In recent years, considerable research and development efforts are devoted to improving the performance of polymer electrolyte fuel cells. However, the power density and catalytic activities of these energy conversion devices are still far from being satisfactory for large-scale operation. Here we report performance enhancement via incorporation, in the cathode catalyst layers, of a ring-structured backbone matrix into ionomers. Electrochemical characterizations of single cells and microelectrodes reveal that high power density is obtained using an ionomer with high oxygen solubility. The high solubility allows oxygen to permeate the ionomer/catalyst interface and react with protons and electrons on the catalyst surfaces. Furthermore, characterizations of single cells and single-crystal surfaces reveal that the oxygen reduction reaction activity is enhanced owing to the mitigation of catalyst poisoning by sulfonate anion groups. Molecular dynamics simulations indicate that both the high permeation and poisoning mitigation are due to the suppression of densely layered folding of polymer backbones near the catalyst surfaces by the incorporated ring-structured matrix. These experimental and theoretical observations demonstrate that ionomer’s tailored molecular design promotes local oxygen transport and catalytic reactions.
Polymer electrolyte fuel cells (PEFCs) are promising power sources for automobiles. Owing to intensive research and development of fuel cell systems and materials, several automakers have commercialized fuel cell vehicles (FCVs) with the required power density and durability. However, they are still more expensive than vehicles with internal combustion engines. To reduce the system costs, it is essential to reduce the use of expensive materials and components, such as platinum, supports, membranes, ionomers, gas diffusion layers (GDLs), and bipolar plates. An effective method of cost reduction is the use of PEFCs with high power density. Hundreds of cells are currently stacked in a FCV to ensure the availability of the maximum power required sporadic aggressive acceleration. Obtaining higher power density in individual cells allows automakers to reduce the stack cost by decreasing the number of cells or by reducing the geometric electrode area. In addition, the amount of precious Pt catalyst per cell needs to be reduced, and the cells must exhibit the required durability. Motivated by these demands, the US DRIVE Fuel Cell Tech Team has set a 2025 power density target of 1.8 W cm$^{-2}$, and the New Energy and Industrial Technology Development Organization in Japan recently set a 2030 power density target of 2.5 W cm$^{-2}$ with 0.12–0.25 mg cm$^{-2}$ Pt loading. In addition, Million Mile Fuel Cell Truck (M2FCT) consortium has set a 2025 efficiency and durability target of 2.5 kW g$^{-1}$ power (1.07 A cm$^{-2}$ current density) at 0.7 V after 25,000 hour-equivalent accelerated durability test for heavy-duty vehicle applications.

The cathode catalyst layers (CLs) of PEFCs are known to strongly influence fuel cell performance. Figure 1 shows a schematic of a single cell and CL. The CL is a porous medium composed of Pt or Pt alloy nanoparticles deposited on carbon supports and perfluorinated ionomers. Oxygen molecules diffuse through the pores in the CL and dissolve in the ionomers. The dissolved oxygen molecules permeate the ionomers and react with protons and electrons on the Pt surface to produce water. Although the mechanism is not entirely clear, it is commonly accepted that oxygen transport resistance in the ionomer causes an unfavorable voltage drop. The simplest method of suppressing the voltage drop is to increase the specific Pt surface area, for example, by decreasing the Pt particle size, and thus reduce the local oxygen fluxes. However, this change has a detrimental effect on the durability because smaller particles degrade more rapidly by Ostwald ripening and particle coalescence.

An alternative method of solving this trade-off problem is to eliminate the ionomer/Pt contacts. Ionomer-free nanostructured thin films fabricated by 3M exhibit such desired environments. The ionomer-free nanostructured thin films and/or mesoscopic CL model assuming highly reduced transport in thin films compared to that in bulk ionomers because of confinement effects and/or substrate interactions.

Although the mechanism is not entirely clear, it is commonly observed that oxygen transport resistance in the ionomer causes an anomalous voltage drop owing to oxygen transport resistance in the cathode CL. The measured resistance was found to be mathematically equivalent to that of the film-like resistive layer coated on the Pt surface. In this study, the resistive layer was attributed to the ionomers, which appear as films covering the Pt surface (Fig. 1). However, the origin of the high resistance of the ionomers remains controversial. The measured high resistance cannot be explained without assuming much thicker ionomer films and/or larger carbon agglomerates than those observed in the micrographs. To elucidate the mechanistic origin of the anomalous voltage drop, intensive experiments and mathematical simulations have thus been undertaken. Kudo et al. measured the oxygen transport resistance of Nafion thin films (see its molecular structure in Fig. 2a) using microelectrodes and observed a large interfacial resistance. On the basis of experimental results, Suzuki et al. incorporated the interfacial resistance into a mathematical model and reproduced the experimental current–voltage curves reasonably well. Later, Liu et al. showed negligible resistance at the gas/ionomer interface by experiments on Nafion thin films. In order to clarify the origin of the interfacial resistance, Jinnouchi et al. and Kurihara et al. performed molecular dynamics (MD) simulations and showed that the interfacial resistance originates from the dense ionomer layer created at the ionomer/Pt interface. By contrast, a more significant bulk ionomer resistance was recently proposed on the basis of hydrogen pump experiments and a mesoscopic CL model assuming highly reduced transport in thin films compared to that in bulk ionomers because of confinement effects and substrate interactions.

