ denote polarization37 and diffuse40 basis set functions, respectively). Output files were converted to vibrational mode animations using the Maestro graphical user interface (Schrödinger Inc., New York, NY). Calculations were carried out on the high performance computing cluster at the University of Texas Rio Grande Valley with 72 nodes of Dual 2.67 GHz processors; each node with 48 GB RAM and 250 GB disk. DFT calculated normal mode peaks are denoted by superscript (∗) (e.g., 983 cm⁻¹). Only normal modes with normalized intensity above 1% of the largest peak were selected for Maestro animation viewing.

Non-PGM catalyst preparation.—Non-platinum group (non-PGM) catalysts were prepared and provided by Barton, et al.41 Briefly, in their preparative method, Ketjen black 600JD (Alfa Aesar, Ward Hill, MA) and melamine (6.3 wt% N) (Alfa Aesar) were heat treated at 800 °C. These catalysts were used as received.
MEAs were prepared by immersing sheets in boiling 8 M nitric acid followed by two hours in boiling NanopureTM water. Catalyst inks were prepared by diluting the catalyst in 5 wt% Nafion ionomer solution (Sigma Aldrich, Milwaukee, WI), water, and isopropyl alcohol (Sigma Aldrich). 4 mg/cm² Pt black (Johnson Matthey, London, UK) and 1.6 mg/cm² non-PGM catalyst were used as the anode and cathode catalysts, respectively. Catalyst inks were applied to a 5 cm² area of a sheet of Nafion 117 (E. I. DuPont) immobilized on a heated vacuum table (NuVant Systems, Inc., Crown Point, IN). Toray carbon paper (200 μm) was used for the gas diffusion layers. MEAs were initially conditioned by cycling the potential from 200–800 mV in the operando Raman cell operating at 50°C with humidified H₂ (50 sccm) and O₂ (200 sccm) flowing over the anode and cathode, respectively.

Cell design.—The operando Raman fuel cell design (Fig. 3) is a modification of the operando IR-XAS cell described by Lewis et al.21 Briefly, the upper flow field connects to the working electrode and contains an aperture that accommodates a GE 124 fused quartz window (General Electric). The lower flow field connects to the counter/reference electrode to which humidified hydrogen is delivered. The counter and reference electrodes of the EZstat Pro potentiostat/galvanostat (NuVant Systems Inc., Crown Point, IN 46307) are shorted together and connected to the counter/reference electrode. The cell is connected to a gas manifold that delivers the reactant feeds to the anode and cathode graphite flow fields. The cell is equipped with heater elements and a thermistor for temperature control. A DB9 connector interfaces the EZstat Pro to the operando cell. The cell is positioned at the working distance of the microscope objective (Fig. 3).

Operando Raman spectroscopy.—All operando Raman spectra were acquired using a WITec Inc. (Ulm, Germany) Confocal Raman Microscope (CRM 200). A 488 nm (23 mW) solid state laser (WITec Inc.) was used as the excitation source, which was coupled into a Zeiss (Thornwood, NY) microscope via a 50 μm wavelength-specific single-mode optical fiber. The incident laser beam was focused onto the sample using a Nikon (Tokyo, Japan) Fluor (10x/0.25, WD: 7.00 mm) objective with a z resolution of 23 μm and confocal volume of 33 μm³. The Raman backscattered radiation was focused through a holographic notch filter, onto a 50 μm multimode optical fiber, and into a 300 mm focal length monochromator (600/mm grating, blazed at 500 nm). The Raman spectrum was detected via a back-illuminated, deep-depletion CCD camera (1024 × 128 pixels) operating at −82°C. Single Raman spectra were acquired for 30s, except that spectra of the Fe based catalyst under O₂ conditions were obtained with a 30 second acquisition time and a hardware accumulation of 2s. Confocal microscope depth profiling was performed with a step size of 50 μm. Because the confocal volume of the 10x objective is 33 μm³, spectra are correlated to overlapping layers of the assembly structure as shown in the Results section.

