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In situ, simultaneous thermal imaging and infrared molecular emission studies of solid oxide fuel cell electrodes

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Highlights
- Thermal images and emission spectra are simultaneously measured in situ from SOFCs.
- Spatially resolved anode cooling is correlated with the dry reforming product CO.
- Anode cooling and CO decrease with increased operating current.
- Molecular and electrochemical processes are spatially resolved in real time.

Abstract
Various in situ probes of solid oxide fuel cells (SOFCs) have advanced recently to provide detailed, real time data regarding materials and chemical processes that relate to device performance and degradation. These techniques offer insights into complex fuel chemistry at the anode in particular, especially in the context of model predictions. However, cell-to-cell variations can hinder mechanistic interpretations of measurements from separate, independent techniques. The present study describes an in situ technique that for the first time simultaneously measures surface temperature changes using near infrared thermal imaging and gas species using Fourier-transform infrared emission spectra at the anodes of operating SOFCs. Electrolyte-supported SOFCs with Ni-based anodes are operated at 700°C with internal, dry-reformed methane at 75% maximum current and at open circuit voltage (OCV) while electrochemical and optical measurements are collected. At OCV, more cooling is observed coincident with more CO reforming products. Under load, CO decreases while the anode cools less, especially near the current collectors. The extent of cooling is more sensitive to polarization for electrolyte-supported cells because their anodes are thinner relative to anode-supported cells. This study exemplifies how this duplex technique can be a useful probe of electrochemical processes in SOFCs.

1. Introduction

Solid oxide fuel cells (SOFCs) have recently attracted significant attention because of their ability to cleanly and efficiently (>70%) convert chemical energy to electrical energy using a wide variety of hydrocarbon feedstocks, including reformed methane and alcohols [1–3]. Solid oxide electrolysis cells (SOECs) are closely related devices that have also seen strong research investment because of their ability to efficiently produce fuels from greenhouse gases such...
as CO₂ and H₂O using electricity [4]. These assemblies traditionally use materials including Ni/yttrium stabilized zirconia (YSZ) cermet as the fuel electrode, lanthanum strontium manganite (LSM)/YSZ as the oxygen electrode, and YSZ as the electrolyte [4]. High operational temperatures (600–800 °C) are required to overcome the energy barriers for oxide diffusion through the electrolyte material as well as to activate electrode reactions [5,6]. However, these high temperatures tend to aggravate degradation of component materials. Ni/YSZ electrodes in SOFCs, for example, are well investigated but continue to experience significant challenges that include delamination, Ni agglomeration, and deactivation stemming from oxidation/reduction cycles, reactions with contaminants, and carbon growth. Much study has focused on developing new, robust materials that sustain high electrochemical performance [4,7,8], but efforts of this nature have been hampered by uncertainty regarding the mechanisms that lead to performance changes [9].

Traditionally, SOFC anode chemistry has been inferred from a combination of ex situ measurements, electrochemical measurements, and/or theoretical models. The primary reason is that the high operational temperatures pose challenges to in situ observation [10]. However, notable advancements have provided direct insights in real time, particularly in regard to molecular and material changes on electrode surfaces. Pomfret et al. were the first to collect Raman spectra from the anode surface of SOFCs operating near 715 °C [11,12] and Kirtley et al. later increased the limiting temperature to over 800 °C [13]. This innovative technique has provided information about electrochemical changes (including voltage and impedance) accompanying materials changes (such as carbon growth and electrode oxidation) [14,15]. Li et al. have extended this technique by implementing in situ surface enhanced Raman spectroscopy to strengthen signals from carbon and hydrocarbon intermediates, spatially resolved with regard to the Ni/YSZ interface. Their Ni based SOFCs were operated with propane at 450 °C and under various biases [16]. As another example, Cumming et al. have pioneered diffuse reflectance infrared Fourier transform spectroscopy for in situ measurements of electrochemical intermediates (including surface hydroxyls, carbonates, and bicarbonates) in SOEC applications [17]. Using atmospheric pressure X-ray photoelectron spectroscopic (APXPS) techniques, Geller et al. measured in situ the reduction of ceria in SOECs operating at 1–2 Torr in different environments [18]. Pomfret et al. demonstrated that Fourier-transform infrared emission spectroscopy (FTIRES) could be used to directly observe gas phase products and a surface intermediate from a SOFC operating with methane [19].