The interfacial resistance decreases Pt loading is accompanied by an anomalous voltage drop owing to oxygen transport resistance in the cathode CL. The measured resistance was found to be mathematically equivalent to that of the film-like resistive layer coated on the Pt surface. In this study, the resistive layer was attributed to the ionomers, which appear as films covering the Pt surface (Fig. 1). However, the origin of the high resistance of the ionomers remains controversial. The measured high resistance cannot be explained without assuming much thicker ionomer films and/or larger carbon agglomerates than those observed in the micrographs. To elucidate the mechanistic origin of the anomalous voltage drop, intensive experiments and mathematical simulations have thus been undertaken. Kudo et al. measured the oxygen transport resistance of Nafion thin films (see its molecular structure in Fig. 2a) using microelectrodes and observed a large interfacial resistance. On the basis of experimental results, Suzuki et al. incorporated the interfacial resistance into a mathematical model and reproduced the experimental current–voltage curves reasonably well. Later, Liu et al. showed negligible resistance at the gas/ionomer interface by experiments on Nafion thin films. In order to clarify the origin of the interfacial resistance, Jinnouchi et al. and Kurihara et al. performed molecular dynamics (MD) simulations and showed that the interfacial resistance originates from the dense ionomer layer created at the ionomer/Pt interface. By contrast, a more significant bulk ionomer resistance was recently proposed on the basis of hydrogen pump experiments and a mesoscopic CL model assuming highly reduced transport in thin films compared to that in bulk ionomers because of confinement effects and substrate interactions.

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operation because of the lack of proton conduction pathways in the absence of liquid water.

Several research groups have reported significant improvements in fuel cell performance without any remarkable adverse effects by using highly oxygen-permeable ionomers (HOPIs)\(^\text{38-41}\). For example, a recent study by Katzenberg et al.\(^\text{41}\) showed that a HOPI incorporating an oxygen-permeable glassy amorphous matrix based on a perfluoro-(2-methylene-4-methyl-1,3-dioxolane) (PFMMD) backbone shown in Fig. 2b reduced the oxygen transport resistance in the CL and enhanced the power density of fuel cells. These results motivate the molecular design of ionomers to promote the local oxygen and proton transport required by the device architecture. For advanced design of cathode CL, however, further understanding of the role of the HOPI is necessary. The permeability is determined by both the bulk and interfacial permeabilities, which are strongly affected by multiple properties such as the oxygen solubility, diffusivity, interfacial permeation rate constants, and ionomer distribution in the CL\(^\text{20-22,24,42}\). Changes in the interfacial structure caused by the new ionomers can also influence the ORR activity\(^\text{43-46}\). Clarification of these relevant effects is significant for optimal arrangement of catalysts, ionomers, and support materials in the CL as well as molecular design of ionomers.

In this work, by combining analyses of single cells, microelectrodes, and single-crystal surfaces with MD simulations, we show that an HOPI incorporating a ring-structured monomer, perfluoro-(2,2-dimethyl-1,3-dioxole) (PDD)\(^\text{47}\), significantly enhances both the interfacial oxygen permeation and ORR activity. The high permeation is shown to originate from the high oxygen solubility, and the high ORR activity is attributed to the mitigation of catalyst poisoning by sulfonate anion adsorption. All these improvements originate from the PDD matrix, which prevents layered folding of the ionomer backbones on the Pt surface.