Prior to obtaining spectra, the cell potential was cycled from 0 to 1200 mV at 50°C with humidified H₂ (50 sccm) and N₂ (200 sccm) fed to the counter/reference and working electrodes, respectively. The working electrode reactant feed was then switched to humidified O₂ (200 sccm). Raman spectra were obtained between 100 mV and 0 mV and collected in decreasing 100 mV increments. The fuel cell anode was used as the reference electrode by shorting the counter and reference electrodes of the potentiostat (EZstat Pro, NuVant Systems, Crown Point, IN 46307) as described by Gurau et al.42

Results

Location of optimal focal point for study of catalytic layer.—Our interest in cathode catalytic layer processes within the operando cell required determination of the optimal position of the Raman microscope laser beam focal point. Figure 4 shows a cross sectional
Figure 3. Left: Exploded view of the operando Raman cell. (1) Top plate, (2) Upper flow field, (3) Membrane electrode assembly, (4) Lower flow field, (5) Assembly gasket, and (6) Assembly stage. Right: Operando Raman cell in position for confocal Raman microscopy.

Figure 4. Left: Schematic of MEA installed in the operando spectroscopy fuel cell. Right: Confocal Raman microscope depth profiling spectra of Fe-Nx/C cathode with humidified O2 flow.

schematic of the MEA loaded into the operando cell (Fig. 4, left). The microscope focal point was varied along the z-axis until the Nafton spectrum attained a maximum intensity (black spectrum). This is the “reference” position for additional spectra obtained as the focal point was sequentially lifted above the reference (Fig. 4, right). This is “device” depth profiling over four complex regions (membrane, catalytic layer, gas diffusion layer and graphite flow field region). The Nafton membrane is a $\sim 178 \, \mu m$ condensed phase that, within the torques applied to fuel cell (35 in-lbs /8 bolts: 4 in. on edge flow field blocks), is incompressible. The nevertheless complex optics for membrane(s) layers is discussed by Peng et al.$^{31}$ The catalytic layer is a $\sim 10 \, \mu m$ porous composite layer with optical characteristics that substantially vary with electrode potential.$^{22}$ The gas diffusion layer is a $\sim 200 \, \mu m$ porous carbon paper that is homogenous over a length scale of microns. The final layer is a dense graphite layer with millimeter flow field grooves and an aperture to fit a quartz window.

The focal point position (or depth) cannot be directly correlated to a position within the fuel cell assembly. The $z$ resolution of 23 $\mu m$ and confocal volume of 33 $\mu m^3$, compounded by the physical characteristics of the different layers (e.g., thickness, diffraction, scattering, etc.) add to Raman signal distortion.$^{31,34}$ Each focal point location (Fig. 4, Right) yields signal over a bracketed region of the fuel cell assembly. Fortunately, bracketed regions can be calibrated by knowledge of the nominal compositions of the device regions (e.g., pure polymer regions, carbon support, gaseous dioxygen, etc.). Gaseous dioxygen is not observable within the incompressible membrane. At a focal point of $+150 \, \mu m$ (from the reference position), a dioxygen peak emerges at 1556 cm$^{-1}$. Gaseous oxygen resides in the porous cathode layer, the gas diffusion layer and in the flow field. The oxygen band is not observed within the Nafton membrane region with detection limits of 1000 ppm.$^{31-33,36}$

Peaks related to the carbon support in the catalytic layer start to emerge at $+100 \, \mu m$ with no attenuation of the Nafton peaks. The two prominent features of the graphite are the E$_{2g}$ vibration mode at 1600 cm$^{-1}$ and disorder peak (D peak) at 1360 cm$^{-1}$. The D peak, which arises from an A$_{1g}$ breathing mode, is observed at the edges of graphene planes on clusters smaller than 200 Å.$^{46}$ The catalytic layer is rendered ionically conductive by Nafton ionomer originating from the catalyst ink.$^{3}$

Our objectives required that we select the highest focal point available that exhibited dioxygen peaks simultaneously with Nafton peaks. Based on Figure 4 (Right), we selected $+350 \, \mu m$ above the reference.

