Supporting Information

Pd–H species on electrode stabilized by solvent co-adsorption: observation by operando IR spectroscopy

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**Experimental**

*Materials*

All chemicals were used without further purification. \(n\)-Octane, benzene, toluene, and deuterated water (D\(_2\)O) were purchased from Fujifilm Wako Pure Chemical, and \(n\)-heptane was purchased from Wako Pure Chemical Industries. Deuterated \(n\)-octane (C\(_8\)D\(_{18}\)) was kindly provided by Taiyo Nippon Sanso. Cyclohexane, diphenylacetylene, and 4-octyne were purchased from Tokyo Chemical Industry. Nafion perfluorinated membrane (Nafion NRE212) and Nafion perfluorinated resin ionomer solution (5 wt% in a mixture of lower aliphatic and water, Nafion DE521) were purchased from Sigma-Aldrich. Carbon-supported catalysts (46 wt% Pt/C and 29 wt% Pd/C) were purchased from Tanaka Kikinzoku Kogyo. Carbon separator sheets used as diffusers (Sigracet GDL35BC) were purchased from SGL CARBON.

*Assembly of PEM reactor for operando IR observation*

Details of the preparation method for the PEM reactor are available elsewhere.\(^1\) The procedure is briefly illustrated in Figure 1. Further details of the modification are shown for only one side of the PEM in Figure S1. Pt/C and Pd/C catalysts were spread in an area 40 × 40 mm\(^2\) at the center of each side of a Nafion film (120 × 120 mm\(^2\)) to fabricate an MEA. The MEA was covered by a carbon diffuser sheet (40 × 40 mm\(^2\)) with a hole (10 mm diameter) at the center to allow the transmission of the incident IR beam. A Teflon gasket (80 × 80 mm\(^2\)) with a space to fit the carbon sheet was then sandwiched between the MEA and a carbon separator (90 × 90 mm\(^2\)) with a central hole (12 mm diameter). Finally, the PEM reactor assembly was stabilized by end plates on both sides of the reactor; the end plates were also holed at their center. CaF\(_2\) windows were placed within the carbon separator by sealing with O-rings (not shown for simplicity.) Potentiostatic electrolyses were carried out using a potentiostat (Hokuto Denko HABF-501A).

*Acquisition of IR spectra of the MEA*

IR spectra were recorded using a Shimadzu IR Tracer-100 equipped with an MCT detector; the resolution was 4 cm\(^{-1}\), and 64 scans were averaged. The PEM reactor was pretreated by flowing humidified H\(_2\) through a water bubbler to the anode at 0 V for 60 min with the cathode chamber empty. The as-observed IR spectra before and after pretreatment are shown in Figure S2, where the range below 850 cm\(^{-1}\) is filtered by the absorption of CaF\(_2\) windows 10 mm in diameter. All the absorption bands originate from Nafion films and water-related species.\(^2\)\(^-\)\(^4\) In the spectrum of the MEA before the
pretreatment, a wide band was observed in the region 3800–2500 cm\(^{-1}\), together with another broad band at approximately 1750 cm\(^{-1}\). The former is attributed to stretching vibrations of hydrogen-bonded OH groups of \((\text{H}_2\text{O})_n\text{H}^+\) species and \(-\text{SO}_3\text{H}\) groups, whereas the latter is attributed to a bending mode of \((\text{H}_2\text{O})_n\text{H}^+\). The band at 1059 cm\(^{-1}\) arises from symmetric stretching of the \(-\text{SO}_3^-\) group, and the doublet at 979 cm\(^{-1}\) is attributed to symmetric stretching of \(\text{O}--\text{C}--\text{O}\) groups on the polymer side chains and that of \(\text{S}--\text{OH}\) of \(-\text{SO}_3\text{H}\) groups. An intense absorption saturated in the range 1400–1100 cm\(^{-1}\) includes asymmetric stretching modes of \(-\text{SO}_3^-\) and \(\text{O}--\text{C}--\text{O}\) groups and symmetric \(\text{S}=\text{O}\) stretching; however, the majority of this absorption is ascribed to symmetric and asymmetric stretching vibrations of \(\text{CF}_2\) groups. This range is completely filtered by the strong absorption of Nafion, and no information was obtained.