**Results and discussion**

Figure 2c shows the molecular structure of our HOPI. Its \(^{19}\)F Nuclear Magnetic Resonance (NMR) spectrum is compared to those of the Nafion ionomer and HOPI in Fig. 2a. The peak assignments of the NMR spectra were carried out using the values reported in past studies\(^\text{48-50}\). Our HOPI contains a symmetric PDD matrix, which is expected to introduce highly oxygen-permeable amorphous domains similar to those in the PFMMD matrix\(^\text{41}\). The obtained \(^{19}\)F-NMR spectra indicate the presence of the perfluorinated sulfonic-acid (PFSA)\(^\text{48}\) matrix and PDD matrix\(^\text{49,50}\) in the synthesized HOPI ionomer. A previous study\(^\text{41}\) showed that an ionomer with PFMM MD backbones had a low density of 1.86–1.89 g cm\(^{-3}\) under dry conditions compared to that of Nafion (2.04 g cm\(^{-3}\)). The density of our HOPI is also lower than that of Nafion (1.93 g cm\(^{-3}\)). The number-average molecular weights (\(M_n\)) of the Nafion ionomer and HOPI were 2.8 \times 10^4 and 3.9 \times 10^4, respectively, and the equivalent weights (EWs) were 952 and 735 g mol\(^{-1}\), respectively. The measured \(M_n\) of the Nafion ionomer is smaller than the reported value\(^\text{51}\) because of the difference in the standards used in the calibration (see details of the calibration in SI). The relative difference between Nafion and HOPI in our study indicates that the molecular weight of the HOPI does not significantly differ from that of Nafion. Although the EW of the HOPI is lower, the HOPI does not differ greatly in proton conductivity and water uptake from Nafion, as shown in Supplementary Fig. 3. This is due to the presence of the amorphous PDD domains, which do not contribute to proton conduction\(^\text{41}\). As shown in Supplementary Fig. 2c, the wide-angle X-ray scattering (WAXS) indicates that the HOPI does not exhibit the crystalline matrix peak at 0.8–1.4 Å\(^{-1}\); the PDD domains presumably suppress the backbone crystallization as in the case of the PFMMD domains\(^\text{41}\).

Figure 3a shows the current–voltage curves of membrane electrode assemblies (MEAs) with the Nafion ionomer and HOPI. The HOPI outperforms Nafion over the entire current density range at 30% and 60% relative humidity (RH) and high current density range at 90% RH. The improvement under high-current-density conditions is attributed to the reduction in the local oxygen transport resistance \(R_{other}\) by the HOPI. As shown in Fig. 3b, the \(R_{other}\) value of the MEA employing HOPI is smaller in comparison to Nafion, particularly at 30% RH. The \(R_{other}\) value of Nafion increases significantly when the RH decreases from 100% to 30%, indicating that the dry Nafion forms highly resistive films on the Pt surfaces. By contrast, the HOPI retains a low \(R_{other}\) under low-RH conditions. Unlike \(R_{other}\) as shown in Fig. 3c, the HOPI exhibits ohmic resistance of the CL higher than Nafion. Hence, the observed improvement in the current–voltage performance is attributed to the lower local oxygen transport resistance of the HOPI. The reduction in \(R_{other}\) was also observed for the HOPI with the PFMMD domains\(^\text{41}\). Detailed comparison indicates that our HOPI exhibits more significant reduction (40–50% reduction) to \(R_{other}\) than the PFMMD-based HOPI (17% reduction).

Our previous analyses using microelectrode techniques\(^\text{21,22,24}\) indicated that the local oxygen transport resistance in the CL with the Nafion ionomer is dominated by the interfacial permeation resistance of the ionomer thin film. The current study also suggests the same conclusion. Figure 4a shows the inverse of the measured limiting current density as a function of the ionomer thickness. The inverted current density approximately obeys the linear Eq. (2), and the slope and intercept provide the bulk and interfacial gas diffusion resistances, respectively (see details in the “Methods”). As summarized in Fig. 4b, the interfacial resistance of the Nafion ionomer (black solid line) is one order of magnitude higher than the bulk resistance (black dashed line). Hence, the small \(R_{other}\) of the MEA with the HOPI must be attributed to the enhanced interfacial oxygen permeation. Indeed, the interfacial resistance of the HOPI (red solid line) is only one-fifth to one-half of the resistance of Nafion (black solid line), as shown in

![Fig. 2 Molecular structures of ionomers. a-c Molecular structures of Nafion ionomer (a), HOPI with PFMMD matrix reported in ref. \(^\text{41}\) (b), and HOPI synthesized in this work (c). Density (\(\rho\)), number-average molecular weight (\(M_n\)), EW (ionomer mass per sulfonate group), and proton conductivity (\(\sigma_p\)) are also shown. The density was measured under dry conditions, and the proton conductivity shown here was obtained at 97% RH and room temperature.](https://doi.org/10.1038/s41467-021-25301-3)
Fig. 3 Electrochemical characterizations of MEAs. a Current-voltage (with closed dots) and current-power density (with open dots) curves of MEAs with Nafion ionomer (black) and HOPI (red) at 353 K and 30, 60, and 90% RH. b Local oxygen transport resistance $R_{\text{other}}$ as a function of RH. c Ohmic resistance of CLs in MEAs. All measurements were conducted twice, and the differences between two measurements were shown as error bars in all figures.

