

Effects of Microstructure on Electrochemical Reactivity and Conductivity in Nanostructured Ceria Thin Films

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ABSTRACT

The proton conductivity in functional oxides is crucial in determining electrochemistry and transport phenomena in a number of applications such as catalytic devices and fuel cells. However, single characterization techniques are usually limited in detecting the ionic dynamics at the full range of environmental conditions. In this report, we probe and uncover the links between the

microstructure of nanostructured ceria (NC) and parameters that govern its electrochemical reaction and proton transport, by coupling experimental data obtained with time-resolved Kelvin probe force microscopy (tr-KPFM), electrochemical impedance spectroscopy (EIS), and finite element analysis. It is found that surface morphology determines the water splitting rate and proton conductivity at 25 °C and wet conditions, where protons are mainly generated and transported within surface physisorbed water layers. However, at higher temperature (i.e., ≥ 125 °C) and dry conditions, when physisorbed water evaporates, grain size and crystallographic orientation become significant factors. Specifically, the proton generation rate is negatively correlated with the grain size, whereas proton diffusivity is facilitated by surface {111} planes and additional conduction pathways offered by cracks and open pores connected to the surface.

KEYWORDS. nanostructured ceria, water splitting reaction, proton conduction, microstructure, energy discovery platforms, tr-KPFM

1. INTRODUCTION

The electrochemical reaction and transport phenomenon of solid ionic conducting materials is crucial in many energy applications, ranging from energy storage and conversion materials, to catalysts and membranes.¹⁻³ Particularly, nanostructured ceria (NC), a mixed ionic-electronic conductor, has been extensively studied as electrolyte in solid oxide fuel cells, catalytic devices, gas sensors, etc.⁴⁻⁷ Being a polar oxide, NC can strongly interact with the environment, e.g., with water vapor, which may significantly affect the material properties during device operation.⁸⁻¹¹ Typically, water can be physi- or chemisorbed on the NC surface and grain boundaries. In external electric field, the adsorbed water may split into protons and/or hydroxyl groups (in addition to oxygen and hydrogen gas) that transport along the material. It is believed that the mechanisms of water splitting and transport process are controlled by the nanoscale details of the NC structure.¹² ¹³ However, the direct correlation of the NC's microstructure with conduction properties is still under debate. For example, it is still debatable whether the proton conductivity occurs along the grain boundaries, residual pores and cracks, or along specific facets of the nano-crystals.¹³⁻¹⁸

In this study, energy discovery platforms¹⁹ – nanofabricated devices for combined in situ microscopy and spectroscopy characterization – were utilized to uncover the correlation between microstructure and the ionic conduction properties. Energy discovery platforms enable multiple characterization techniques on a single sample through a simple set-up, which not only allows the detection of full range of environmental conditions, and also eliminates the data fluctuation originated from different samples used for different characterization methods: using the same preparation method, two batches of samples are not necessarily identical in their microstructure, composition, etc. Here, time-resolved Kelvin probe force microscopy (tr-KPFM) and

electrochemical impedance spectroscopy (EIS) were employed to study the conductivity of NC under controlled environmental (temperature and humidity) conditions.

EIS, with a well-established measurement and analysis procedure, is one of the most widely used techniques in electrochemical studies. However, it is often of a more limited scope at low temperatures, especially for thin films' characterization on the nanoscale, due to the relatively weak ionic conductivity in these conditions.¹³ On the other hand, tr-KPFM detects the temporal- and spatial-resolved surface potential variation on the nanoscale, and can detect minute potential changes due to charge transport along the surface, when the flowing currents are below the detection limit of modern current amplifiers.²⁰ In recent years, tr-KPFM has been successfully used in studying surface transport phenomena in functional oxides, and it is believed to be an important supplementary technique for EIS due to its high resolution and sensitivity.^{19, 21}

To understand the relationship between the NC microstructure and its electrochemical reactivity in different environmental conditions, thin films with different surface roughness, grain size and the crystallographic orientation were prepared through pulsed laser deposition (PLD), chemical solution deposition (CSD) and sputtering (SD). The fundamental parameters for electrochemical reactions and transport phenomena were obtained through tr-KPFM and EIS measurements at controlled temperature and humidity conditions, and correlated to the microstructure. It was found that all the considered microstructural features impact the conductivity in NC films, but their effects are dominant at different environmental conditions due to activation of different electrochemical processes.

2. EXPERIMENT

2.1. Thin Film Fabrication. An insulating Si_3N_4 layer (≈ 500 nm thick) was deposited onto a Si (100) wafer by low-pressure chemical vapor deposition (LPCVD) in a mixture of NH_3 ($17 \text{ cm}^3/\text{min}$ at $T=273.15 \text{ K}$ and $p=101325 \text{ Pa}$, or sccm) and H_2SiCl_2 ($100 \text{ cm}^3/\text{min}$ at $T=273.15 \text{ K}$ and $p=101325 \text{ Pa}$, or sccm), at 21 Pa (158 mTorr) and $835 \text{ }^\circ\text{C}$. NC thin films with thickness of ≈ 100 nm were fabricated on $\text{Si}_3\text{N}_4/\text{Si}$ substrates via PLD, CSD and SD. For PLD, a KrF excimer laser with a wavelength of 248 nm and a pulse width of 25 ns was focused on the target with a spot area of about 2 mm^2 . The CeO_2 target was prepared by pressing CeO_2 powders (99.99 % Reactor Grade) into a $1 \frac{1}{4}$ " (31.75 mm in dia.) disk, and annealing at $1200 \text{ }^\circ\text{C}$ for 24 hours. The PLD thin films were prepared at $500 \text{ }^\circ\text{C}$ and $700 \text{ }^\circ\text{C}$ substrate temperature under 13.3 Pa (0.1 Torr) oxygen base pressure, and at $700 \text{ }^\circ\text{C}$ substrate temperature under high vacuum ($<0.13 \text{ mPa}$ or 10^{-6} Torr). The target-to-substrate distance was 40 mm , and silver paste was used to provide thermal contact between the sample holder and the deposition substrate. The laser energy density was about $1.5 \text{ J}/\text{cm}^2$ with a repetition rate of 10 Hz . The total deposition time was 5 min and the estimated growth rate was about 0.3 nm/s . For CSD thin films, a 0.2 mol/L ceria precursor was prepared by dissolving $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in ethylene glycol, followed by mixing at $80 \text{ }^\circ\text{C}$ in an oil bath for 3 days. The as-prepared solution was spin-coated onto the substrate at a rotation speed of 3000 min^{-1} for 30 s , followed by pyrolysis at $400 \text{ }^\circ\text{C}$ on a hot plate surface for 1 minute. After 6 deposition and pyrolysis steps, the sample was rapid thermally annealed for 1 min at $700 \text{ }^\circ\text{C}$ (ramp rate $\approx 100 \text{ }^\circ\text{C/s}$) to crystalize the film and remove the eventual remaining organics. For SD films, a PVD RF Sputterer with a $99.9 \text{ } \%$ CeO_2 target was used. The $\text{Si}/\text{Si}_3\text{N}_4$ substrate was placed about 10 cm above the target. Ceria was deposited at 80 W for 40 min in argon atmosphere (0.67 Pa , or $5 \cdot 10^{-3} \text{ Torr}$).

2.2. Lateral Electrode Device Fabrication. Lateral Cr/Pt electrodes (20 nm/80 nm thick) were created by evaporation and patterned by a lift-off method. The electrodes were 10 μm wide and with inter-electrode distance of 50 μm . Each die was glued to a chip holder and the appropriate ground and bias electrode were wire-bonded to the chip-level contacts.