Potential-dependent Raman bands.—The polarization curve, obtained with the focal point set at $+350 \, \mu m$ from the reference, (Fig. 5) shows a current onset at 750 mV (a striking 20-fold improvement over carbon with no iron-based catalyst).$^{47}$ At cathode potentials positive of 800 mV (Fig. 6) there is no current and thus no oxygen reduction reaction (ORR). Figure 6 compares potential-dependent Raman spectra of $+150 \, \mu m$ (from the reference position), a dioxygen peak emerges at 1556 cm$^{-1}$. Gaseous oxygen resides in the porous cathode layer, the gas diffusion layer and in the flow field. The oxygen band is not observed within the Nafton membrane region with detection limits of 1000 ppm.$^{31-33,36}$

*The expected solubility of oxygen within the membrane (50°C and $\sim 30$ water molecules/exchange site) is 8.9 ppm.*
Figure 5. Polarization curve obtained in the operando spectroscopy fuel cell. Pt anode (humidified H2); Fe-Nx/C cathode (humidified O2).

At potentials negative of 700 mV, Raman bands at 1066 cm\(^{-1}\) and 969 cm\(^{-1}\) emerge. These bands, also observed in the hydrated Nafion (red) IR spectrum, are the \(C_{1V, HF}\) and \(C_{1V, LF}\) group modes respectively. These group modes are consequent of a dissociated Nafion exchange site (sulfonate form) with \(C_{1V}\) local symmetry.\(^{22,48,51–55}\)

\(C_{1}\) normal mode eigenvector animation snapshots.—The dehydrated Nafion spectrum (blue) features bands at 1414 cm\(^{-1}\) and 910 cm\(^{-1}\). These are group modes that have motional participation of the exchange group in the sulfonic acid form (\(C_{1}\) local symmetry). Eigenvector animation extrema screenshots (Fig. 7, top panels) provide details of the vibrational motions with the dominant motions within solid circles and secondary contributions within dotted circles. These high and low frequency bands (\(C_{1, HF}\) and \(C_{1, LF}\), respectively) correspond to group modes that involve the side-chain functional group contributions (e.g., COC-A, -CF\(_3\), exchange site, etc.). The \(C_{1, HF}\) and \(C_{1, LF}\) group modes are both dominated by sulfonic acid stretching (asymmetric and symmetric, respectively) with secondary contributions from COC-A stretching (asymmetric and symmetric, respectively). The lower panels show eigenvector extrema snapshots of molecules that make up the pure modes contributing to the \(C_{1}\) group modes, along with associated calculated normal mode frequencies. The mirrored similarities of dehydrated Nafion group modes and side chain pure modes is evident (Fig. 7). Comparison of the pure modes (bottom panels) with the calculated normal modes (top panels) correctly show that the pure mode frequencies contributing to the \(C_{1, LF}\) are on average substantially higher than the pure modes contributing to the \(C_{1, HF}\), in support of the assignments. The relationships between the pure modes and the calculated normal modes (actually group modes) are more explicit by visualization of the video animations (Supplemental Material (Figs. S6, 8, 11–12, 14–17). A similar analysis for \(C_{1V}\) peaks that emerge as the fuel cell potential is decreased follows. All of the assignments are summarized in Table I.

