Careful Choices in Low Temperature Ceramic Processing and Slow Hydration Kinetics Can Affect Proton Conduction in Ceria

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Low-temperature ceramic proton conductors such as ceria are important for applications ranging from sensors and resistive switches to new devices like implantable solid-oxide glucose fuel cells. Spray pyrolysis offers a promising fabrication route for proton-conducting ceria, with direct liquid-to-solid synthesis and control over crystallinity and grain size. To date, there are conflicting reports on ceria's proton conduction mechanism, particularly whether the interior contributes to proton conduction or transport occurs exclusively along a surface water layer. In this work, proton conductivity is observed in sprayed ceria thin films at 125 °C and below. Post-annealed films exhibit higher conductivity than as-deposited films of 3.3×10^{-5} S cm⁻¹ at 25 °C, which is comparable to previous reports and ascribed to the increase in crystallinity and grain size by post-annealing. This indicates that the interior of ceria in fact contributes to proton conduction. Remarkably slow hydration kinetics of ceria are observed, with time-dependent conductivity equilibrating to 9.53×10^{-6} S cm⁻¹ after up to 76 h. This implies kinetics may have suppressed proton conduction in previous studies, explaining the strong fluctuations in reports to date. Slow protonation kinetics must be considered when designing functional ceria ceramics, for example, in electrochemical bio-energy conversion, sensing or neuromorphic computing.

1. Introduction

Proton conducting ceramics define a plethora of functionalities for today's electrochemical devices in energy and information processing, ranging from protonic ceramic fuel cells (PCFCs),^[1,2] sensors,^[3–6] or memristors^[7–11] to magnetic switches^[12,13] for memories and neuromorphic computing. In particular, hydrated fluorite-structured oxides such as ceria (CeO₂) or yttria-stabilized zirconia (YSZ) show promising proton conductivity at low temperatures, with the potential to be used in new types of low-temperature energy harvesting

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devices.^[14] Recently, we have developed a new type of implantable glucose fuel cell based on free-standing ceria membranes as the proton-conducting electrolyte, demonstrating that this bio-compatible material class can open up new avenues to biomedical applications unattainable for other proton-conducting ceramics.^[15] Hydration plays a key role in defining the electronic and ionic properties of many ceramics, and strongly impacts device performance parameters such as lowtemperature proton conductivity in fluorites,^[16-21] as well as resistive switching behavior in SrTiO₃,^[7,8,11] HfO₂,^[10] and Ta_2O_5 ,^[10] or magneto-ionic switching in a Gd₂O₃/CoO₂ system.^[13] To understand and guide the further development of protonconducting ceramics, mechanistic insights are needed. Two aspects of proton conduction in low temperature ceramic proton conductors have been largely unexplored so far: First, the initial choices made for processing and the degree of intrinsic hydration and respective protonation level.

And second, the kinetics of hydration from interaction with the ambience (or device operation environment), which largely control the proton uptake and the corresponding material equilibration times. Sensors and resistive switches rely on stable and reproducible behavior, so that only the switching pulse or sensing species affects the device response and not an uncontrolled conductivity change due to slow or poorly controlled hydration. Similarly, stable and long-term operation of fuel cells requires a stable, high electrolyte conductivity. Slow hydration kinetics can be prohibitive to these performance requirements, through high device-to-device and cycle-to-cycle variability due to the reliance on transient states instead of equilibria.