2.3. Microstructure Characterization. The surface topography of NC thin films was characterized by an atomic force microscope (AFM) in tapping mode. The crystal structure was characterized by an X-ray diffractometer (Cu $K\alpha=0.15418\text{ nm}$). The surface and cross sectional microstructure were imaged in a scanning electron microscope (SEM).

2.4. Electrochemical Reactivity and Conductivity Measurements. The tr-KPFM measurements were performed on a commercial AFM. Cantilevers with conductive Cr/Pt coated tips (resonance frequency $\approx 75\text{ kHz}$) were used. An external lock-in amplifier was used for signal processing, and a function generator applied AC waveforms to the tip. A 50 $\text{M}\Omega$ resistor was connected in series to the NC device to prevent short circuit. Data processing was performed using custom-written codes. Some of the outlier points in the mappings and averaged data that corresponded to abrupt changes in topography (SPM tip encountering surface particle or electrode edge) were removed manually. Measurements were performed in a temperature ranging from 25 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$, and relative humidity (RH) ranging from 0 % to 90 % (as measured at 25 $^{\circ}\text{C}$) using a gas cell.

A schematic of the tr-KPFM setup is shown in Figure 1a. During measurements, a 15 V of DC bias and 1V of AC bias ($\omega=44\text{ kHz}$) were applied to the cantilever. The tip is sequentially positioned on each pixel of a rectangular grid (30×3 pixels in this study) overlaid on the NC surface spanning the two electrodes. Meanwhile, a step function of DC bias – 30 V for the first 10

s and 0 V for the next 10 s – was applied between the two lateral electrodes, and repeated for all the pixels (30×3). The surface potential change as a function of time was then recorded at each pixel, and averaged over points equidistant from each electrode to create potential profiles, shown in Figure 1b as an example. These profiles show that in proximity of the biased electrode, the surface potential increases during the bias-on stage (polarization) and decreases during the bias-off stage (relaxation), presumably due to the accumulation and dissipation of protons (Equation 1). Detailed description of tr-KPFM and discussions of ionic dynamics on NC surface have been previously reported.^{19, 25}



The complex impedance measurements were performed on the same samples for tr-KPFM measurements at controlled RH in a gas cell. The amplitude of the exciting signal was 1 V, with a frequency ranging from 0.1 Hz to 7 MHz.

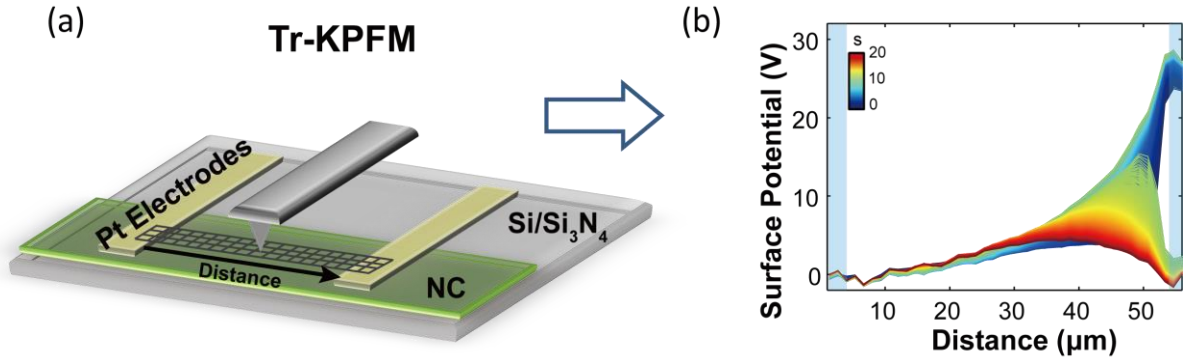


Figure 1. (a) Schematics of tr-KPFM set-up and (b) a representative averaged surface potential mapping as a function of distance and time obtained from tr-KPFM. The two blue stripes represent lateral electrodes.

3. RESULTS AND DISCUSSION

3.1. Crystal structure

The surface topography and cross sectional microstructure were characterized by scanning electron microscopy (SEM), and are shown in Figure 2. All films have similar thickness ranging from approximately 80 nm to 100 nm, and show good adhesion to the substrate, regardless of the preparation method. The microstructure of the films, however, is largely dependent on the preparation method and growth conditions. The films grown by PLD at 500 °C and 13.3 Pa (0.1 Torr) oxygen pressure (PLD500, Figures 2a and 2f) have an extremely rough surface, with grain size ranging from 20 to 50 nm. The films deposited by PLD at 700 °C and 13.3 Pa (0.1 Torr) O₂ (PLD700, Figures 2b and 2g) have lower surface roughness, and exhibit a similar grain size. The PLD films deposited in a vacuum at 700 °C (PLD700HV, Figures 2c and 2h) have columnar grains, but a ~~smoother~~ **smoother** surface, albeit with cracks and porosity area connecting to the surface. The films prepared by CSD and SD have smaller grains, with an average grain size of about 10 nm. The surface roughness of each film was measured by AFM and summarized in Table 1. The PLD500 films have the highest surface roughness (R_g), ≈ 9.8 nm. The PLD700 and CSD films have lower R_g , ≈ 2.6 nm and 1.9 nm, respectively. And the PLD700HV and SD films have the lowest R_g , ≈ 1.0 nm and 0.8 nm, respectively.