Figure 6. Left: Potential dependent Raman spectra of Fe-Nx/C cathode catalyst with O\(_2\) at cathode; H\(_2\) at the anode. Right: Transmission spectra of Nafion 212. Fully dehydrated (top), partially dehydrated (middle) and fully hydrated (bottom). Group theory labels refer to exchange site local symmetry.
**C3V normal mode eigenvector animation snapshots.**—The fully hydrated Nafion spectrum (red) features bands at 1061 cm$^{-1}$ and 969 cm$^{-1}$ that correspond to the sulfonate form (C3V local symmetry) of the exchange site. Eigenvector animation extrema screenshots (Fig. 8, top panels) provide details of the vibrational motions. These high (C3V, HF) and low frequency (C3V, LF) bands correspond to group modes that involve the same side-chain functional group contributors. Figure 8 depicts extrema of the C3V normal mode eigenvector animations of hydrated Nafion and Nafion side chain composition analog structures. The lower panels show extrema snapshots of molecules that make up pure modes contributing to the C3V group modes along with associated calculated normal mode frequencies. Both the C3V,LF and C3V,HF modes are group modes with participation of a dissociated sulfonate group with C3V symmetry. The lower frequency 969 cm$^{-1}$ (C3V,LF) is dominated by a symmetric sulfonate stretch. (Fig. 8) The higher frequency 1061 cm$^{-1}$ (C3V,HF) has a major contribution from COC-A.

Historically, 969 cm$^{-1}$ was ascribed solely to the COC $\nu_{as}$, and the 1061 cm$^{-1}$ was ascribed solely to the $\text{SO}_3^{-1} \nu_{s}$. In contrast, normal mode analyses of Nafion, DTFME, and triflate show why these bands cannot be properly assigned as single function group modes. The mirrored similarities of hydrated Nafion group modes, and its side chain pure modes, are evident in extrema snapshots (Fig. 8). As expected, our assignments are in line with the DTFME COC $\nu_{as}$ and triflate $\text{SO}_3^{-1} \nu_{s}$ modes at 1136 cm$^{-1}$ and 981 cm$^{-1}$, respectively. Comparison of the pure modes (bottom panels) with the calculated normal modes (top panels) correctly show that the pure mode frequencies contributing to the C3V,LF are on average substantially higher than the

| Table I. Group mode assignments, DFT calculated normal modes, Transmission IR, Raman bands for hydrated Nafion-[H], dehydrated Nafion-[H], TPS$^-$, TPSH, triflate, triflic acid and DTFME. |
|---------------------------------|------------------|-----------------|---------------|-----------------|
| Hydrated Nafion-[H]            | CF$_3$ $\delta_u$, COC-B $\delta_s$, COC-A $\delta_u$ | 738$^*$          | 730            | Video S1        |
|                                | BB               | 883$^*$         | 806            | Video S2        |
| C$_{3v}$,LF                    | SO$_3^{-1} \nu_{s}$, COC-A $\nu_{as}$ | 983$^*$         | 969            | Video S3        |
| C$_{3v}$,HF                    | COC-A $\nu_{as}$, SO$_3^{-1} \nu_{s}$ | 1059$^*$        | 1061           | Video S4        |
|                                | CF$_3$ $\delta_u$, COC-B $\rho$, COC-A $\rho$ | 731$^*$         | 730            | Video S5        |
| C$_{1}$,LF                     | SO$_3$ $\nu_{as}$, COC-A $\nu_{as}$ | 786$^*$         | 910            | Video S6        |
|                                | COC(B) $\omega$, BB | 820$^*$         | 806            | Video S7        |
| Dehydrated Nafion-[H]          |                  |                 |                |                 |
|                                | SO$_3$ $\nu_{as}$, COC-A $\nu_{as}$ | 1405$^*$        | 1414           | Video S8        |
|                                | BB               | 972$^*$         |                | Video S9        |
| TPS$^-$                        | SO$_3^{-1} \nu_{s}$, COC $\nu_{as}$ | 1075$^*$        |                | Video S10       |
|                                | COC $\nu_{as}$, SO$_3^{-1} \nu_{s}$ |                |                | Video S11       |
|                                |                  | 766$^*$         |                | Video S12       |
| Pure Modes                     |                  |                 |                |                 |
| Triflate                       | SO$_3^{-1} \nu_{s}$ | 981$^*$         |                | Video S13       |
| Triflic Acid                   | SO$_3$ $\nu_{as}$ | 795$^*$         |                | Video S14       |
|                                | SO$_3$ $\nu_{as}$, COC $\nu_{as}$ | 1398$^*$        |                | Video S15       |
| DTFME                          | COC $\nu_{as}$   | 1136$^*$        | Video S16      |                 |
|                                | COC $\nu_{as}$   | 1256$^*$        | Video S17      |                 |