To give an overview over the wide range of ionic conductors used in the aforementioned applications, we summarize different classes of ionic conductors in **Figure 1**a.^[1,22–25] Displayed are typical ionic conductivity ranges as a function of device operating temperature for various materials, including intermediate temperature proton-conducting ceramics such as BaZrO₃ and low-temperature proton conductors such ceria and YSZ. These low-temperature proton conductors offer advantages over state-of-the-art polymeric proton exchange membranes (PEMs), in particular for the integration into glucose fuel cells: ceria is non-toxic, can be easily thermally sterilized, can be processed



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Figure 1. a) lonic conductivity of various ionic conductors as a function of temperature.^[1,22–25] b) Schematic of a hydrated ceramic showing the two types of proton transport mechanisms: the vehicular mechanism in which hydroxyl or hydronium ions carry charge along the surface water layer and the Grotthus mechanism where protons hop between water molecules. Regions where proton transport occurs in the hydrated ceramic are shown as 1) bulk 2) grain boundary 3) proton enriched layer in the grain 4) surface of bulk 5) surface of grain boundary

via standard semiconductor manufacturing techniques, and offers greater mechanical and thermal stability than PEMs.^[15] There has been a spur in research of low-temperature protonconducting oxides such as ceria,^[18-20,26] YSZ,^[16,21,27-29] and TiO₂^[30] in recent years, driven by the push toward new lowtemperature fuel cells, as well as effective resistive switches and sensors. The measured proton conductivity of these materials ranges from 10⁻³ S cm⁻¹ for gadolinia-doped ceria at 25 °C^[18] to 9×10^{-6} S cm⁻¹ at 25 °C for YSZ^[21] and 10^{-3} S cm⁻¹ at 30 °C for TiO₂.^[30] In these materials, various modes of proton transport can contribute to the overall conductivity in this low temperature range, see schematic in Figure 1b and Refs. [18,20] for further details. In general, the transport of protons can be classified by either i) the regions where proton transport occurs of the ceramic and its microstructure (e.g., surface, grain boundary, etc.) or ii) by the mechanism by which protons are transferred spatially within and between these regions.

- i) Classification by regions where proton transport occurs: Proton conduction has been proposed to occur via the grain or grain boundary in the interior of the ceramic (modes 1 and 2 in Figure 1b, respectively) or within either an enriched water layer near (mode 3) or an adsorbed water layer above its surface (modes 4–5, Figure 1b). Within this water layer, one can in turn separate the contributions from the surface above the bulk (mode 4) and the surface above the grain boundary (mode 5).
- ii) Classification through the mechanism by which protons are transferred: Here, two mechanisms have been shown to dominate proton transport: First, a Grotthuss-type mechanism^[31] where protons hop from water molecule to water molecule along the surface or from protonic defect site to protonic defect site within the ceramic interior. Second, a vehicular mode where hydroxyl and hydronium ions move and

thereby transport charge, within a water layer at the surface of the ceramic.

Dependent on the ceramic and its structure, different contributions may be dominant to the H+-conduction. Specifically, for fluorite structure-type oxides such as pure and doped variants of ceria and zirconia, there is a debate whether the water layer adsorbed to the surface dominates or whether grain boundary transport through the ceramic interior also plays a role in the observed proton conductivity at low temperature: i) It has been proposed that proton conduction exclusively occurs via the surface water layer along pores and cracks in the surface.^[18,20,21] In particular, Gregori et al.^[18] observed that an enhancement in conductivity under moist air only occurred in porous films and not in dense films, concluding that low temperature proton conduction occurs along adsorbed water in the residual pores and cracks in the film. ii) On the contrary, other reports in thin films as well as pellets demonstrate that the interior, predominantly grain boundaries, contributes to proton conduction in fluorites.^[16,26,27,32] This includes a study by Oh et al. that demonstrates orientation dependence of proton conductivity,[26] contradicting conduction in an isotropic water layer, as well as studies on dense YSZ pellets with a polymeric capping layer, preventing the formation of a conducting surface laver.^[16] These reports demonstrate the contribution of grain boundaries to proton conduction and contradict the model i) where only the surface contributes to proton conduction in ceria and YSZ. In summary, it remains unclear which mechanism of proton conduction dominates under which exact conditions, and the literature indicates that a solely surface-dominated description fails to fully explain enhanced low-temperature proton conductivity in fluorite-type oxides.