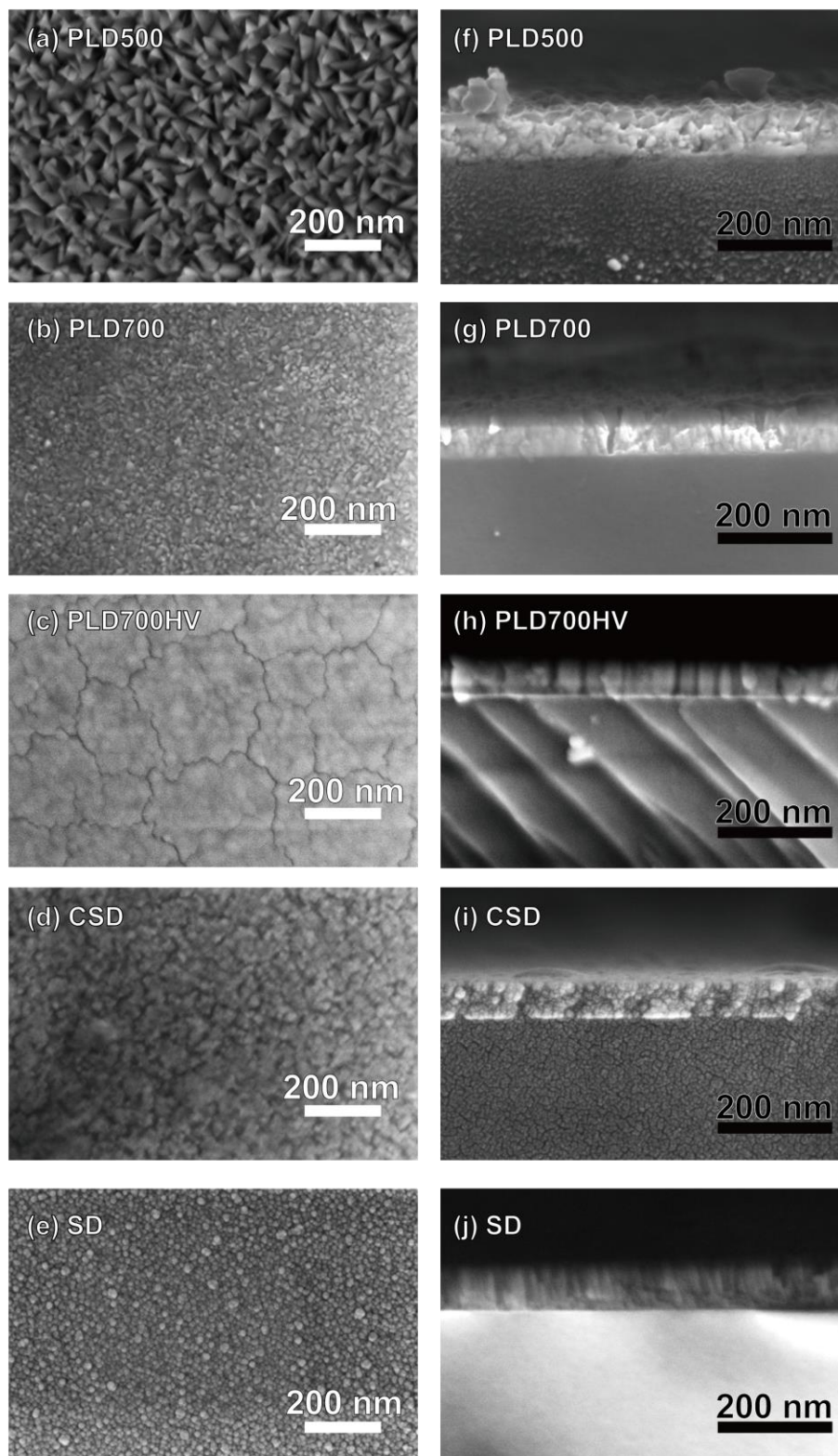


Figure 2. Representative surface (a-e) and cross sectional (f-j) SEM images for PLD500 (a, f), PLD700 (b, g), PLD700HV (c, h), CSD (d, i) and SD (e, j) films. The scale bar length is 200 nm.

Table 1. Structural properties of NC thin films.

	PLD500	PLD700	PLD700HV	CSD	SD
Surface roughness R_g (nm)	9.8	2.6	1.0	1.9	0.8
Grain size (nm)	24 ± 2	41 ± 2	37 ± 3	14 ± 1	9 ± 1
Lotgering factor for {111}	0.06	-0.27	0.92	0.45	0.72

Figure 3 illustrates representative X-ray diffraction (XRD) patterns for the films processed through the different approaches. The patterns are compared with the Joint Committee on Powder Diffraction Standards data of 34-0394, and confirm the presence of polycrystalline ceria. The average grain size for each film is estimated from the Scherrer equation, $D = \frac{k\lambda}{\beta \cos\theta}$ – where β is the full-width at half maximum (FWHM), $k=0.9$ is a constant, λ is the wavelength of the X-ray radiation and θ is the Bragg angle – as reported in Table 1. The films deposited by PLD show sharper peaks, and the calculated grain sizes are approximately $24 \text{ nm} \pm 2 \text{ nm}$, $41 \text{ nm} \pm 2 \text{ nm}$ and $37 \text{ nm} \pm 3 \text{ nm}$ for PLD500, PLD700 and PLD700HV films, respectively. The films prepared by CSD and SD have much wider peaks, and the corresponding grain sizes are estimated at $14 \text{ nm} \pm 1 \text{ nm}$ and $9 \text{ nm} \pm 1 \text{ nm}$, respectively. The calculated grain sizes have error bars that reflect one standard deviation from multiple XRD measurements, and are consistent with the SEM observations. To quantify the preferred crystallographic orientation of the samples, the Lotgering factors for {111} planes, $f_{\{111\}}$, were calculated.^{22, 23} A Lotgering factor of 0 means that the crystals are randomly oriented. As summarized in Table 1, PLD700HV, SD, CSD and PLD500 samples has {111} preferred orientation, with $f_{\{111\}}$ being 0.92, 0.72, 0.45, and 0.06, respectively. PLD700

sample does not have {111} preferred orientation. It is {110} preferred, with $f_{\{110\}}$ being 0.21. However, for better understanding of the effect of {111} orientation, the $f_{\{111\}}$ is still calculated, which is -0.27.

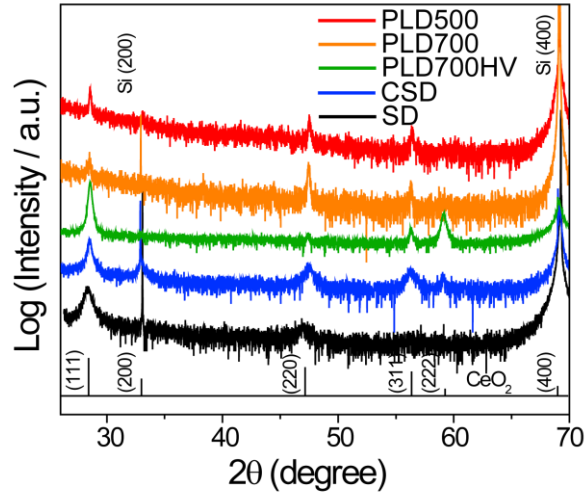


Figure 3. XRD patterns for NC thin films deposited via different methods.

3.2. Electrochemical properties

The surface potential mappings of all the NC films at 25 °C and high humidity, and at 125 °C and in absence of humidity are shown in Figure 4. The former condition corresponds to conduction through the physisorbed water layer, while the latter require conduction facilitated by the chemisorbed water on the NC surface.^{15, 24} The dark blue to light blue curves represent the polarization response, i.e. under biased electrodes, while the curves from green to red indicate the relaxation after grounding of both electrodes.²⁰ Detailed introduction of the tr-KPFM measurement is shown in the experimental section. At 25 °C and wet condition, PLD500 and PLD700 films (Figures 4a and 4b) exhibit strong changes in the surface potential over time throughout the whole NC surface. A large surface potential variation during polarization suggests that a considerable

number of protons are injected at the biased electrode, and are transported towards the grounded electrode under the electric field. Note, that the surface potential mapping at RH of 60 % rather than RH of 90 % is shown for PLD500 film, because when RH is above 70 %, the sample becomes so conductive that its resistivity is even smaller than the protective resistor. Thus, the potential gradient over the the sample is almost zero, and the tr-KPFM data is not comparable with other samples. In comparison, for CSD films (Figure 4d), the polarization and relaxation behavior is substantially weaker, and mostly concentrated in proximity to the biased electrode area. At the grounded electrode, the surface potential is mostly invariant over time, indicating that charge concentration does not significantly vary in this region. For PLD700HV and SD films (Figures 4c and 4e), the surface potential variation only exists in immediate proximity to the biased electrode, and is invariant in the rest of the film.

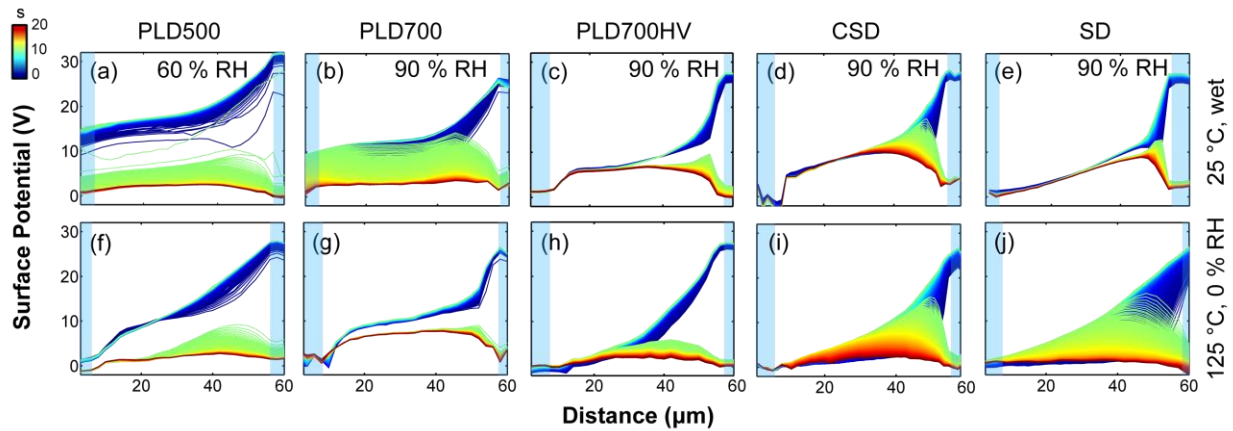


Figure 4. Surface potential mappings as a function of time and distance for PLD500 films (a, f), PLD700 films (b, g), PLD700HV films (c, h), CSD films (d, i) and SD films (e, j) as measured at 25 °C and wet conditions (a-e, relative humidity marked in each plot) and 125 °C and RH of 0 % (f-j). Blue stripes represent lateral electrodes.