In the spectrum of the MEA after pretreatment, a folding feature was observed in the OH stretching region (3600–3200 cm\(^{-1}\)), originating from extremely strong absorption. The increase in intensity of the broad OH band is accompanied by the appearance of a band at 1638 cm\(^{-1}\), both of which are typical of \(\text{H}_2\text{O}\) molecules. The increase in intensity of the bands due to \(\text{H}_2\text{O}\) was only observed after the pretreatment, which indicates that the MEA was humidified. The silent feature of the other bands due to Nafion in the subtracted spectra enabled us to detect signals from surface species and solvents. The spectrum measured after pretreatment was used as a background spectrum hereafter.

The flow rate of humidified water (described as \(\text{H}_2/\text{H}_2\text{O}, \text{D}_2/\text{H}_2\text{O}, \text{H}_2/\text{D}_2\text{O}, \text{and } \text{D}_2/\text{D}_2\text{O},\) depending of the isotope used) at the anode was set at 25 mL min\(^{-1}\). At the cathode, a solvent was introduced to the reactor at optimized flow rates between 0.03 and 0.25 mL min\(^{-1}\), depending on the type of solvent. Hydrogenation of 4-octyne was carried out with a concentration of 0.4 mol L\(^{-1}\) in octane.

**NMR analysis of reaction products**

From the sample solution vent port of the reaction apparatus, a few drops of the sample solution were collected at the specified reaction times and dissolved in CDCl\(_3\) until the total volume of the solution was ~0.6 mL. The prepared solution was transferred to an NMR sample tube 5 mm in diameter, and the \(^1\text{H}\) NMR (400 MHz) spectra were acquired with a JNM ECA400 (JEOL) spectrometer. The reaction rate was estimated on the basis of the areas of the peaks assigned to octane, \textit{cis}-4-octene, and 4-octyne (Figure S6).
Supporting References


Figure S1. (a) Schematic of the structure of a half-side of an IR cell. The numbers in parenthesis are dimensions in mm. A CaF\textsubscript{2} window (\(\varnothing 10\) mm) was adjusted at the central hole. (b) Photograph of the side view of the electrochemical cell for operando IR measurement. (c) Photograph of the electrochemical cell settled in the IR system.
Figure S2. Background IR spectra of the PEM reactor before (a) and after (b) pretreatment. The region between 1400 and 1100 cm\(^{-1}\) is filtered by strong absorption of the Nafion sheet, and that below 850 cm\(^{-1}\) is filtered by CaF\(_2\) windows.
Figure S3. Comparison of intensified IR spectra reproduced from Figures 2(c), (e), and (f) so that the intensity of the band at 2030 cm$^{-1}$ is equal across the spectra. Spectra (a), (b), and (c) correspond to spectra (c), (e), and (f), respectively, in Figure 2.
Figure S4. Change in the IR spectra when the flow of gas at the anode was switched; octane solvent was constantly flowed and a bias of +200 mV was applied at the cathode. H₂/H₂O was flowed for 30 min (a), then switched to D₂/H₂O for 10 min (b) and 30 min (c). The flow was switched from D₂/H₂O again to H₂/H₂O for 10 min (d) and 30 min (e).
Figure S5. Change in the IR spectra when the flow of gas at the anode was switched; octane solvent was constantly flowed and a bias of +200 mV was applied at the cathode. H₂/H₂O was flowed for 30 min in the absence of octane (a), octane was provided for 30 min (b), and then the supply of H₂ was stopped for 30 min (c). H₂ was then supplied again for 30 min (d).
Figure S6. $^1$H NMR (400 MHz, CDCl$_3$) spectra of a) octane, b) cis-4-octene, and c) 4-actyne. The symbols “*” and “♯” mark the residual CHCl$_3$ and H$_2$O signals in CDCl$_3$, respectively. For the estimation of the reaction rate, areas of the peaks assigned to $H_a + H_c + H_d$ in octane (in (a)), $H_d$ in cis-4-octene (in (b)), and $H_c$ in 4-octyne (in (c)) were used.