A second challenge in the field of proton-conducting oxides is the uncertainty of how the processing and fabrication routes





of the ceramics affect the degree of protonation, and thereby effectively the proton conductivity. For instance, fabrication routes of ceria vary widely throughout reports on proton conduction to date, ranging from solution-based processing and sol-gel methods to vacuum based techniques, and frequently involve thermal annealing or sintering steps. Here, processing techniques that would allow to control and possibly increase the initial protonation level of ceramics during the manufacturing process would be beneficial. However, this discussion has yet to start. The potential benefit of such studies can be exemplified by considering the effect of processing temperature and densification on the protonic defect density. For instance, ceria pellets require sintering temperatures upwards of 1200 °C to densify the ceramic from pre-made powders. At this temperature organic residues, hydration and protonic defects are effectively removed. In contrast, thin films deposited via spray pyrolysis are deposited at much lower temperatures, between 200 and 500 °C, resulting in residues from the organic precursor as well as control over the degree of crystallinity and grain size. Thus, the question arises whether it is possible to use rational ceramic processing techniques during the synthesis to enhance the overall proton conductivity.

There are some first indications in literature that initial processing choices may indeed affect the degree of protonation and resulting proton conductivity. Gregori et al.^[18] employed spin coating, through use of cerium nitrate dissolved in an organic precursor, to deposit porous ceria films, and these films were compared to thin films deposited via pulsed laser deposition. A difference of conductivity between the PLD-deposited and spin coated samples was attributed to the difference in porosity, however, differences in film processing chemistry and the resulting impact on protonation were not further discussed. Scherrer et al. similarly found that in YSZ, differences in protonic conductivity can be attributed to differences in the porosity of the samples, when comparing a variety of differently processed films ranging from spray pyrolysis and PLD to aerosol-assisted chemical vapor deposition, as well as pressed and sintered pellets and commercial tapes.^[29] In addition, the data indicates a trend that samples prepared at lower temperatures and with smaller crystallite size show a higher protonic conductivity, which was also observed by Shirpour et al.^[19] Remarkably, Scherrer et al. describe that some residual precursor solution from the spray pyrolysis deposition is still present in some films and affects the conductivity. Also, they observe that biphasic amorphouscrystalline films tend to have a higher protonic conductivity than their fully crystalline counterparts and a fully amorphous sample shows a protonic conductivity that lies along the average of all their presented data.^[29] All this indicates that the sample fabrication route, processing temperature, sample crystallinity, and synthesis chemistry may affect proton conductivities. Despite these singular reports, it remains unresolved whether low-temperature-manufactured amorphous phases of ceria or zirconia exhibit significant proton conductivity. This motivates this present study to explore low temperature processing routes, specifically spray pyrolysis, and understand the relationship between structure and protonic transport behavior in the ceria model system. Ultimately, we see the perspective that by understanding these fundamental transport properties better, this may contribute to an effort of designing proton-conducting ceramics towards novel energy conversion devices, sensors or resistive switches. By investigating the in-plane conductivity of ceria thin films deposited via spray pyrolysis as a model system, we explore the hydration kinetics of ceria and the impact of the processing route and microstructure on proton transport behavior. This work does not aim to reproduce previous indepth structure and crystallinity studies of sprayed ceria,^[33–37] but rather aims to shed new light into how thermal processing, microstructure, and extremely slow hydration kinetics impact proton conductivity in ceria thin films. It provides new insights towards the open questions on the mechanism of proton conduction in ceria and how it can be controlled through processing and experimental design.