At 125 °C and dry condition, the CSD and SD thin films (Figures 4i and 4j) show the strongest surface potential variation during polarization and relaxation, indicating a high proton

injection rate. PLD500 and PLD700 films (Figures 4f and 4g) have weaker response, and the potential variation is observed close to the biased electrode. PLD700HV films (Figure 4h) also have a relatively small potential variation, however, it spans over the whole surface, indicating a faster proton transport across this film.

The DC current was also measured while obtaining each of the surface potential mappings, and is summarized in Table 2. At 25 °C and in RH of 90 %, the interelectrode current is ≈ 170 nA and ≈ 2.0 nA for PLD700 films and CSD films, respectively, and is not detectable for PLD700HV and SD films. Because the resistivity of PLD500 films is much smaller than the protective resistor, the DC current through the sample cannot be accurately determined by the current settings. At 125 °C and dry condition, current is not detectable for any of the films and therefore not shown in the table.

Table 2. Extracted parameters of the electrochemical reactivity and conductivity of NC thin films

		PLD500	PLD700	PLD700HV	CSD	SD
25 °C RH of 90 %	DC current @ 30 V (nA)	>600	170	$< 1 \cdot 10^{-3}$	2.0	$< 1 \cdot 10^{-3}$
	Proton injection rate (<i>S</i>) (mmol/m ³ s)	>80	80 ± 20	10.0 ± 3.0	40 ± 6	5.0 ± 0.8
	Proton diffusivity (<i>D</i>) (μm ² /s)	>1000	1000 ± 250	5.0 ± 0.8	30 ± 8	2.0 ± 0.4
	Resistance <i>R_F</i> (Ω)*	$5.0 \cdot 10^4$	$1.6 \cdot 10^8$	$>1.0 \cdot 10^{12}$	$1.9 \cdot 10^{10}$	$>1.0 \cdot 10^{12}$
125 °C RH of 0 %	Proton injection rate (<i>S</i>) (mmol/m ³ s)	10 ± 1.0	3.0 ± 0.2	7.0 ± 1.5	35 ± 10	45 ± 10
	Proton diffusivity (<i>D</i>) (μm ² /s)	30 ± 5	10.0 ± 1.0	200 ± 30	60 ± 15	100 ± 20

*See Figure 5.

The observed surface potential variation over time is a result of two processes, i.e. proton generation at biased electrode (see Eq. 1 above), and the subsequent proton transport toward grounded electrode under the electric field and chemical gradients. These physical processes can be expressed by Equations 2 and 3:¹⁹

$$\frac{\partial n}{\partial t} = \nabla \cdot (-D\nabla n + \mu n \nabla \Phi) + (S - k_r n^2) \quad (2)$$

$$\nabla^2 \Phi = -\Sigma n F / \epsilon_0 \epsilon_r \quad (3)$$

where t is time, n is proton concentration, Φ is surface potential, D is diffusivity, μ is proton mobility, S is proton injection rate, and k_r is the reaction constant for proton dissipation. From Equation 2, the proton concentration change over time is determined by diffusion and electrical migration (first term), as well as electrochemical reaction (Equation 1) at the biased electrode (second term). The rates of the forward and reverse reactions of Equation 1 are given by S and $k_r n^2$, respectively, where $S = k_f \cdot [\text{H}_2\text{O}]$ ($[\text{H}_2\text{O}]$ is water concentration on NC surface and k_f is the reaction constant for proton generation). Equation 3 is Gauss's law, which defines the surface potential variation due to proton concentration change over time. We assume that μ is linearly dependent on D according to the Nernst-Einstein relationship, and k_r is the same for different samples at a specific temperature. To resolve the time-dependent surface potential and proton concentration, the remaining two unknown parameters, S and D , vary with different samples. These parameters are directly correlated with the electrochemical processes taking place on the NC, and thus determine the shape of the surface potential curves.

Finite element methods are used to find S and D parameters for each film and environmental condition through maximization of correlation coefficients, as summarized in Table 2.²⁵ The correlation coefficient is also used to determine the error bars of each fitting, as detailed

in the supplementary information. The S and D values of PLD500 films in 25 °C and RH of 90 % are too high to be accurately simulated, so they are not available in the table.

To further quantify the proton conduction behavior, EIS is performed at a variety of RH values and 25 °C, as summarized in Figure 5. For all cases, the real part of impedance decreases with increasing sweeping frequency, so the direction of frequency sweep on the Nyquist plots are not marked on each plot. For PLD500 films (Figure 5a), at low RH (<50 %), the Nyquist plot shows a semicircular shape, indicating that the device can be described by the Randles equivalent circuit as shown in Figure 5d.^{26, 27} In this circuit, R_s corresponds to a series resistance, such as the contact resistance between Pt and NC; R_F and C_F are the resistance and capacitance of the sample, or more specifically, of the adsorbed water on NC. At higher RH, a linear tail appears at lower frequencies accompanied by a significant decrease of the semicircular part. The Warburg impedance element, Z_w , is added in series with R_F to the equivalent circuit, as shown in Figure 5e, which represents the involvement of semi-infinite diffusion of protons at the NC-electrode interface. The linear tail is not seen in PLD700 and CSD films (Figures 5b and 5c), possibly due to the limited water layer on the NC surface: the equivalent circuit is represented by Figure 5d. The impedance spectra for PLD700HV and SD films are not shown in this study, because their impedance was too high to be measured (note, again, that despite high impedance, tr-KPFM allowed probing their transport properties). The EIS plots are fitted to the proposed equivalent circuits and the resistivity values for R_F are plotted as a function of RH, as shown in Figure 5f. At the same RH, PLD500 films have the lowest resistivity and CSD films have the highest resistivity. For all films, R_F decreases with increasing humidity, which is consistent with proton conduction within the physisorbed layer. The R_F value at 25 °C and 90 % RH is also summarized in Table 2. The R_F is $5.0 \cdot 10^4 \Omega$, $1.6 \cdot 10^8 \Omega$ and $1.9 \cdot 10^{10} \Omega$, respectively. The high sensitivity to humidity makes

these films good candidates for H₂O sensors. And by controlling the microstructure through different deposition methods and parameters, the resistivity range can also be controlled as needed. It is worth noting that EIS measurements at 125 °C and in absence of humidity showed almost purely capacitive signal originated from the substrate instead of proton transport on NC films, and no DC current between electrodes was detectable.