Symmetric stretching, $\nu_{s}$; Asymmetric stretching, $\nu_{as}$; Waggling, $\omega$; Bending, $\delta$; Umbrella bending, $\delta_u$; Rocking, $\rho$; Backbone, BB; Calculated value$^*$
pure modes contributing to the $C_{3v,LF}$, in further support of the assignments. The relationships between pure modes and calculated normal modes (actually group modes) are more easily seen by visualization of the full animations, which are available as Supplemental Material. All of the assignments are summarized in Table I.

Intermediate states-of-hydration show coexistence of the $C_{3v}$ and $C_1$ modes (Fig. 6 purple spectrum). Both $C_{3v}$ and $C_1$ modes exist in the Raman spectra between 900 and 700 mV, consistent with the onset current (Fig. 5) and intermediate hydration. Thus $C_1$ and $C_{3v}$ modes together are indicators of membrane state-of-hydration at intermediate and extreme levels. This is the most important revelation of Figure 6.

**Nafion Raman bands at 730 cm$^{-1}$ and 806 cm$^{-1}$.—**Prior to this work, the bands at 730 cm$^{-1}$ and 806 cm$^{-1}$ had not been assigned by visualization of normal mode eigenvector animations. Although these Raman bands appear at all potentials (Fig. 6, left), there are band shape and intensity transitions concurrent with the onset of water formation (Fig. 6, dotted line region). Eigenvector animations (Figs. S1–2, 5, 7) reveal a pair of near degenerate normal modes that make up the 730 cm$^{-1}$ band and another normal mode pair contributing to the 806 cm$^{-1}$ band. While both observed bands are assigned by Peng et al. as “due to Teflon skeleton structure”, the eigenvector animations enable a more detailed set of assignments.

The animations show that the 731 cm$^{-1}$ (sulfonic acid side-chain normal mode analysis) and the 738 cm$^{-1}$ (sulfonate side-chain normal mode analysis) both contribute to the 730 cm$^{-1}$ band (Table I) to extents that depend on the state-of-hydration. Above 900 mV, the mode corresponding to the dehydrated exchange site dominates contributions (side-chain rocking) to the 730 cm$^{-1}$ band. Between 900 and 700 mV, modes due to the dehydrated and hydrated states contribute to the band as the cathode initiates water formation. Below 700 mV, the modes associated with the dehydrated states are entirely supplanted by modes calculated from the hydrated state of the exchange site. The hydrated form of the exchange site becomes the dominant contributor (side-chain bending) to the 730 cm$^{-1}$ band. Thus, there is a transition in the 730 cm$^{-1}$ band as the membrane state of hydration increases. The band shape changes from a side-chain rocking dehydrated mode to a side-chain bending hydrated mode (low intensity, broad peaks to narrower, sharp peaks). The overall changes in modes are indirectly related to exchange site local symmetry because the animations show little contribution of exchange site motions to the modes. However high and low states of hydration do have substantial impact on the overall morphology of the membrane (e.g., a three phase model, core-shell structure, etc.).

Similarly, normal mode animations confirm that the 820 cm$^{-1}$ (sulfonic acid form) and 883 cm$^{-1}$ (sulfonate form) normal modes contribute to the 806 cm$^{-1}$ band (Table I). Above 900 mV, the 820 cm$^{-1}$ mode dominates contributions (side-chain/backbone) to the 806 cm$^{-1}$ band. Between 900 and 700 mV, the 820 cm$^{-1}$ and 883 cm$^{-1}$ modes co-contribute to the 806 cm$^{-1}$ band as the cathode initiates water formation. Below 700 mV, the 820 cm$^{-1}$ mode is entirely supplanted by the 883 cm$^{-1}$ mode. In summary, as the membrane becomes hydrated, the dominant contributor to the 806 cm$^{-1}$ band gradually shifts from the calculated 820 cm$^{-1}$ to the 883 cm$^{-1}$ normal modes. The band shape changes (although not as distinctly as in the 730 cm$^{-1}$ band) from a side-chain/backbone dehydrated mode to a backbone hydrated mode.