2. Results and Interpretation

2.1. Microstructure and Phase Analysis

Ceria thin films were deposited at 305 $^\circ$ C by spray pyrolysis and we compare an as-deposited film and another after



Figure 2. a) Optical micrograph of the as-deposited film deposited via spray pyrolysis. b,c) Top view scanning electron micrograph of the b) as-deposited and c) the post-annealed film, confirming that smooth, dense, thin films were deposited. d) X-ray diffraction patterns of the as-deposited (black) and post-annealed (red) films with fluorite structure ceria reference for comparison (black). As films are annealed, peak width decreases, and intensity increases as a result of increasing grain size and crystallinity.



post-annealing at 500 °C to investigate the effect of thermal processing and microstructural evolution on proton conductivity. We turn to microscopy to examine the film deposition for ceria via spray pyrolysis. Figure 2a shows a top view optical micrograph of the as-deposited thin film. The observed color pattern with droplet feature sizes on the scale of microns stems from the droplet-by-droplet type deposition of the spray pyrolysis process itself, and are in agreement with other reports.^[38] The SEM top view micrographs and optical microscope images in Figure 2 confirm that smooth, on the scale of microns, ceria thin films were deposited with the spray pyrolysis technique independent of the post annealing. The thickness of the films as measured via profilometry was 490 ± 60 nm, immediately after deposition. The as-deposited film is crack free, and the post-annealed film showed a very low crack-density (see Supporting Information), stemming from bubbles of precursor evaporating during the post-annealing process. Judging by the small size, local nature and low overall occurrence of cracks, they do not affect the electrochemical results presented here. Figure 2d shows the X-ray diffraction (XRD) patterns of ceria films as-deposited and after being post-annealed at 500 °C, respectively. Peaks corresponding to the (111), (200), and (220) Miller indices are present, confirming the fluorite crystal structure of ceria, and a sharp silicon substrate peak is observed at $2\theta = 33^{\circ}$. No preferred orientation can be determined and there are no detectable changes in peak position between the postannealed and as-deposited films. Using the Scherrer equation on the (111) peak, grain sizes are estimated to be on average 3.8 and 2.4 nm for the post-annealed and as-deposited sample, respectively. Small grain sizes obtained from XRD analysis explain why distinguishable grains were not visible in SEM micrographs. Significant peak broadening of the ceria peaks can be observed, with full width half maximum peak values for the (111) peak of 2.13° for the post-annealed film and 3.39° for the as-deposited film, in addition to a weak overall signal. Data extrapolated from Ref. [33] indicates that the post-annealed film is more crystallized: the Johnson-Mehl-Avrami-Kolmogorov (JMAK) analysis^[39,40] from the reference determines that a 5 h post-anneal at 500 °C fully crystallizes amorphous ceria thin films, if dispersed seed crystallites are present. The dispersed seed grains do exist as can be seen from the presence of ceria peaks in the XRD pattern. According to the same analysis, the as-deposited film remains largely amorphous with small, dispersed crystallites. This is confirmed qualitatively by XRD since the post-annealed film shows narrower and more intense peaks than the as-deposited film. However, the XRD data obtained remains inconclusive in quantitatively confirming the fraction of crystallized material, as the overall peak areas are suppressed too strongly for a quantitative analysis of active X-ray scattering volume. Overall, we conclude that thermal post-annealing increased the crystallized fraction as well as the grain size compared to the as-deposited film, and the influence of these properties on the ionic conductivity will be probed in the following.

2.2. Temperature-Dependent Impedance under Dry and Moist Air

Impedance measurements of the biphasic, as-deposited ceria film were taken between 25 and 400 $^\circ\text{C}$ in both, dry and moist



atmospheres. The film was heated at a rate of 10 °C min⁻¹ with a 90 s stabilization time at each temperature prior to each impedance measurement. To assure equilibration, films were held under moist air for 21 h at 25 °C ($P_{\rm H2O} = 0.027$ atm) prior to temperature dependent moist air impedance measurements. Impedance data was fit using an equivalent circuit composed of three parallel RC circuits in series, representing bulk, interface, specifically grain boundary and amorphous-to-crystalline interfaces, and electrode impedance contributions. **Figure 3**a shows the Arrhenius plot of the extracted conductivities from impedance measurements, and Figure 3b,c show exemplary impedance spectra at 25 and 50 °C, and at 400 °C, respectively.