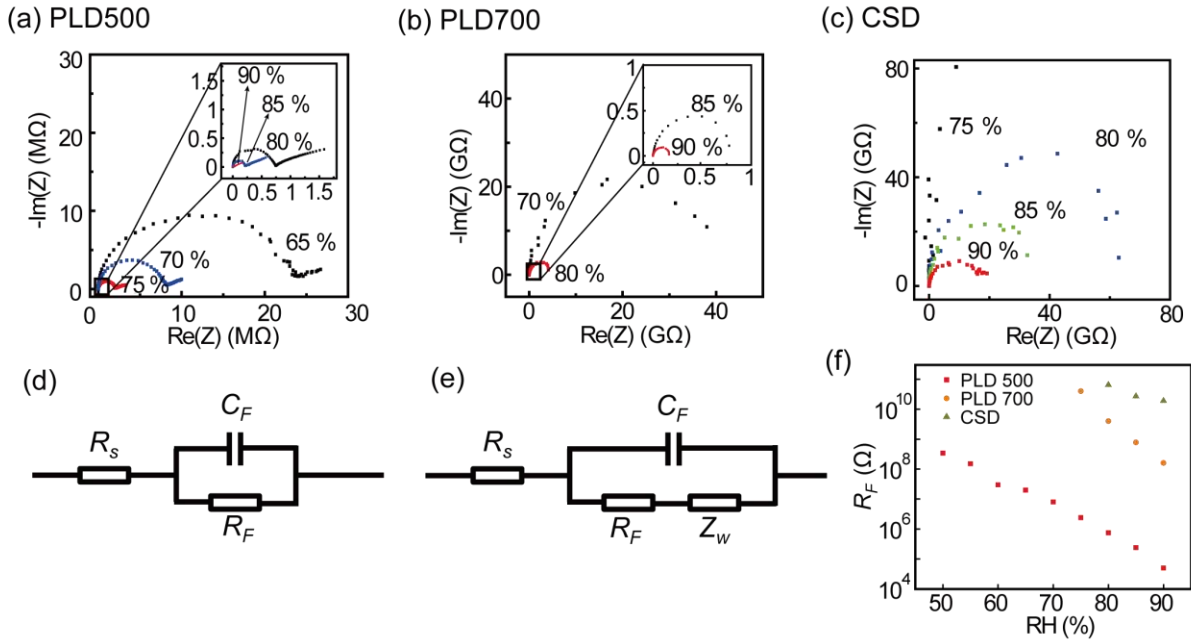


Figure 5. (a)-(c) Impedance spectra of PLD500, PLD700 and CSD films at various relative humidity; (d) equivalent circuits for (b) and (c); (e) equivalent circuit for (a); (f) resistance (R_F) as a function of relative humidity (RH) for different NC thin films. Measurements were performed at 25 °C.

3.3. Structure-property correlations

The correlation between the fitting parameters (S and D) and microstructure, including surface roughness, grain size and $f_{\{111\}}$, is studied according to the data provided in Tables 1 and 2, as plotted in Figure 6. For the ease of comparison, all graphs are plotted using the same scale for all vertical axes. It is clearly seen that at 25 °C and RH of 90 % (Figures 6a-c), the change of

S and D for different samples is substantially larger than at 125 °C and RH of 0 % (Figures 6d-f), which indicates a crucial role of the relatively thick physisorbed water layer in the former conditions, as elaborated in the following discussion.

Effects of surface topography

The correlation between the surface roughness and proton injection rate, S , and proton diffusivity, D , for each of the samples are plotted in both environmental conditions, as shown in Figures 6a and 6d. At 25 °C and RH of 90 %, both parameters are positively correlated with the surface roughness (Figure 6a). However, at 125 °C and dry condition, these parameters have no significant correlation with the surface roughness (Figure 6d).

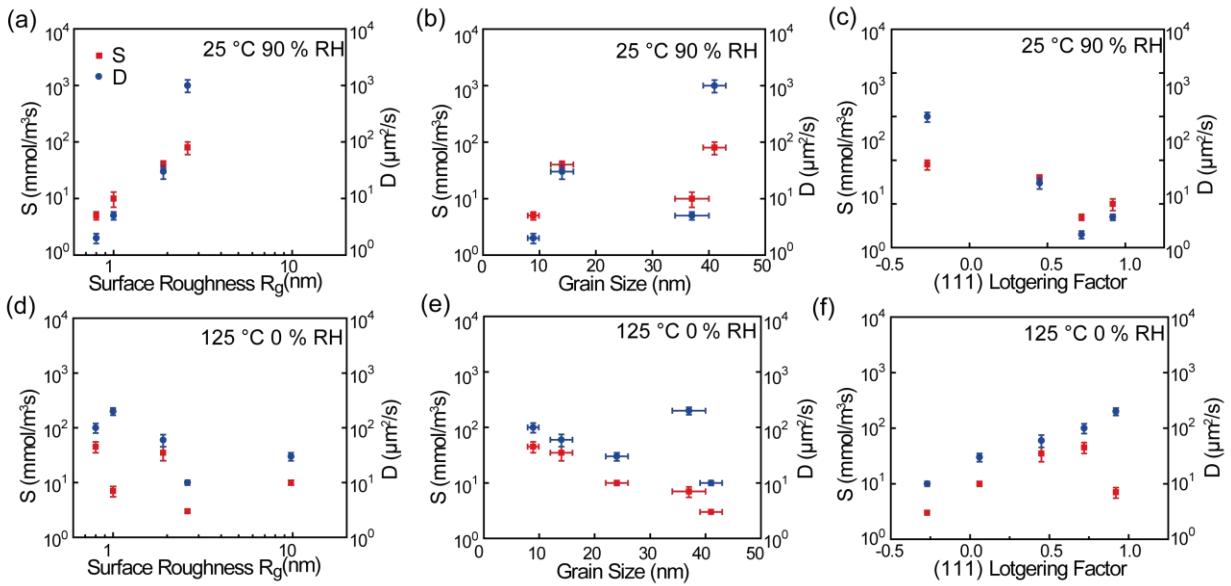


Figure 6. Calculated proton injection rate, S , and proton diffusivity, D , as a function of surface roughness (a, d), grain size (b, e) and Lotgering Factor of {111} (c, f) at 25 °C and RH of 90 % (a-c) and 125 °C and RH of 0 % (d-f).

The positive correlation between surface roughness and S and D at 25 °C is most likely a result of the water layer formed on the NC surface. A rough surface provides more porous and

capillary-filled regions, resulting in a larger amount of condensed water in contact with the sample. Under an applied electric field, water molecules are decomposed (Equation 1), generating protons that undergo transport through this water layer. As previously stated, the proton generation rate S is equal to $k_f \cdot [\text{H}_2\text{O}]$. While k_f is considered constant and relatively small at low temperature, $[\text{H}_2\text{O}]$ is largely dependent on the surface topography of the sample. More water is overall absorbed on the surface – and specifically, at the Pt-NC interfaces, where the electrochemical water splitting occurs – in the samples with higher surface roughness (PLD500, PLD700 and CSD). Therefore, the electric field-induced water splitting generates more protons in the samples, resulting in a relatively high S (Table 2). For PLD700HV and SD films, however, due to the low surface roughness and therefore limited amount of adsorbed water, S is much smaller, resulting in much smaller changes in the surface potential.

Proton diffusivity, D , follows overall the same trends in microstructural dependence as S , since D is expected to increase within a larger volume of absorbed water layer on NC surface. When liquid water is formed on the surface, protons can be transported through multiple pathways including water and water-NC interface, resulting in a larger D than that of samples with smaller amount of surface water, and thus limited proton pathways. For samples with lower surface roughness, since the condensed water is much thinner, the conduction pathways for protons are also limited. Therefore, D is also considered a qualitative measure of the thickness of water on the surface.¹¹ The obtained D value is consistent with DC current and resistance R_F : with increasing D , the inter-electrode current also increases, and the resistance between electrodes decreases, as shown in Table 2. At higher T , water is mostly evaporated from the surface, so the surface diffusion of protons is less important. That is why no correlation between surface roughness and D is

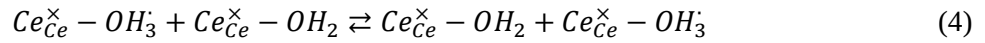
observed. However, other conduction pathways may exist in these conditions, as discussed in the following section.