Near infrared (NIR) thermal imaging is another in situ technique that has been pioneered by several groups as a way to probe surface temperature and emissivity changes. The first to utilize this technique in fully operational SOFCs were Pomfret et al. [20]. This group also collaborated with Geller et al. later to attribute surface emissivity changes near electrochemically active regions of an SOEC to a change in a ceria electrode's oxidation state [18]. Tachikawa et al. implemented a combined visible/NIR imaging technique to distinguish between thermal and emissivity changes in situ [21], while Cumming and Elder used this technique in SOEC applications to observe temperature changes that were sensitive to different cathode environments [22].

In recent studies Kirtley et al. integrated in situ Raman, NIR thermal imaging, and FTIRES to provide the first direct optical measurements of methane dry reforming on Ni-based, anode supported SOFCs [13,23]. This work directly showed that more surface cooling during dry reforming correlated with higher operating temperature, and less carbon formation. In the case of unreformed methane, minimal cooling and significant carbon accumulation was observed. The former result contrasts with other work that correlated surface cooling with increased carbon formation from alcohols [15,24]. Any carbon accumulation during the dry reforming reactions was monitored using in situ Raman, often simultaneously with NIR thermal imaging, and also after the reaction when carbon was electrochemically oxidized. In this case, relative carbon accumulation was inferred after exposure by comparing oxidation products measured by FTIRES with changes in electrochemical potential. This work provides an example of how several in situ optical techniques can provide direct insights into SOFC anode processes.

The present study advances the in situ optical techniques available for SOFC studies by simultaneously measuring NIR thermal images with FTIRES. The approach is relatively straightforward. A CaF₂ window is inserted in the emission beam path such that the small amount of reflected light is used for thermal imaging while most of the radiation is transmitted for FTIRES. This new capability enables direct correlation of surface temperature changes, products, intermediates, and electrochemical measurements in real time. This work is motivated by challenges associated with cell-to-cell variations, observed previously, that have led to difficulties interpreting results collected from independent measurements from multiple techniques. In this study, dry reforming processes are again investigated but now using Ni-based electrolyte-supported SOFCs to demonstrate that this duplex technique can provide deeper mechanistic insights that reflect electrochemical processes. Because electrolyte-supported SOFCs are constructed with thin anodes compared to anode supported designs studied previously, they provide closer optical access to the electrochemically active anode/electrolyte interface. For the first time, this work directly attributes spatially-resolved surface cooling with endothermic dry methane reforming from observations that the CO reforming product increases with more cooling. Furthermore, operation with a load suppresses cooling preferentially near current collectors while CO decreases relative to OCV. This result suggests that the electrochemical oxidation of CO is spatially resolved in situ with this technique.

2. Experimental

2.1. SOFC samples and assembly

Results from two electrolyte-supported SOFCs (Cells A and B) purchased from Fuel Cell Materials are reported in this work. The ~50 μm thick anodes (areas 1.35 and 1.38 cm², respectively) of Cells A and B were composed of a NiO/YSZ (8 mol%) outer layer and a NiO/gadolinium doped ceria (GDC) inner layer. The ~50 μm thick cathodes were composed of a lanthanum strontium manganite (LSM) outer layer and a LSM/GDC inner layer. The electrolytes of Cells A and B were 300 μm thick, 2.5 cm diameter YSZ and 150 μm thick, 2.0 cm diameter Hionic™ ceramic disks, respectively. Gold leads for electrochemical measurements were attached with Au contact paste/Au mesh to the anode and with Pt contact paste/Pt mesh to the cathode. The area of the gold current collector for Cell A (~0.27 cm²) and Cell B (~0.24 cm²) varied slightly, as did their shapes, though care was taken to center each on the anode (see Figs. 3 and 4). The SOFC was subsequently sealed with alumina paste to an alumina test rig equipped with a CaF₂ window for direct optical access to the anode. Further details regarding the SOFC assembly can be found elsewhere [10,25].