Conductivity measured in dry air and moist air follow Arrhenius type behavior above ≈150 °C, and in dry air, is only measurable above this temperature; in contrast, we clearly observe increasing conductivity with decreasing temperature below 150 °C under moist air. At 25 °C under moist air, total conductivity (σ) was 7.95 ·× 10⁻⁶ S cm⁻¹ and a single compressed impedance arc with a peak frequency of 2.00 Hz and a low frequency tail is observed, as shown in Figure 3b. This arc indicates one dominating transport mechanism, however, there are conflicting reports on the exact interpretation, which we mostly extract from sparse reports on the case of doped zirconia: For example, a study on the impedance of YSZ showed that in moist air proton conductivity takes place along grain boundaries, bypassing the bulk, yielding a single arc, while at higher temperatures oxygen ions are conducted through the bulk and grain boundaries resulting in two arcs.^[27] Another report on the conductivity of dense nanocrystalline YSZ films concluded that the single semicircle arc in moist air correlates to surface proton conductivity.^[28] From these impedance results alone, we cannot distinguish whether the single arc is a result of proton conduction within ceria or a surface conductivity mechanism, however we can conclude that protons are the dominating conducting species based on the moisture dependence in this temperature region. At temperatures from 300 to 400 °C in both dry and moist air, two distinct arcs are observed, corresponding to grain bulk and transport across interfaces within the ceria film, namely interfaces between the crystallites and the amorphous matrix, and where developed, grain boundaries (Figure 3c).

After impedance contributions are assigned, we now analyze the evolution of conductivity over the different temperature regions for the as-deposited film measured in dry and moist atmospheres. Figure 3a shows two distinct regions of different conduction behavior, referred to as Regions I and II as specified in Figure 3a. In Region I, within the temperature range of roughly 150 to 400 °C, we observe an Arrhenius-type behavior of thermally activated conductivity, with activation energies of 0.96 ± 0.06 and 0.91 ± 0.17 eV in dry and moist air, respectively, and a maximum conductivity of 1.64×10^{-4} S cm⁻¹ at 400 °C in dry air. Reported activation energy errors correspond to the linear fit error of the Arrhenius trend in Region I. These values of the activation energy are in good agreement with those of the total apparent conductivity of ceria observed in literature,^[41] indicating that oxygen ionic transport is the dominant conduction mechanism in this temperature range. However, inspection of the high temperature impedance spectra leads to interesting observation: In Figure 3a it can be seen that the conductivity at the highest temperatures at and above 300 °C differ significantly between the moist and dry case, with a



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Figure 3. a) Arrhenius plot of extracted conductivities from impedance measurements taken in dry and moist atmospheres for the as-deposited film. Two temperature regions are shown: Region I with Arrhenius-like conduction behavior indicating oxygen ion conduction, and Region II with increasing conduction for decreasing temperature indicating proton conduction. In Region II, dry air conductivity was below the detection limit of the potentiostat used and hence not seen in the plot. b,c) Exemplary impedance spectra under moist and dry air at low (25 and 50 °C) and high (400 °C) temperatures, respectively, with peak frequencies labeled. At low temperatures under moist air, a compressed impedance arc is observed, attributed to proton conductivity. At higher temperatures under both dry and moist air, two arcs are observed, with the low frequency arc attributed to oxygen ion conduction along the interfaces within the film and the high frequency arc to oxygen ion conduction through the grain bulk. d) Equivalent circuit used for fitting impedance spectra, representing grain bulk, interface (grain boundary and amorphous-to-crystalline interfaces), and electrode impedance contributions.