Effects of crystal size and orientation

To further study the effects of crystallinity on the ionic dynamics in NC, the fitting parameters, S and D , are also plotted as a function of grains size and $f_{\{111\}}$ for both environmental conditions studied, as shown in Figures 6b, c and e, f. At 25 °C and 90 % RH, no obvious correlation between crystallinity and fitting parameters are observed (Figures 6b and 6c), since S and D are mostly determined by the physisorbed surface water formed on the NC, providing the primary conduction path. However, at elevated temperatures, the proton injection rate S decreases with increasing grain size (Figure 6e): the water layer on NC surface and connected pores have mostly evaporated, leaving only chemisorbed water that dominates the electrochemical reactivity.²⁵ Such layer does not necessarily exist only on the surface, but can be present also at the grain boundaries within NC.^{15, 18} Here, the total amount of chemisorbed water is proportional to the area of grain boundaries. So $S=k\cdot[\text{H}_2\text{O}]=k'\cdot A$, where A is the grain boundary area at the reaction site (close to the Pt/NC interface), and is inversely proportional to the grain size, as observed experimentally.

In contrast, the proton diffusivity does not have a perfect correlation with grain size at 125 °C and RH of 0 %, as is shown in Figure 6e. The “outlier”, PLD700HV sample, has the highest D . Admittedly, the remaining four samples appear to exhibit a negative correlation between D and grain size; however, considering the “outlier” and the fact that D does not depend on the area of grain boundaries according to the definition of diffusivity, D might have a more direct correlation with other factors instead of grain size. The exceptionally high diffusivity observed in PLD700HV

sample might be due to an addition of water diffusion pathways through large and deep cracks in this sample, as observed in Figure 2c (note, that this is the only sample that shows large cracks). Furthermore, since most of the protons are expected to exhibit hopping transport in the first water molecules layer that is chemisorbed on the NC surface lattice, according to the Grotthuss mechanism:^{24, 25, 28, 29}



the overall diffusivity can also be affected by the interaction between water and the NC surface termination. Indeed, according to Figure 6f, a positive correlation between D and $f_{\{111\}}$ is observed, suggesting the dependence of surface crystal orientation on proton diffusion in NC.

The ceria $\{111\}$ surface is known to be the most stable surface among the low index surfaces of ceria, and strong water adsorption to ceria $\{111\}$ plane has been observed experimentally.^{30, 31} Such adsorption can be in the form of molecular, dissociative or a mixture of both,⁸⁻¹⁰ but the properties of each crystallographic orientation such as water coverage and defect concentration is unknown. Due to this complexity, direct comparison of the water-ceria interaction of different surface orientation has been limited and contradictory.³² However, two possible reasons for the positive correlation of $f_{\{111\}}$ and D can be identified: first, water adsorption on ceria surface is energetically favorable, and water is bonded more strongly to $\{100\}$ and $\{110\}$ than to $\{111\}$ oriented surface, due to lower adsorption energies for water association.⁹ It is true that weaker water adsorption energy on $\{111\}$ surface may result in a poor water layer continuity and thus decrease the value of D ; however, since water adsorption is energetically favorable on all surfaces,⁹ we assume that chemisorbed water is well dispersed onto ceria, and any variation in D value due to water discontinuity is a minor factor. On the other hand, protons can move more freely along the surfaces with lower adsorption energy, i.e. $\{111\}$, resulting in a higher D than other

crystallographic planes. Second, due to the close packing on {111} surface in the fluorite-structured ceria, the distance between a proton (from adsorbed water, either associative or dissociative) and its nearest oxygen atom is smaller than in other crystallographic planes.⁹ According to Equation 4, proton transport is enabled through Grotthuss mechanism, and a smaller proton-oxygen distance is expected to result in a lower proton hopping energy barrier, thus leading to a higher D value for ceria {111} surface.

As a result, within the exposed surfaces, the {111} planes might allow for higher proton diffusivity, while addition of cracks and open porosity resulting in increased pathways for water and proton diffusion could also have similar effects. However, further investigation is needed to systematically understand the correlation between proton diffusivity and specific crystallographic surfaces.

4. CONCLUSIONS

In this study, five NC thin films with different microstructure were prepared by PLD, CSD and SD, and the effects of their microstructure on electrochemical reactivity and proton conductivity at temperatures below 200 °C are studied. It is found that the surface roughness is positively correlated with the proton generation and conductivity at 25 °C and RH of 90 %, due to the proton transport through the physisorbed water layer on the NC surface. In contrast, at elevated temperature (125 °C) and dry conditions, when the surface physisorbed water evaporates, the ionic dynamics are mainly dependent on the grain size and crystallographic orientation. The proton generation rate is negatively proportional to the grain size, while the proton transport through chemisorbed water is mainly affected by the surface plane orientation and the cracks and open

pores connected to the surface. The proton diffusivity is positively correlated with the Lotgering factor of {111} plane, most possibly due to the ease of proton transport along {111} oriented NC surfaces.

From a broader perspective, this study highlights the importance of combinatorial approach in electrochemical materials characterization. A heuristic combination of complimentary novel (tr-KPFM) and established (EIS) characterization techniques, as well as synthetic methods and sample design (Energy Discovery Platforms), allows probing different parameters affecting electrochemical activity of NC. This approach is also envisioned to be applied to a wide range of energy-related materials, including proton conductors, electrolytes in SOFCs, hydrogen separation membranes, ferroelectric and flexoelectric materials, etc. They enable not only furthering of the fundamental scientific understanding of transport behavior at the nanoscale, but additionally facilitate material and device design paradigms for reliable performance of the final energy devices.

ASSOCIATED CONTENT

Supporting Information: Additional details, Figures S1-S3.

ACKNOWLEDGEMENT

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Captions:

Figure 1. (a) Schematics of tr-KPFM set-up and (b) a representative averaged surface potential mapping as a function of distance and time obtained from tr-KPFM. The two blue stripes represent lateral electrodes.

Figure 2. Representative surface (a-e) and cross sectional (f-j) SEM images for PLD500 (a, f), PLD700 (b, g), PLD700HV (c, h), CSD (d, i) and PLD (e, j) films. The scale bar length is 200 nm.

Figure 3. XRD patterns for NC thin films deposited via different methods.

Figure 4. Surface potential mappings as a function of time and distance for PLD500 films (a, f), PLD700 films (b, g), PLD700HV films (c, h), CSD films (d, i) and SD films (e, j) as measured at 25 °C and wet conditions (a-e, relative humidity marked in each plot) and 125 °C and RH of 0 % (f-j). Blue stripes represent lateral electrodes.

Figure 5. (a)-(c) Impedance spectra of PLD500, PLD700 and CSD films at various relative humidity; (d) equivalent circuits for (b) and (c); (e) equivalent circuit for (a); (f) resistance (R_F) as a function of relative humidity (RH) for different NC thin films. Measurements were performed at 25 °C.

Figure 6. Calculated proton injection rate, S , and proton diffusivity, D , as a function of surface roughness (a, d), grain size (b, e) and Lotgering Factor of {111} (c, f) at 25 °C and RH of 90 % (a-c) and 125 °C and RH of 0 % (d-f).

Table 1. Structural properties of NC thin films.