Fig. 4 Electrochemical characterizations of microelectrodes. a Inverse of the limiting current density as a function of the ionomer thickness at 353 K and 30% RH. The bulk ($R_{\text{bulk}}$) and interfacial ($R_{\text{in}}$) resistances are determined by the slope and intercept of the linear line, respectively. b Interfacial (open symbols with solid lines) and bulk (solid symbols with dashed lines) oxygen permeation resistance of ionomer thin films measured by the microelectrode technique. c, d Oxygen solubility and diffusion coefficient of ionomer thick films measured by the microelectrode technique. In b, the bulk resistance was calculated assuming an ionomer thickness of 5 nm. The error bars shown in (b) were calculated from fitting errors assuming the normal error distributions, and the error bars shown in (c) and (d) show the differences between two measurements.
Owing to the layered folding, the Naflon folded to form a layered structure parallel to the Pt surface. By becomes 10% thinner than the HOPI thin study on the Naflon(0.3 - 0.67 nm) from the Pt surface) is 20% higher than the density of the HOPI thin film. Near the Pt surface in particular (Z = 0.3 - 0.67 nm), the density of the HOPI is low. The MD snapshots and density profiles indicate that the polytetrafluoroethylene (PTFE) backbones of the Nafion ionomer are folded to form a layered structure parallel to the Pt surface. By contrast, the HOPI backbones form a more disordered structure. Owing to the layered folding, the Nafion ionomer thin film becomes 10% thinner than the HOPI thin film. In addition, the local density of the Nafion adlayer near the Pt surface (0.3 - 0.67 nm from the Pt surface) is 20% higher than the density of the HOPI in the same region. As demonstrated in our previous study on the Nafion ionomer, the dense ionomer layer significantly reduces the oxygen solubility and increases the permeation barrier at the interface between Pt and ionomer. Accordingly, the PDD matrix prevents backbone folding and enhances the interfacial oxygen permeability near the Pt surface. Another notable conclusion provided by our MD simulations is that the enhanced solubility greatly contributes to the high oxygen solubility, which enhances the oxygen permeation through the ionomer/Pt interface. The MD simulations also indicated that the interfacial oxygen permeation remains a bottleneck of the oxygen transport in the HOPI. Electrochemical measurements using single-crystal electrodes indicated that high ORR activity is realized by the mitigation of catalyst poisoning by sulfonate anions. MD simulations give evidence that both effects arise from the ring-structured backbone matrix, which prevents the layered backbone folding of the ionomer near the catalyst surface. The experimental and theoretical observations presented herein indicate that a tailored molecular design of the ionomer makes it possible to simultaneously realize high interfacial oxygen transport and high ORR activity.

Methods

**Ionomer synthesis.** The ionomer was synthesized in two steps, polymerization and hydrolysis, as shown schematically in Supplementary Fig. 1. PDD (97%, P&M) and perfluorooctanoate(3-oxapent-4-ene) sulfon fluoride (PSVE) (99%, SynQuest) were distilled prior to use. Polymerization was performed under inert atmosphere by stirring a mixture of PDD (4.0 g, 16.4 mmol), PSVE (13.7 g, 48.9 mmol), and a solution (0.08 cm³, 0.08 mol dm⁻³) of a polymerization initiator, [CF₃(CF₂)₂C(O)Cl (Tokyo Chemical Industry Co., Ltd) in a Vertrel® XF solvent mixture of PDD (4.0 g, 16.4 mmol), PSVE (13.7 g, 48.9 mmol), and a solution (0.08 cm³, 0.08 mol dm⁻³) of a polymerization initiator, [CF₃(CF₂)₂C(O)Cl (Tokyo Chemical Industry Co., Ltd) in a Vertrel® XF solvent mixture. After the solvent was removed, the residual solid polymer was immersed in a HCl aqueous solution (1 mol dm⁻³) and heated at 373 K after polymerization, and the copolymerized polymer with the side-chain end of the SO₂F group(2.5 g) was obtained. The copolymerized polymer (1.05 g) was mixed with a NaOH aqueous solution (1 mol dm⁻³) in a Teflon crucible and hydrolyzed by heating the solution at 403 K for 17 h. After the solvent was removed, the residual solid polymer was immersed in a HCl aqueous solution (1 mol dm⁻³) and heated at 353 K. After the polymer was washed with ultrapure water several times and dried at 353 K, an ionomer with the side-
chain end of the SO3H group (0.86 g) was obtained. After synthesis, the molecular weight, 19F-NMR, WAXS, EW, density, water uptake, and proton conductivity were measured. The measurement methods are summarized in Supplementary Information Section 2.

