A. Sample preparation

First, square Ni coupons (~8 mm) were prepared from Ni foil (Alfa Aesar) and polished to a grade of 0.1 µm using diamond media, after which the coupons were cleaned ultrasonically in acetone, washed with ethanol and purified water, and then dried under a compressed air stream. The coupons were exposed to flowing gas mixture (>100 sccm flow rate) composed of 15% H₂ and 10% C₃H₈ in dry Ar for 5 minutes at 550°C in a quartz tube to induce chemically-driven carbon deposition over the polycrystalline Ni surface.

For the patterned strip electrode samples, YSZ substrates were first prepared by tape-casting a slurry of YSZ powder (Daiichi). The tape was cut into 1.7 cm discs, after which stacks of 3 discs were laminated by uniaxial pressing. The laminated stacks were
sintered into dense pellets at 1450ºC for 5 hours in air. The dense pellets had a thickness of ~400 µm. The pellets were subsequently cleaned and patterned with Ni strips deposited using photolithography methods like those described elsewhere\textsuperscript{1,2}.

Samples with Ni mesh electrodes were also prepared. Squares of Ni mesh (Alfa Aesar, size 50) that were <1 cm in size were sandwiched between packs of YSZ powder and uniaxially co-pressed with the packed powder into 13-mm disc pellets (~1 mm thickness). The pellets were sintered at 1440ºC for 5 hours in a tube furnace under a flowing reducing gas atmosphere (4% H\textsubscript{2}/bal. Ar) to prevent degradation of the mesh by oxidation. After firing, one face of each pellet was mechanically ground away to reveal the embedded Ni mesh. The embedded mesh surface was then further polished and cleaned by the same method used for the Ni coupon samples. A modification was applied to the Ni mesh samples for some samples by heating them to 1200ºC for 2 hours in reducing atmosphere (4% H\textsubscript{2}/bal. Ar) with BaO powder present in the tube furnace. While the BaO powder was not in physical contact with the samples, vapor evolved and deposited on the revealed Ni mesh surface. For the purpose of \textit{ex situ} measurements, a selection of the patterned Ni and plain/modified Ni mesh pellets were heated to 625ºC in flowing C\textsubscript{3}H\textsubscript{8} gas for 2 hours.

**B. Analysis details**

Raman spectroscopy and mapping was performed using a Renishaw RM-1000 microspectroscopy system with 633 nm laser excitation set at ~17 mW of power (Thorlabs HRP170) or 514 nm laser excitation set at ~5 mW (Modu-Laser StellarPro 150). Spectra were collected through a 50X objective lens. This lens was also used to capture optical images that could be correlated with Raman maps. For Raman mapping,
full spectra were quickly collected from different spots on the sample with the laser at maximum focus. Sample movement was controlled by an XYZ stage with submicron precision (Prior Scientific). The beam diameter was ~2 µm; thus, spectra were collected at 2-µm intervals.

For in situ Raman analysis, a modified high-temperature diffuse reflectance infrared spectroscopy sample chamber (Harrick Scientific) was used. The chamber allows for atmosphere control and sample heating, while its standard dome top was replaced by a custom-built flat quartz window top that gives the laser beam access to the sample surface. A schematic and a photograph of the chamber are displayed in ESI-1. The YSZ pellets with strip-patterned Ni or Cu as well as those with embedded Ni mesh were used for these measurements. The former samples were heated in the chamber at 625°C with flowing CH₄ gas for 12 hours, while the mesh samples were treated at 625°C in a flowing mixed gas containing 4% H₂, 5% C₃H₈, and 3% H₂O balanced by Ar for 15 hours. Raman signal was collected while the samples were held at high temperature.

Scanning electron microscopy (SEM, Hitachi S800) and atomic force microscopy (AFM, Veeco Nanoscope IIIA) were also employed for Ni surface characterization purposes.