2.2. Experimental assembly

A schematic describing the experimental assembly is presented in Fig. 1. A tube furnace was used to heat the SOFC assembly, while infrared radiation from the hot anode and surrounding surfaces was transmitted through the CaF₂ window. This window sealed the
−5 mm thick headspace over the anode from the furnace cavity and also transmitted infrared light from the anode chamber with a lower frequency limit near 1000 cm⁻¹. The infrared light exited the furnace through a second CaF₂ window sealed to a purged alumina tube; the window helped prevent convective heat loss from the furnace aperture. The emission passed through the alumina cylinder and into a Fourier-transform infrared (FTIR) spectrometer (Mattson Instruments), from which the original infrared source had been disengaged. The emission was directed onto a CaF₂ flat, oriented at 45°. Approximately 4% of the radiation was reflected from the front surface of the flat to a CCD camera equipped with a long pass filter to block light <720 nm. The back surface of the CaF₂ flat was anti-reflective coated (Evaporated Coatings, Inc., #289 NIR) to avoid doubling of the infrared image. The majority of the infrared light was passed through the flat to a parabolic gold mirror and reflected to an interferometer and mercury cadmium telluride (MCT) detector for collection of emission spectra. The furnace was purged with Ar, while the spectrometer and connecting alumina cylinder were purged with N₂ to reduce interference from background atmosphere. Other related details can be found in previous publications [13,23].

2.3. Gas flows and experiment sequence

All gas flows were supplied via mass flow controllers to the SOFC, nominally near atmospheric pressure. At the cathode, gas flows remained at 20 mL min⁻¹ O₂ and 65 mL min⁻¹ Ar throughout the experiment. At the anode, the Ar flow remained at 150 mL min⁻¹. Before any trials began, the anode was initially reduced by adding 20 mL min⁻¹ H₂ for at least 15 min and then fully reduced under 100 mL min⁻¹ H₂ until OCV was stable.

Each trial followed a sequence similar to that used in previous dry reforming studies [13,23]. First, each trial began with benchmark electrochemical measurements (described in Section 2.5) under 100 mL min⁻¹ H₂ at the anode. Hydrogen flow was then lowered to 20 mL min⁻¹ for 10 min at OCV to more closely match the CH₄ mole fraction used in the next step. Surface temperatures vary as much as 1 °C with H₂ flow (20–100 mL min⁻¹). This extra step provided a more representative baseline to compare cooling trends from dry reformed methane. Hydrogen was replaced with 25 mL min⁻¹ CH₄ and 25 mL min⁻¹ CO₂. Under CH₄/CO₂ flow, the cell was set to operate at OCV or at 75% maximum current (see Section 2.5) for 600 s. The current (75% I_max) was chosen to maximize optical responses to electrochemical processes while avoiding oxidation of the anode. Additional electrochemical benchmarks were also completed under this fuel. After CH₄/CO₂ exposure, anode flows were returned to 20 mL min⁻¹ H₂ for 10 min to purge the anode headspace of fuel while minimizing any carbon oxidation. Any carbon deposits were then removed electrochemically by drawing current at 67% I_max (relative to H₂ benchmarks) under Ar only. This current was chosen to follow previous studies and to allow for clear electrochemical equivalence points [14] (signaling a loss of electrochemically accessible carbon) without overly stressing the cell when no gaseous fuel was present. The cell was returned to OCV once an electrochemical equivalence point was reached. The trial was complete when the anode was again reduced and prepared for electrochemical benchmarks with 100 mL min⁻¹ H₂ flow. Multiple such trials were completed on each cell.