**Membrane electrode assembly.** A Pt/Vulcan catalyst (TEC10V30E, Tanaka Kikinzoku Kogyo, Tokyo, Japan), an ionomer solution (Nafion D2020, Chemours, or HOPI), and a solvent were mixed and agitated by ultrasonic vibration so that the final solvent composition became water/ethanol/propanol 0.50/0.44/0.06 weight ratio for Nafion and water/ethanol/propanol/proplylene glycol 0.50/0.02/0.38/0.10 weight ratio for HOPI. In the HOPI solution, propylene glycol was mixed to prevent formations of cracks in the catalyst layer, and propanol weight ratio was increased to dissolve the ionomer homogeneously. The ionomer/carbon weight ratio was 0.75. This ink was applied to a PTFE sheet by a doctor blade process and dried to form a catalyst layer sheet with a Pt loading of 0.12 mgPt cm$^{-2}$. This catalyst sheet (1 cm$^2$) was transferred to a Nafion membrane (NR-211) by a decal method using hot pressing (60 kgf cm$^{-2}$, 413 K, 5 min). An anode CL was formed similarly using Pt/Vulcan at 0.2 mgPt cm$^{-2}$ and an ionomer/carbon weight ratio of 0.75 to form an MEA. A single cell was assembled using the MEA and GDL substrates (TGP-H-030, Toray) with microporous layers and gold-plated copper current collectors with a straight channel flow field (0.4-mm-wide channels and lanes).

Electrochemical measurements of the single cells were performed using protocols similar to those recommended by Fuel Cell Commercialization Conference of Japan (FCCJ)$^{54}$ and EU harmonized testing protocols$^{55}$. Detailed conditions were modified to adapt the protocols to our single cell and targets of this study. Details are described in Supplementary Information Section 3. All measurements were carried out using a charge/discharge unit (Hokuto Denko, Japan) with a fuel cell testing system (Chino Co., Tokyo, Japan). The reactant gas (hydrogen or oxygen) and nitrogen were mixed and humidified by bubbling through water at controlled temperatures. The current–voltage characterizations of the MEA are described in detail in Supplementary Information Section 3. The local oxygen transport resistance in the MEA was measured using the method proposed by Ono et al.$^{18}$. In this method, the total oxygen transport resistance $R_{\text{total}}$ at the limiting current defined by Baker et al.$^{38}$ is separated into the molecular diffusion
resistance \( R_{\text{bulk}} \) and remaining resistance \( R_{\text{other}} \):

\[
R_{\text{total}} = \frac{4F \Delta G_{\text{f}}}{j_L} = R_{\text{bulk}} + \frac{p}{p_0} + R_{\text{other}},
\]

where \( F \) is the Faraday constant (C mol\(^{-1}\)), \( \Delta G_{\text{f}} \) is the concentration of oxygen molecule (mol m\(^{-3}\)), \( j_L \) is the limiting current (A m\(^{-2}\)), \( p_t \) is the total pressure (Pa), and \( p_0 \) is the reference total pressure (0.1 MPa). The first resistance in Eq. (1) is attributed mainly to intermolecular diffusion in the GDL, which possesses relatively large pores, where diffusion coefficients are inversely proportional to the total pressure. The second resistance is attributed to the diffusion in the CL having small pores and thin ionomer, where the gas transport is dominated by pressure-independent Knudsen diffusion and diffusion in the ionomer and liquid water\(^{21,22,24,26,27} \). To determine \( R_{\text{other}} \), the limiting current density \( j_L \) of the MEA was measured by varying the total pressure \( p_t \). \( R_{\text{bulk}} \) and \( R_{\text{other}} \) were determined as the slope and intercept, respectively, of a plot of \( R_{\text{total}} \) versus \( p_t \). The measurement is explained further in Supplementary Information Section 3. In the local oxygen transport resistance, the ohmic resistance of the proton exchange membrane (PEM) and CLs was measured by the AC impedance method\(^{25} \). The experimental conditions are also described in Supplementary Information Section 3.

**Microelectrodes.** The interfacial oxygen permeation resistance of the ionomer was measured using the microelectrode technique developed in ref. \(^{21} \). Assuming the presence of constant bulk and interfacial oxygen permeation resistances through the ionomer, the limiting current density \( j_L \) of the ORR should obey the following equation:

\[
\frac{4F \Delta G_{\text{f}}}{j_L} = \frac{RTD_{\text{O}_2}}{K_{\text{O}_2}} \Delta \bar{\delta} + \frac{1}{RTK_{\text{O}_2}} \left( \frac{1}{k_{\text{new}}/\rho_t} + \frac{1}{k_{\text{old}}/\rho_{\text{gas}}} \right),
\]