**Raman bands (560 – 631 cm$^{-1}$).—**Figure 6 shows low intensity bands at 564 cm$^{-1}$, 600 cm$^{-1}$, and 635 cm$^{-1}$. To facilitate analysis, Figure 9 shows operando spectra with cathode catalytic layers of: (left) Fe-Nx/C (O$_2$ flow), (middle) C/(no Fe-Nx/C) (O$_2$ flow), and (right) Fe-Nx/C (N$_2$ flow). Johnson Matthey Pt/C was used at the MEA anode. The absence of peak frequency potential dependence (Stark tuning) justifies signal averaging of the left, middle and right panel spectra. “Average” spectra are shown in separate panels below their respective source panels.

The peak at 564 cm$^{-1}$, attributed to Fe-O$_2$ stretching modes, is present at all cell potentials under O$_2$ flow (left). It is non-discernable from the background under N$_2$ flow (right). There is total absence of intensity at 564 cm$^{-1}$ when a carbon cathode is under O$_2$ flow (middle). This is totally consistent with the presence of iron in the catalytic layer. However, the absence of Stark tuning of the Fe-O$_2$ stretching modes, and the appearance of the peak at potentials from open circuit to short circuit currents is unexpected for a site associated with the oxygen reduction current onset.

A literature search revealed no reports of Fe-O$_2$ stretching modes within the 600 cm$^{-1}$ to 635 cm$^{-1}$ range. However, a Hester and Krishnan report on vibrational spectra of divalent metals in molten sulfates elucidates an analogy between metal complexation in molten...
Figure 9. Potential dependent Raman spectra, from 650 to 550 cm$^{-1}$, of the Fe-N$_2$/C cathode catalyst operating under O$_2$ (left), C (no Fe) cathode catalyst operating under O$_2$ (middle), and Fe-N$_2$/C cathode catalyst operating under N$_2$ (right).

**Conclusions**

Hydrogen/oxygen fuel cell operando Raman spectroscopy shows the potential-dependent spectroscopy of the Nafion ionomer within the MEA cathode catalytic layer: The ionomer state-of-hydration increases as the fuel cell voltage decreases. Density functional theory calculated normal mode analysis, of the Nafion repeat unit and side-chain molecular fragment analogs, provides eigenvector animations that enable Nafion band assignments in terms of the exchange site local symmetry. Dehydrated Nafion features C$_2$V modes that are associated with the sulfonic acid form of the exchange site. Hydrated Nafion features C$_3$V modes that are associated with the sulfonate form. At intermediate stages of hydration the C$_1$ and C$_3$V modes coexist. The study highlights a less understood wavenumber region between 550 and 650 cm$^{-1}$.

The proper positioning of the Raman microscope laser focal point is determined by a coarse depth profiling of the Raman fuel cell that is calibrated by Raman peaks associated with materials that comprise layered regions of the fuel cell device. This technique can advance the fundamental understanding of the processes such as oxygen reduction reaction (ORR), carbon corrosion, and catalysis process of ORR in PEMFCs catalyzed by Pt or non-PGM catalysts operating under realistic conditions.

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**Figure 9.** Potential dependent Raman spectra, from 650 to 550 cm$^{-1}$, of the Fe-N$_2$/C cathode catalyst operating under O$_2$ (left), C (no Fe) cathode catalyst operating under O$_2$ (middle), and Fe-N$_2$/C cathode catalyst operating under N$_2$ (right).

**Table 1.** Summary of operando Raman spectroscopy studies on PEMFCs.

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