2.4. Duplex measurements

NIR thermal images were recorded with in-house software written in LabView (v8.5). Emission intensities were temperature calibrated using a thermocouple (type K) surface located near the anode. Images were collected with >4 Hz temporal resolution. NIR thermal imaging data were processed post-experiment in two ways: 1) temperatures within a region of interest were averaged over the course of a trial to show a temperature difference against time, and 2) an image collected under initial conditions (20 mL min⁻¹ H₂) was subtracted from an image collected near a
trial's end to show a difference in spatially resolved (~100 μm) temperatures over the entire anode surface. Temperature resolution can approach 0.1 °C. Though the background variation from the furnace heating elements often increased the noise level, the time scales of chemical processes approaching steady state were sufficiently large to reject the furnace variation. As a result, most of the data showing ΔT against time were boxcar smoothed temporally over 100 data points (~21 s).

Two Fourier-transform infrared emission spectra were collected before the start of fuel flow to serve as a reference and a blank measurement, while additional spectra were collected at approximately 100, 300, and 500 s after the start of fuel flow. Spectra were averaged over 16 scans (~35 s) with 0.5 cm⁻¹ nominal resolution and over a range of 700–5000 cm⁻¹. The maximum temporal resolution of the current FTIR spectrometer system is ~90 s under this configuration. Each spectrum was subtracted from the first reference to account for background radiation. Post-experiment leveling of spectra to bring the baseline near zero was also applied. Other details regarding collection of NIR images and infrared emission spectra can be found elsewhere [19,20].

2.5. Electrochemical measurements

A Gamry Reference 3000 Potentiostat/Galvanostat/ZRA measured and controlled all electrochemical parameters. Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) provided benchmarks for the SOFC under H₂ and CH₄/CO₂ fuels. LSV measured cell current while sweeping the cell potential from OCV (0 mA) to 0 V (Iₘₐₓ) at a rate of 0.1 V s⁻¹. EIS measurements benchmarked real (Z_{real}) and imaginary (Z_{imag}) impedance losses from 100 kHz to 0.2 Hz with V_{OC} and V_{AC} set to 0.1 V and 0.05 V, respectively. The potentiostat also monitored potential at OCV or at a controlled current (chronopotentiometry) during each trial.

3. Results and discussion

3.1. Electrochemical benchmarks

Benchmarks measured under CH₄/CO₂ are shown in Fig. 2. Data shown in Fig. 2a were used to determine the current when the cells were operated at 75% Iₘₐₓ: 100 mA cm⁻² (Cell A) and 113 mA cm⁻² (Cell B). The lower performance from Cell A (in terms of current and power) is likely due primarily to the ~2 fold thicker electrolyte relative to Cell B. Fig. 2b supports this, in which the resistance associated with ionic transport through the electrolyte (x-intercept) is larger under Cell A (3.8 Ω, or 2.8 Ω cm⁻²) relative to Cell B (2.7 Ω, or 2.0 Ω cm⁻²). The differences in polarization resistance (values greater than the x-intercept) are not explored here, but investigations of this nature have in the past provided insights into transport and activation phenomena at the electrodes [14,15,26]. Based upon a shorted lead EIS measurement, the contact resistance is assumed to be negligible. Furthermore, though the current collector area for Cell A is estimated to be slightly larger than Cell B (0.27 and 0.24 cm², respectively), Cell A shows the lower performance.

3.2. NIR imaging

Fig. 3 shows a false-color NIR image measured under typical baseline conditions (e.g. immediately before a trial and under 20 mL min⁻¹ H₂). The fuel direction, indicated by the arrow, can vary among setups because each is hand-assembled (see also Fig. 4a and b). Red and blue areas correspond to greater and less surface infrared emission, respectively. The anode is the nearly perfect
circle inside the dashed square, while the anode/electrolyte boundary is seen at the perimeter. A gold current collector is visible at the center of the anode. Outside the dashed square, the alumina paste used to seal the cell to an alumina support tube may be carefully discerned.