where \( R \) is the gas constant (J K\(^{-1}\) mol\(^{-1}\)), \( T \) is the temperature (K), \( D_{\text{O}_2} \) is the diffusion coefficient of oxygen molecule in the bulk ionomer (m\(^2\) s\(^{-1}\)), \( K_{\text{O}_2} \) is the Henry constant (mol m\(^{-3}\) Pa\(^{-1}\)), \( \Delta \bar{\delta} \) is the ionomer thickness (nm), and \( k_{\text{new}}/\rho_t \) and \( k_{\text{old}}/\rho_{\text{gas}} \) are the apparent rate constants of oxygen permeation through the ionomer/Pt and ionomer/gas interfaces (m s\(^{-1}\)), respectively. The bulk resistance coefficient \( R = 1/T \Delta \bar{\delta} / K_{\text{O}_2} \) and the interfacial resistance \( R = 1/T \Delta \bar{\delta} / K_{\text{O}_2} \) can be determined from the slope and intercept, respectively, of a plot of \( j_L \) versus \( \Delta \bar{\delta} \). As discussed in our previous study\(^{21} \), the ionomer must be thin enough to resemble the ionomer thin films in the CL, and to enable accurate determination of the resistance. The sample preparation and measurement are described in Supplementary Information Section 4.

Although the thin film measurement provides the bulk and interfacial resistances, these parameters both depend on multiple properties of the ionomer: the solubility, diffusivity, and interfacial permeation rate constants. For further separation, we measured the limiting current transition of the ORR, which flows through the interface between the ionomer thick film and the Pt microelectrode after the potential step measurements under oxygen atmosphere. When the potential is stepped from 1.1 to 0.4 V (vs. RHE), for example, the transitional limiting current controlled by oxygen transport inside the thick ionomer film is observed. Assuming that the ionomer film is thick enough that boundary effects are negligible, the time-dependent limiting current density can be described by the following Cottrell-type equation\(^{38,50} \):

\[
j_L(t) = \frac{4F \Delta G_{\text{f}}}{RT} \frac{K_{\text{O}_2} D_{\text{O}_2}}{R_t} \left[ 1 + \frac{R_t}{\sqrt{\pi D_{\text{O}_2} t}} + 0.2732 \exp \left( -0.3911 R_t / \sqrt{\pi D_{\text{O}_2} t} \right) \right].
\]

where \( t \) is the time from the potential step, and \( R_t \) is the radius of the microelectrode. \( K_{\text{O}_2} \) and \( D_{\text{O}_2} \) can be determined by fitting Eq. (3) to the measured transitional limiting current density. The sample preparation and measurement are also described in further detail in Supplementary Information Section 4.

**Single-crystal model electrodes.** A (111)-oriented Pt single-crystal disk (99.99%, 0.196 cm\(^2\), MaTeck) was annealed by electromagnetic inductive heating for more than 10 min at 1400–1650 K in a mixed H\(_2\) and Ar flow (3% H\(_2\), Taiyo Nippon Sanso: H\(_2\); 99.99999%, Ar: 99.99999%). The annealed specimen was slowly cooled to room temperature in a flow of the same mixed gas, and the Pt(111) surface was covered by a droplet of ultrapure water (Milli-Q, 18.2 MΩ). The Pt(111) surface was then coated with a thin film of an ionomer by dropping 20 μL of a 0.005 wt% ionomer solution (20 wt% dimethylformamide aqueous solution), and the solvent was evaporated from the surface in an Ar stream; finally, the film was heated at 420 K in the Ar stream to improve its physicochemical stability. Further details are given elsewhere\(^{35} \). Equal amounts by weight of the ionomers were deposited on the Pt(111) surface to a thickness of ~35 nm. Cyclic and linear-sweep (positive scan) voltammetries were carried out in a 0.1 mol dm\(^{-3}\) HClO\(_4\) solution without an ionomer (blue dashed line in c). The plots in bar graphs are the measured data, and error bars show their root mean square differences. Bars show their averages based on two to four separate measurements.
oxygen gas was applied to the ionomer thin film. During the MD simulation, some oxygen molecules permeated the ionomer and reached the Pt surface. By translating these oxygen molecules back to the upper limit of the gaseous oxygen layer, steady-state oxygen permeation was obtained during the MD simulation. From the number of transferred oxygen molecules, the oxygen permeation flux was calculated and directly compared with the experimentally measured limiting current density. During the MD simulations, the temperature was maintained at 353 K by an NVT ensemble realized by the weak coupling method. For each condition, three initial structures were prepared, and a 150 ns MD simulation was executed for each initial structure to calculate the oxygen permeation flux. The obtained fluxes were averaged and used to calculate the limiting current density. In addition to the Pt/ionomer interfaces, the bulk ionomers were simulated to compute the ionomer densities and diffusion coefficients of oxygen molecule in the ionomers. Oxygen molecules were located in the bulk ionomer models, and the diffusion coefficients were calculated from the slopes of the mean square displacements versus time. The ionomer density was calculated from the system volume. Similar to the ionomer/Pt interfaces, three initial structures were prepared, and a 10 ns MD simulation for each structure was executed. Obtained densities and diffusion coefficients were averaged. Ionomer thin films isolated in the high-pressure oxygen gas (20 MPa) were also simulated to calculate the solubility of oxygen in the thin films. Two initial structures were prepared for each condition, and a 30 ns MD simulation at 353 K for each structure was carried out. The solubility was calculated by counting the number of oxygen molecules in the region in which the ionomer density is higher than 90% of the bulk density. Further details of the system size, model preparation, and simulations are described in ref. and Supplementary Information Section 5.