C. Characterization of the Ni surface

Fig. ESI-2a displays an image of the polished and cleaned Ni coupon surface prior to any other treatments. In most areas, the surface had a smooth texture although a small number of polishing media particles missed by the cleaning step can be seen. In the smooth areas, topographic variation was 10 nm, as measured by cross-sectional analysis of the AFM image (Fig. ESI-2b).
The Ni surface morphology was changed considerably by carbon deposition, even in areas where coking was not severe. **Fig. ESI-2c** shows a high-magnification SEM image of a lightly coked area on a Ni coupon exposed to C$_3$H$_8$-containing gas at 550°C for 5 minutes. The surface was roughly textured in comparison to the untreated Ni. In addition, AFM images over the same area revealed nanoscale dot features (see inset in Fig. ESI-2c). These features likely represent the sites of initial carbon nucleation. The same analyses performed on a heavily coked area showed an even rougher surface texture (**Fig. ESI-2d**). In this case, much larger granules were observable in the AFM image.

**D. Ex situ mapping of patterned Ni electrodes**

**Fig. ESI-3a** shows an example micrograph of patterned Ni strips on YSZ. The darker strips are the Ni phase and the lighter areas are exposed YSZ substrate. The widths of the Ni strips were ~10-15 µm, while the distances between the strips varied from and 15-30 µm, respectively. **Fig. ESI-3b** displays the same area after exposure to C$_3$H$_8$ gas at 625°C for 2 hours. The Ni strips turned completely black from carbon deposition on the surface. **Fig. ESI-3c** provides a higher magnification of some of the coked strips. A Raman map of the area shown in Fig. ESI-3c was collected for the carbon D-band (**Fig. ESI-3d**). The D-band intensity was much higher along the Ni strips, indicating that carbon preferentially deposited on Ni and that the YSZ surface experienced little or no coking. This finding supports the notion that a heightened susceptibility of Ni to coking is the main cause of related degradation problems.
E. In situ evaluation of coking on Cu electrodes

Raman spectra were collected from the surface of a Cu electrode while held at 625°C and are shown in Fig. ESI-4. No distinct features above the background can be observed either in the spectrum obtained right before CH₄ exposure or the one taken at the 12-hour mark during exposure. The lack of carbon signal, which was in contrast with the considerable amount seen on the Ni electrode under the same conditions, was expected due to Cu’s relative resistance to coking.

F. Coking comparison of BaO-modified/plain Ni exposed to dry C₃H₈

In order to confirm the hypothesis that the BaO modification coking resistance mechanism involves water, modified and plain Ni samples were exposed to dry C₃H₈ at 625°C. The subsequent Raman analysis is summarized in Fig. ESI-5. Unlike the contrast in coking seen in the modified and plain Ni electrodes exposed to wet C₃H₈, the amount of carbon observed on the dry-exposed Ni samples was nearly equal, indicating that BaO nanoparticles only helps remove an appreciable amount of carbon from the anode surface in the presence of water.
**Fig. ESI-1** Schematic of environmental chamber setup for *in situ* Raman analysis (top) along with a photograph of the chamber (bottom).
Fig. ESI-2  (a) SEM image of the surface of a polished Ni coupon. (b) AFM image of a typical area on the surface of a polished Ni coupon. (c+d) SEM images of a lightly coked region and a heavily coked region (respectively) of the Ni coupon after exposure to C_3H_8-containing gas at 550°C. The insets are AFM images of the same regions.
Fig. ESI-3 (a) Optical micrograph of strip-patterned Ni electrode deposited on YSZ substrate; the same Ni electrode is shown in (b) following severe coking caused by exposure to C$_3$H$_8$ at 750°C for 2 hours. (c) Higher magnification of coked Ni electrode, with (d) showing a Raman map of the same area for the carbon D-band.
Fig. ESI-4 Raman spectra collected from the surface of a Cu electrode while heated at 625°C before and after exposure to CH₄.

Fig. ESI-5 Raman spectra collected from Ni samples at room temperature following exposure to dry C₃H₈ at 625°C.

References