Significant information can be gathered using NIR thermal imaging when a change in temperature or emissivity is measured (unlike the raw image seen in Fig. 3). We have measured each under different experimental conditions. Geller et al. recently reported that when Ce$^{4+}$ was electrochemically reduced to Ce$^{3+}$, its surface emissivity decreased reversibly [18]. Kirtley et al. showed that surface cooling associated with endothermic CH$_4$/CO$_2$ reforming on Ni/YSZ anode supported cells is real and not a result of surface emissivity changes from plausible processes such as Ni oxidation or carbon accumulation [13,23]. Separate measurements (not shown) have indicated that cooling on Ni/YSZ anodes is reversible and quickly modulated by varying the CH$_4$/CO$_2$ ratio (or by removing the fuel entirely) which provides further compelling evidence that the intensity changes are due to temperature rather than emissivity changes.

In the present study, the electrolyte-supported cells also indicate a cooling response when operated with CH$_4$/CO$_2$ at OCV and at 75% $I_{\text{max}}$. Fig. 4 shows the change in surface temperatures as Cells A and B approach the end of a 600 s trial with CH$_4$/CO$_2$ fuels, relative to their initial temperatures under H$_2$, OCV (see Section 2.4). Notably, cooling is restricted to the Ni/YSZ anode and not the surrounding YSZ electrolyte. Even across the anode, cooling is not uniform in each example. This heterogeneous cooling likely reflects regions that vary in reforming activity, and may depend upon gas flow fields and anode microstructure. From this standpoint, we predict that reforming is more active on Cell A because of an evidently larger area that cools.

The effects of polarization on cooling are also clear (Fig. 4b and d). Less cooling is observed over the entire anode surface of both cells when 75% $I_{\text{max}}$ current is drawn. Prior studies on CH$_4$/CO$_2$ reforming in anode supported SOFCs did not clearly indicate this electrochemical dependence because the optically-accessible anode surface was much further removed from the electrolyte interface [13,23]. The origin of this decreased cooling relative to OCV will be discussed in Section 3.4.

3.3. Infrared emission spectra

Fig. 5 shows a representative emission spectrum from gas species in the headspace above the anode while Cell A at OCV is exposed to CH$_4$/CO$_2$. Molecular signatures visible between 3400 cm$^{-1}$ and 1800 cm$^{-1}$ have been noted before from in situ anode supported SOFC studies [13,19,23]. These include the antisymmetric stretching mode of CH$_4$ centered near 3007 cm$^{-1}$, the antisymmetric stretching mode of CO$_2$ near 2300 cm$^{-1}$, and the CO stretch near 2150 cm$^{-1}$. The recent replacement of sapphire with CaF$_2$ windows has allowed extension of the lower energy cutoff from 1800 cm$^{-1}$ to 1000 cm$^{-1}$, providing access to the H$_2$O and CH$_4$ bending modes near 1600 cm$^{-1}$ and 1305 cm$^{-1}$, respectively. Greater sensitivity at longer wavelengths also promises access to molecular signatures including carbonates [17,27], and impurities (e.g. sulfur and chlorine products) important in many different SOFC and SOEC studies. Though measurements at lower
frequencies may be hampered by an increased blackbody background leading to reduced sensitivity or spectral distortion [28], our measurements appear largely unaffected by these effects.

Fig. 5 (insets) shows that the rovibrational transitions of CH₄ and CO can be easily resolved. The emission intensities of specific transitions from each gas are chosen to measure how the relative amount of each species varies throughout a trial and as a function of electrochemical current, and are representative of other transitions. Directly quantifying partial pressure with emission intensities remains challenging because background emission will strongly influence signal; a hurdle explored in detail by Ladouceur et al. [28] and possibly circumvented in a specialized measurement chamber by Usseglio et al. [29]. To monitor the relative amount of CH₄, the intensity of its v₃ (1 → 0) and J(8) → J(9) transition at 2926 cm⁻¹ is...
monitored. In this case, \( v_3 \) refers to methane’s asymmetric stretching vibrational mode, “1” and “0” refer to excited and ground vibrational states, respectively, and \( [J'J] \) refers to rotational states. For CO, the vibrational \( (1 \rightarrow 0) \) and rotational \( J(11) \rightarrow J(12) \) transition at 2094 cm\(^{-1}\) is used. Both are chosen for strong signal while avoiding the risk of optical saturation. For this reason, the combination band broadly centered near 3739 cm\(^{-1}\) is chosen to measure CO\(_2\) emission intensities, in lieu of the larger peak at 2300 cm\(^{-1}\). Separate measurements have shown that the 3739 cm\(^{-1}\) emission intensity increases nearly linearly with CO\(_2\) partial pressure, in contrast with the 2300 cm\(^{-1}\) band. Ro-vibrational transitions are not clearly resolved for either CO\(_2\) feature. Finally, for H\(_2\)O, emission signals are too low to allow for accurate comparisons throughout a trial.