Table 2. Extracted parameters of the electrochemical reactivity and conductivity of NC thin films

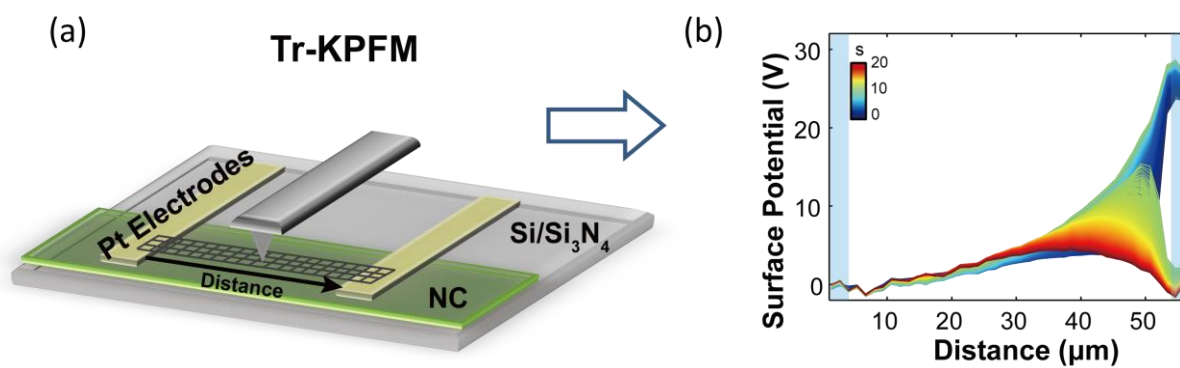


Figure 1. (a) Schematics of tr-KPFM set-up and (b) a representative averaged surface potential mapping as a function of distance and time obtained from tr-KPFM. The two blue stripes represent lateral electrodes.

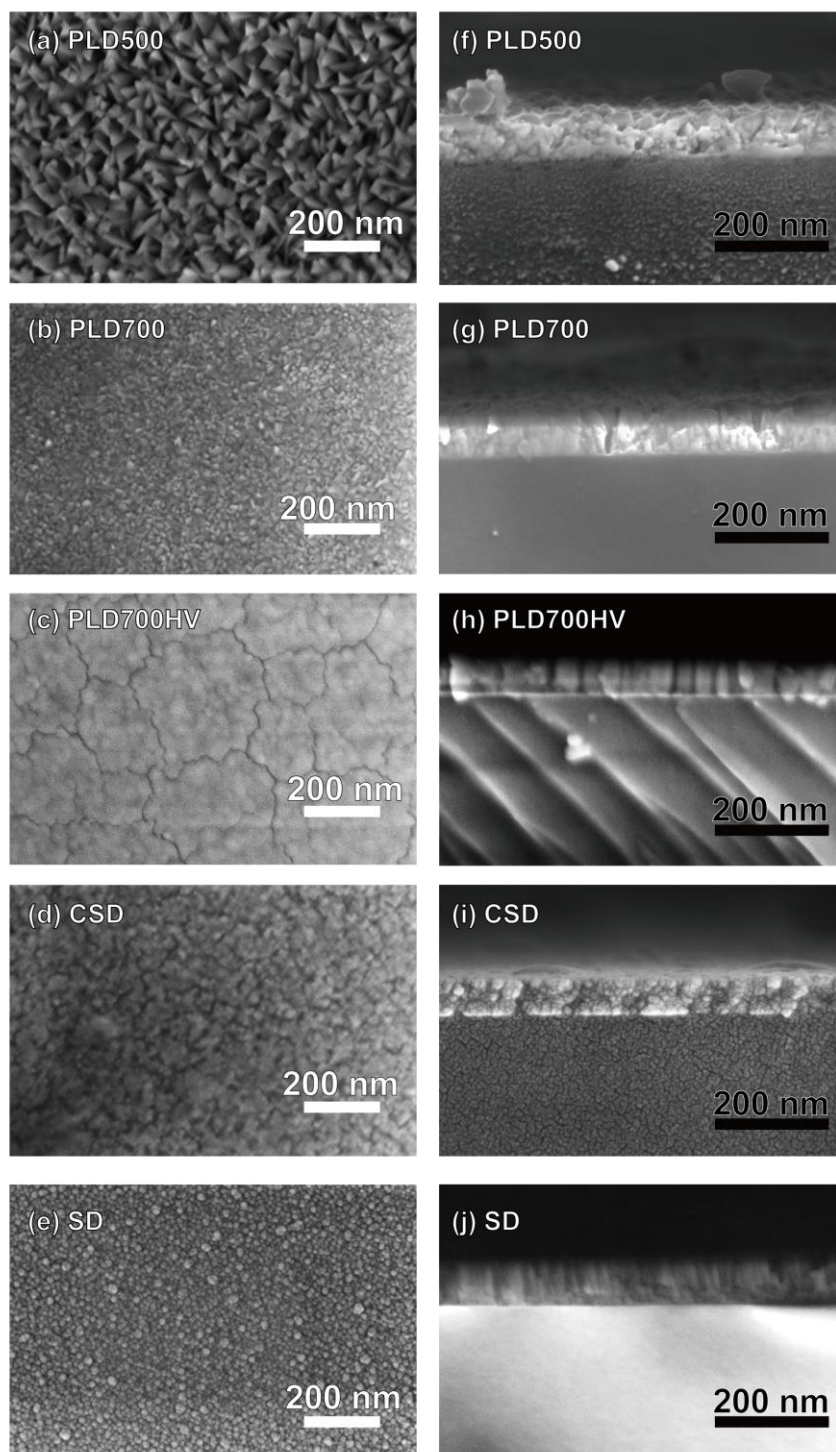


Figure 2. Representative surface (a-e) and cross sectional (f-j) SEM images for PLD500 (a, f), PLD700 (b, g), PLD700HV (c, h), CSD (d, i) and PLD (e, j) films. The scale bar length is 200 nm.

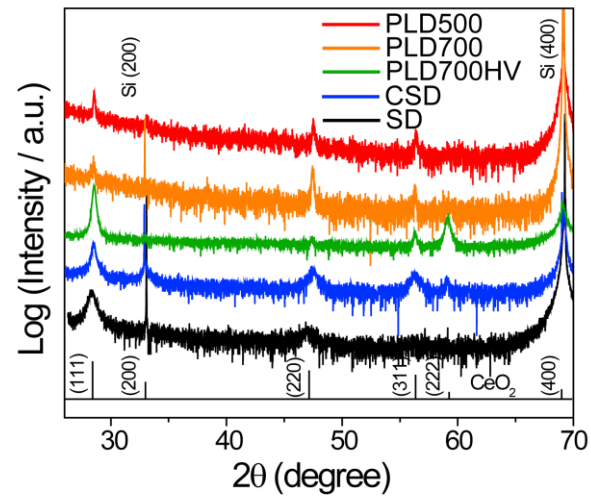


Figure 3. XRD patterns for NC thin films deposited via different methods.