**Reporting summary.** Further information on research design is available in the Nature Research Reporting Summary linked to this article.

**Data availability**

All datasets related to this study are available from the corresponding author upon reasonable request. All electrochemical, spectroscopic, and simulation source data generated in this study are provided in the Supplementary Information/Source Data file. Source data are provided with this paper.

**Code availability**

The molecular dynamics simulation code is a software developed internally in Toyota Central R&D Labs., Inc. and is not publicly available.

Received: 15 December 2020; Accepted: 19 July 2021

**References**

1. Borup, R. et al. Scientific aspects of polymer electrolyte fuel cell durability and degradation. Chem. Rev. 107, 3904–3951 (2007).
2. Gasteiger, H. A. & Markovic, N. M. Just a dream—or future reality? Science 324, 48 (2009).
3. Debe, M. K. Electrocatalyst approaches and challenges for automotive fuel cells. Nature 486, 43–51 (2012).
4. Kongkanand, A. & Mathias, M. F. The priority and challenge of high-power performance of low-platinum proton-exchange membrane fuel cells. J. Phys. Chem. Lett. 7, 1127–1137 (2016).
5. Kusoglu, A. & Weber, A. Z. New Insights into perfluorinated sulfonic-acid ionomers. Chem. Rev. 117, 987–1104 (2017).
6. Kulkarni, A., Siahrostami, S., Patel, A. & Narskov, J. K. Understanding catalytic activity trends in the oxygen reduction reaction. Chem. Rev. 118, 2302–2312 (2018).
7. Yoshida, T. & Kojima, K. Toyota MIRAI fuel cell vehicle and progress toward a future hydrogen society. Interface Mag. 24, 45–49 (2015).
8. Pollet, B. G., Kocha, S. S., Sompalli, B. & Wagner, F. T. Activity benchmarks and requirements for Pt, Pt alloy, and non-Pt oxygen reduction catalysts for PEMFCs. Appl. Catal. B: Environ. 56, 9–35 (2005).
9. Kudo, K., Suzuki, T. & Morimoto, Y. Analysis of oxygen dissolution rate from gas phase into Nafion surface and development of an agglomerate model. ECS Trans. 33, 1495–1502 (2010).
10. Ono, Y. et al. The analysis of performance loss with low platinum loaded cathode catalyst layers. ECS Trans. 28, 69–78 (2010).
11. Greszler, T. A., Caud, D. & Sinha, P. The impact of platinum loading on oxygen transport resistance. J. Electrochem. Soc. 159, F831–F840 (2012).
12. Suzuki, T., Kudo, K. & Morimoto, Y. Model for investigation of oxygen transport limitation in a polymer electrolyte fuel cell. J. Power Sources 222, 379–383 (2013).
13. Kudo, K., Innouchi, R. & Morimoto, Y. Humidity and temperature dependences of oxygen transport resistance of Nafion thin film on platinum electrode. Electrochem. Acta 209, 682–690 (2016).
14. Kudo, K. & Morimoto, Y. Analysis of oxygen transport resistance of Nafion thin film on Pt electrode. ECS Trans. 50, 1487–1494 (2013).
15. Liu, H., Epting, W. K. & Lister, S. Gas transport resistance in polymer electrolyte thin films on oxygen reduction reaction catalysts. Langmuir 31, 9853–9858 (2015).
16. Innouchi, R., Kudo, K., Kitano, N. & Morimoto, Y. Molecular dynamics simulations on O2 permeation through Nafion ionomer on platinum surface. Electrochem. Acta 188, 767–776 (2016).
17. Kurthbauer, Y., Mabuchi, T. & Tokumasa, T. Molecular dynamics study of oxygen transport resistance through ionomer thin film on Pt surface. J. Power Sources 414, 263–271 (2019).
18. Schulter, T. et al. Fuel-cell catalyst-layer resistance via hydrogen limiting-current measurements. J. Electrochem. Soc. 166, F3020–F3031 (2019).
19. Mu, Y.-T., Weber, A. Z., Gu, Z.-L. & Tao, W.-Q. Mesoscopic modeling of transport resistances in a polymer-electrolyte fuel-cell catalyst layer: Analysis of hydrogen limiting currents. Appl. Energy 255, 113895 (2019).
20. Vanyà, P., Sharmam, J. & Elliott, J. A. Mesoscale simulations of confined Nafion thin films. J. Chem. Phys. 147, 214904 (2017).