### 3.4. The duplex: simultaneous, time-resolved optical results

Cooling on the anode surface is observed when both cells operate with CH\(_4/CO_2\) fuel, as noted in Section 3.1. To demonstrate how surface cooling evolves throughout each measurement, temperatures within ROIs (Fig. 4) are averaged throughout each trial. These regions are chosen to represent a similar location with respect to the fuel stream and the gold current collector, but the sampled areas do not attempt to represent the spatially-dependent, heterogeneous cooling across the entire anode of each cell. Fig. 6 shows the cooling \( \Delta T \) in these two regions relative to initial conditions under H\(_2\) and OCV (−90 to −45 s). From −45 s to 0 s, H\(_2\) is replaced with CH\(_4/CO_2\) and a current load is applied if applicable. The desired operating conditions are set at 0 s (indicated by the vertical solid line, Fig. 6a and b). After this point, the magnitude of cooling observed contrasts strongly between the two cells. Cell A (Fig. 6a) at OCV, for example, cools almost three times more than Cell B (Fig. 6b) within the regions sampled. While these data only indicate cooling within the selected ROIs, they reflect the observation from Fig. 4 that the entire anode surface from Cell A cools more than Cell B. When both cells are operated under load, less cooling is observed throughout the 10 min trial. This result contrasts with prior work on anode supported SOFCs [13,23].

Fig. 6 also shows the evolution of emission intensities (normalized) of CH\(_4\), CO\(_2\), and CO species that are observed over the anode during each trial. Because absolute emission signal can vary from one experiment to another, the emission intensities tabulated in Fig. 6 are normalized within each experiment to more directly compare results. A “blank” spectrum is collected (prior to −90 s) under H\(_2\), OCV and subsequently at −100, 300, and 500 s. These data show that as CH\(_4/CO_2\) fuel passes over the Ni/YSZ anode, CO forms through the endothermic dry reforming reaction in both experiments:

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{\text{rxn}} = 260 \text{kJ mol}^{-1}
\]  

(1)

This in situ observation has been made before, but not while surface temperature changes were simultaneously measured [13,23].

Real time correlation of NIR thermal imaging and FTIRES provides in situ confirmation that, with this fuel, surface cooling is related to dry reforming, and that this process can be spatially resolved. At OCV, for example, less extensive surface cooling is observed on Cell B relative to Cell A, both within the selected ROIs (Figs. 4 and 6) and across the anode surface (Fig. 4). At the same time, the normalized CO\(_2\) emission signals are higher while CO responses are lower from Cell B (Fig. 6b), relative to Cell A (Fig. 6a). These data suggest that CH\(_4\) reforming in reaction [1] is less active on Cell B, and that activity is greater in regions of stronger cooling. However, the reasons behind the spatially varied reforming activity remain unclear.

When the cells are operated under load (75% \(I_{\text{max}}\)), FTIRES measurements differ significantly relative to OCV. From Fig. 6a–b, CO signal decreases relative to operation without load, while CO\(_2\) signal increases. In particular, for Cell B, CO decreases −15% when bias is applied, while CO\(_2\) increases 10%. These trends are corroborated by analysis of the exhaust using a quadrupole mass spectrometer and FTIR spectrometer. This result suggests that CO\(_2\) is formed while CO is electrochemically oxidized to generate current, a trend also seen with methanol fuel [30]. Methane emission signal slightly increases under load (e.g., 3% for Cell B and corroborated by exhaust measurements), implying less reforming activity and possible anode degradation. These data suggest that though most of the CO and H\(_2\) formed through reaction [1] is not electrochemically oxidized when bias is applied, measurable CO oxidation is directly observed. Undoubtedly, H\(_2\) is also electrochemically oxidized to produce H\(_2\)O. However, much of the H\(_2\) likely participates in the reverse Water Gas Shift reaction at OCV, as evidenced by the presence of water in situ and in the exhaust:

\[
\text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_{\text{rxn}} = 35 \text{kJ mol}^{-1}
\]  

(2)

In fact, exhaust measurements indicate only 1% more H\(_2\)O produced when bias is added.