difference of over an order of magnitude at 400 °C. Turning to the underlying impedance data in Figure 3c, it is found that the lower frequency arc of the measurement under dry air at 400 °C is significantly smaller than under moist air. Specifically, the extracted resistance of the low frequency arc in the dry case is 2.8 M Ω and in the moist case is 16 M Ω . This arc can be assigned to the contribution of conduction of oxygen ions across interfaces within ceria.^[27] In the case of the ceria thin films presented here, these interfaces are both grain boundaries and amorphous-to-crystalline interfaces. This difference in cross-interface conductivity is remarkable, as it shows that moisture is suppressing the oxygen ion conductivity across grain boundaries. This is in agreement with a study by Chueh et al.,^[42] where it was found that the oxygen ion conductivity across grain boundaries in samarium doped ceria decreased under moisture, over the temperature range of 250-450 °C. Chueh et al. argue that hydration causes an increase in space

charge potential within grain boundaries, resulting in the depletion of oxygen ions in grain boundaries and therefore lower ionic conductivity.

In Region II, at temperatures below 150 °C and only in moist air, the conductivity increased with decreasing temperature, indicating protonic conductivity due to hydration of the ceria film. This behavior, with an apparent negative activation energy of the ionic conductivity, is similar to what was observed in previous studies in literature on polycrystalline ceria thin films,^[18,26] ceria pellets,^[19,20] and YSZ pellets.^[21] The negative activation energy of this process can be interpreted by two competing kinetic processes occurring simultaneously: thermally activated ionic conductivity, yielding lower conductivities at lower temperatures, competes with increasing water adsorption at lower temperatures, which increases the amount of water in the system and thereby the amount of available charge carriers. In dry air and within Region II, the ionic conductivity was

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Table 1. Proton conductivity onset temperatures reported from literature for fluorite-structured oxides with varying synthesis methods, processing temperatures, and microstructures. The onset temperature in this work varies from previous studies due to differences in microstructure, crystallinity, and processing conditions.

T _{onset}	Material and synthesis method	Highest processing temperature	Microstructure	Reference
300 °C	Spin coated CeO ₂ film	600 °C	Porous	[18]
400 °C	Calcinated CeO ₂ pellet	1000 °C	Porous	[20]
<350 °C	Chemical vapor deposition CeO ₂ film	500 °C	Columnar, porous	[26]
~400 °C	Sintered CeO ₂	800 °C	93% Dense	[19]
<50 °C	Pulsed laser deposition CeO ₂ film	720 °C	Dense	[18]
<50 °C	Spark plasma sintered YSZ film	1050 °C	Dense	[28]
125 °C	Spray pyrolysis CeO ₂ films	305 °C	Dense	This work

below the detection limit of the potentiostat used, as exemplified by the impedance spectra at 25 and 50 $^\circ$ C in dry air, shown in Figure 3b.

Interestingly, the onset temperature T_{onset} of proton conductivity observed here differs from other studies, which we exemplify for the fluorite structured oxides ceria and YSZ to have enough data points of comparison. In this work, moist air conductivity begins to diverge from the dry air values at 125 °C, indicating the transition to proton conductivity. As summarized in **Table 1**, for porous and polycrystalline films and porous pellets of ceria and YSZ, moisture dependent proton conductivity was observed at T_{onset} as high as $300^{[18]}$ and $400 \text{ °C}^{[20]}$ respectively and for dense films, low temperature proton conductivity under moist air has been reported with T_{onset} below 50 °C.^[18,28] We consider this as an important observation since the unusual onset temperature of 125 °C when compared to other studies may be a result of the amorphous-crystalline biphasic nature of films synthesized in this work. Proton conduction mechanisms for a film with an amorphous phase fraction likely differ from a fully crystalline film or pellet, due to three main reasons: first, there are by nature of processing more organic residues and OH groups present as space fillers in the local network arrangement of the ceria bonding units. Second, the formation of a local bonding unit network of the amorphous state may be able to accommodate more OH-groups due to increased available volume when compared to any crystalline state, increasing



Figure 4. Nyquist plot of the as-deposited film starting under dry air (red) a) over 5.5 h under moist air (blue) and b) over 74 h after thermal cycling to 400 °C under moist air (blue), revealing the long equilibration times and slow hydration kinetics: Proton conductivity initially stabilized after 5 hours under moist air, however after thermal cycling to 400 °C, conductivity significantly increased and took an additional 47.5 h to reach steady state.