21. Modestino, M. A. et al. Self-assembly and transport limitations in confined Nafion films. Macromolecules 46, 867–873 (2013).
22. Ferreira, P. J. et al. Instability of Pt/C electrocatalysts in proton exchange membrane fuel cells. J. Electrochem. Soc. 152, A2256–A2271 (2005).
23. Tang, L. et al. Electrochemical stability of nanometer-scale Pt particles in acidic environments. J. Am. Chem. Soc. 132, 596–600 (2010).
24. Innouchi, R., Toyoda, E., Hatanaka, T. & Morimoto, Y. First principles calculations on site-dependent dissolution potentials of supported and unsupported Pt particles. J. Phys. Chem. C. 114, 17557–17568 (2010).
25. Shinozaki, K., Morimoto, Y., Privov, B. S. & Kocha, S. S. Suppression of oxygen reduction reaction activity on Pt-based electrocatalysts from ionomer incorporation. J. Power Sources 325, 745–751 (2016).
26. Iden, H. & Ohuma, A. An in situ technique for analyzing ionomer coverage in cathode catalyst layers. J. Electrochem. Chem. 603, 34–41 (2013).
27. Kamitaka, Y., Takeishi, T. & Morimoto, Y. MgO-templated mesoporous carbon as a catalyst support for polymer electrolyte fuel cells. Catalysts 8, 230 (2018).
28. Yarlagadda, V. et al. Boosting fuel cell performance with accessible carbon mesopores. ACS Energy Lett. 3, 618–621 (2018).
29. Takeshita, T., Kamitaka, Y., Shinozaki, K., Kudama, K. & Morimoto, Y. Evaluation of ionomer coverage on Pt catalysts in polymer electrolyte membrane fuel cells by CO stripping voltammetry and its effect on oxygen reduction reaction activity. J. Electroanal. Chem. 871, 114250 (2020).
30. Yamada, K., Hommura, S. & Shimohira, T. Effect of high oxygen permeable ionomers on MEA performance for PEFC. ECS Trans. 50, 1495–1501 (2013).
31. Shimizu, R., Park, Y.-C., Kakinuma, K., Iyama, A. & Uchida, M. Effects of both oxygen permeability and ion exchange capacity for cathode ionomers on the performance and durability of polymer electrolyte fuel cells. J. Electrochem. Soc. 165, F3063–F3071 (2018).
32. Rolli, A., Oldani, C., Merlo, L., Facchi, D. & Ruffo, R. Point of view on high performance and permeability for application in catalytic polymeric electrolyte membrane fuel cell. J. Power Sources 396, 95–101 (2018).
33. Katzenberg, A. et al. Highly permeable sulfonated sulfuric acid ionomers for improved electrochemical devices: insights into structure–property relationships. J. Am. Chem. Soc. 142, 3742–3752 (2020).
34. Ott, S. et al. Ionomer distribution control in porous carbon-supported catalyst layers for high-power and low Pt-loaded proton exchange membrane fuel cells. Nat. Mater. 19, 77–85 (2020).
Acknowledgements
We would like to thank Dr. Masashi Harada for the WAXS measurements and Dr. Ryuichi Murase for his careful proofreading of the manuscript.

Author contributions
A.S. synthesized a HOPI and measured its physical properties through discussion with N.H. N.K. and S.M. fabricated the MEAs and performed the electrochemical characterizations. Kenji Kudo developed the microelectrode techniques. Kenji Kudo and N.K. fabricated thick and thin ionomer films and performed the microelectrode measurements. Kensaku Kodama performed the electrochemical characterizations of single-crystal electrodes. R.J. conducted the MD simulations, analyzed the experimental and theoretical data through discussing with N.K., Kenji Kudo, Kensaku Kodama, K.S. and T.S. R.J. and A.S. wrote the manuscript. All authors discussed the results and checked the manuscript.

Competing interests
The authors declare no competing interests.

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Peer review information
Nature Communications thanks Claudio Oldani, Graham Smith and the other anonymous reviewers for their contribution to the peer review of this work. Peer reviewer reports are available.

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