The conclusion that CO is electrochemically oxidized to CO\(_2\) is supported by less cooling observed under load. CO oxidation is an exothermic process [31] ¹:

\[
\text{CO} + \text{O}^{2-} \rightarrow \text{CO}_2 + 2\text{e}^- \quad \Delta H_{\text{rxn}} = -44 \text{kJ mol}^{-1}
\]  

(3)

This conclusion is also supported by additional measurements that show rapid changes in CO emission intensity and surface temperature changes when the applied current is varied throughout a single trial. However, these experiments do not conclusively rule out resistive heating from electronic or oxide conduction through the Ni or YSZ, respectively. Additionally, the electrochemical oxidation of H\(_2\) is also slightly exothermic ¹:

\[
\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \quad \Delta H_{\text{rxn}} = -8 \text{kJ mol}^{-1}
\]  

(4)

Whatever the molecular origin, electrochemically induced heating is most pronounced near the current collectors (Fig. 7). This observation underscores the importance of the current collector size, shape, and position. Interestingly, this effect is not consistently affected by proximity to the fuel stream or regions of strong cooling. To better understand a molecular basis behind location-dependent cooling, spatially-resolved molecular probes, such as in situ Raman spectroscopy, will be advantageous.

### 4. Conclusions

This work reports a newly advanced in situ capability that simultaneously collects NIR thermal images and FTIRES during SOFC operation. The duplex technique is used to probe Ni/YSZ anodes of electrolyte-supported cells operated with dry reformed, methane fuel as an example of how this technique can correlate surface temperature changes with infrared emission intensities of CH\(_4\), CO\(_2\), and CO in real time. In particular, these studies reveal that surface cooling is not homogeneous across the anode surface, and the amount of surface cooling varies between cells. These measurements directly indicate that more cooling on the Ni/YSZ anode surface is associated with more CO and less CO\(_2\) at the anode and

¹ Calculated using Hess’s law. O\(^{2-}\) is assumed to be O\(_{14}\) on Ni. Specific enthalpy for O\(_{14}\) is estimated from Ref. [31], Table 3.
provides a way to spatially resolve the endothermic dry reforming reaction.

These measurements also demonstrate sensitivity to electrochemical control, aided by thin anodes and closer proximity to electrochemically active regions relative to thick, anode-supported designs. When each cell is operated at 75% Imax, CO decreases and CO2 increases relative to operation at OCV. This result suggests that CO as a reforming product is subsequently oxidized to CO2 when the cell is operated under load with CH4/CO2 fuel. Each anode surface also experiences less cooling under load, especially near the current collectors, and may be related to electrochemical, exothermic oxidation of CO.

These results provide one example of how this duplex technique can reveal detailed, in situ insight that directly correlates evolving anode products and intermediates with surface temperature changes. This technique is resilient to cell-to-cell performance variations (e.g. electrochemical performance and catalytic activity) that can undermine efforts to compare data sets from independent techniques on different cells. Instead, this technique promises a means to explain performance variations. This work also suggests that this technique may provide a way to spatially resolve processes in a wide variety of high temperature systems. Further insights could plausibly come from quantitative, in situ gas measurements, especially if complemented with molecularly-resolved surface mapping techniques such as Raman spectroscopy.

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Glossary

APXPS Atmospheric Pressure X-ray Photoelectron Spectroscopy

Fig. 7. The difference in surface cooling at 75% Imax relative to OCV. Regions are sampled from the left edge of the anode (ROI 0) to the anode/Au interface (ROI 3) in Cell A (black circles) and Cell B (red triangles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
9–21.