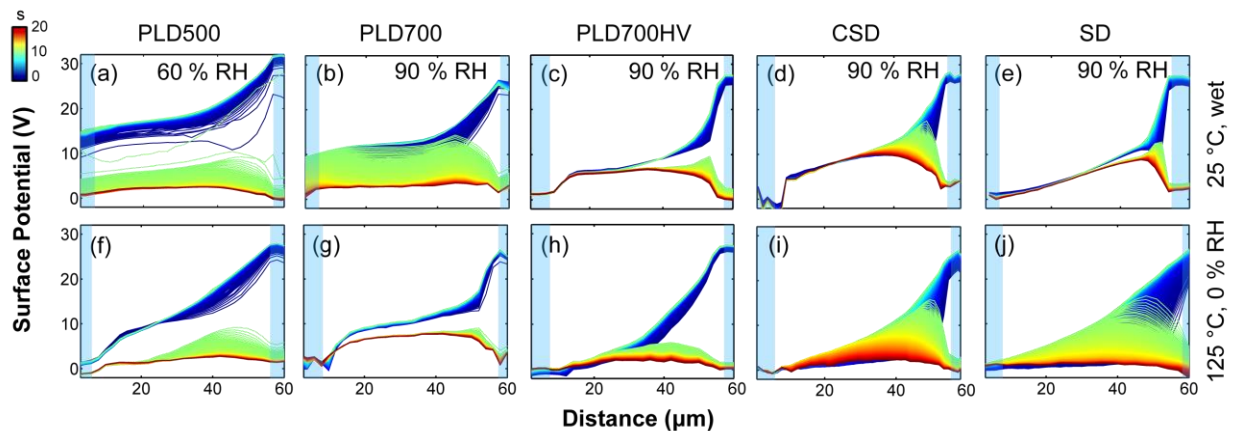


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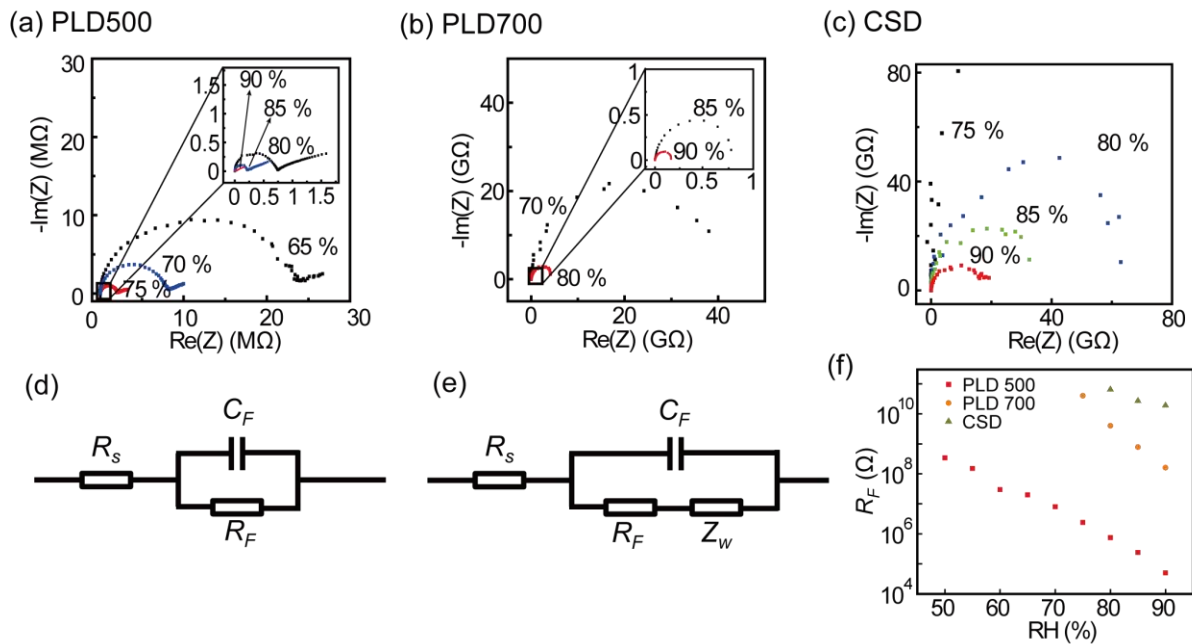


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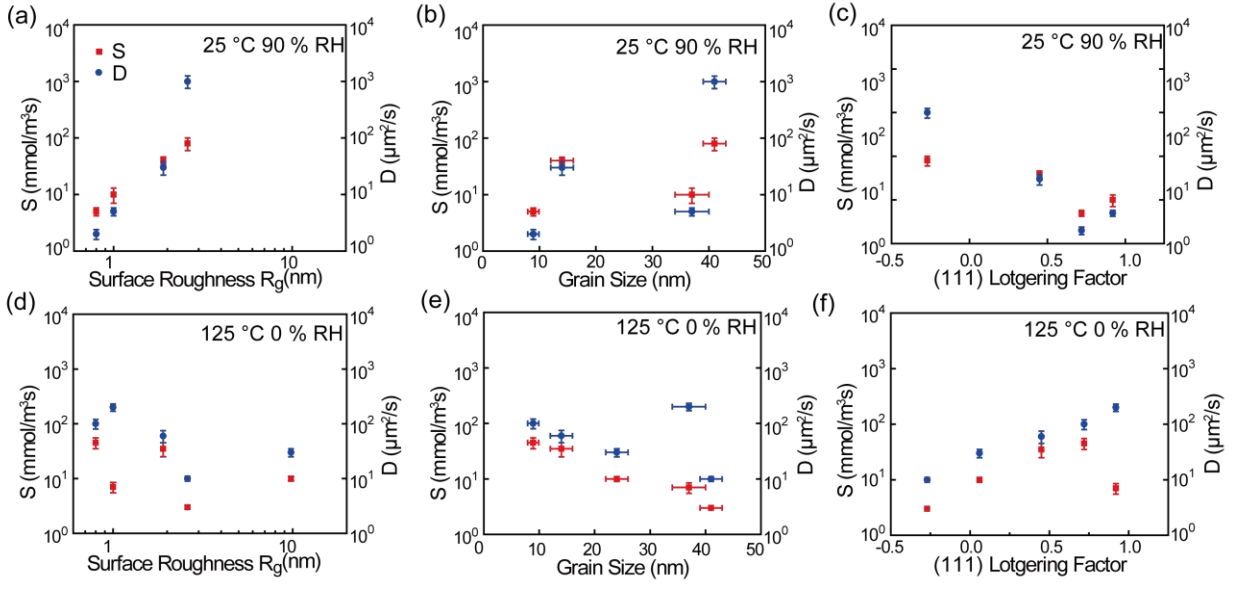


Figure 6. Calculated proton injection rate, S , and proton diffusivity, D , as a function of surface roughness (a, d), grain size (b, e) and Lotgering Factor of {111} (c, f) at 25 °C and RH of 90 % (a-c) and 125 °C and RH of 0 % (d-f).

Table 1. Structural properties of NC thin films.

	PLD500	PLD700	PLD700HV	CSD	SD
Surface roughness R_g (nm)	9.8	2.6	1.0	1.9	0.8
Grain size (nm)	24 ± 2	41 ± 2	37 ± 3	14 ± 1	9 ± 1
Lotgering factor for {111}	0.06	-0.27	0.92	0.45	0.72

Table 2. Extracted parameters of the electrochemical reactivity and conductivity of NC thin films

		PLD500	PLD700	PLD700HV	CSD	SD
25 °C RH of 90 %	DC current @ 30 V (nA)	>600	170	$< 1 \cdot 10^{-3}$	2.0	$< 1 \cdot 10^{-3}$
	Proton injection rate (S) (mmol/m ³ s)	>80	80 ± 20	10.0 ± 3.0	40 ± 6	5.0 ± 0.8
	Proton diffusivity (D) (μm ² /s)	>1000	1000 ± 250	5.0 ± 0.8	30 ± 8	2.0 ± 0.4
	Resistance R_F (Ω)*	$5.0 \cdot 10^4$	$1.6 \cdot 10^8$	$>1.0 \cdot 10^{12}$	$1.9 \cdot 10^{10}$	$>1.0 \cdot 10^{12}$
125 °C RH of 0 %	Proton injection rate (S) (mmol/m ³ s)	10 ± 1.0	3.0 ± 0.2	7.0 ± 1.5	35 ± 10	45 ± 10
	Proton diffusivity (D) (μm ² /s)	30 ± 5	10.0 ± 1.0	200 ± 30	60 ± 15	100 ± 20