Figure 5. Conductivity of the as-deposited film as a function of time at 25 °C a) over >100 h under moist air and b) magnification of the first 6 hours under moist air, before thermal cycling to 400 °C. After 76 h of exposure to moist air (47.5 h after thermal cycling) conductivity stabilized to a value of $9 \cdot 10^{-6}$ S cm⁻¹, showing the extremely slow kinetics of the equilibration process. An exponential relaxation was fitted to guide the eye.

the effective protonation. Third, we also attribute this strong fluctuation of proton conductivity onset temperatures to the microstructure: proton conductivity is influenced by the degree of porosity and the grain boundary density. Here, we characterized mostly dense films in the SEM micrographs (Figure 1), however since it has been suggested that low temperature proton conduction occurs along water adsorbed through open pores and cracks, the proton conduction temperature range likely depends on the degree of porosity. The onset temperature of proton conduction was lower than previous reports of more porous samples and higher than fully dense samples. It is worth noting that an explanation for the low onset temperature in dense samples so far was that only liquid water on the surface contributes to this conductivity. The findings here contradict this, and a reason for not seeing protonic conductivity in the bulk at higher temperatures could lie in slow hydration kinetics: samples simply take too long to fully hydrate and show appreciable conductivity within the measurement times of previous studies.

2.3. Time-Dependent Proton Conductivity

To further explore this hypothesis, we analyzed the low temperature conductivity of sprayed ceria films over time. Timedependent impedance measurements were taken at 25 °C for the as-deposited sample to determine the equilibration time of the protonic conductivity of ceria thin films under moist air. **Figure 4**a displays the impedance reported as Nyquist plots: one measurement was taken in dry air, and immediately afterwards, the atmosphere was switched to moist air. Under moist air, the impedance was monitored over a period of 5.5 h. We observed that the conductivity continuously increased over the first 5 h of this measurement campaign, and then stabilized between 5 and 5.5 h to $\sigma = 4.8 \times 10^{-7}$ S cm⁻¹ with impedance yielding a half semicircle. Subsequently, over the next 23 h, the sample was subject to two heating and cooling cycles, where the sample was heated to 400 °C and then cooled back to 25 °C, all under moist air. This heating program served to simulate the Arrhenius-type measurement campaign. The sample was then held again at 25 °C with $\sigma = 4.03 \times 10^{-6}$ S cm⁻¹ immediately after heating, and Figure 4b shows the electrochemical impedance over 74 h after heating. Remarkably, it took 47.5 h after the heating cycle for the sample to stabilize to around 9×10^{-6} S cm⁻¹ indicating extremely slow hydration kinetics of the ceria films. To better visualize the time scale, we are reporting the total conductivity as a function of time in Figure 5, as extracted from the impedance measurements. Figure 5a shows the entire measurement campaign, and Figure 5b is a magnification of the period before the sample was exposed to heating. We have fitted an exponential profile to visualize the conductivity relaxation behavior over the reported time and that the equilibration is only reached at over 76 h of exposure to moist air with a maximum conductivity of 9.53×10^{-6} S cm⁻¹. To the best of our knowledge, such long equilibration times have not previously been reported and should guide further experimentation and interpretation of conductivity data of ceria.

The long equilibration time observed to reach steady-state proton conductivity may also explain the differences in our reported proton conductivity temperature range from literature (Figure 3 and Table 1). As we show in Figure 5a, equilibration of apparent conductivity can take up to three days, which means that the measurement protocol of the temperature-dependent impedance heavily influences the observed impedance, and data may not reflect true steady-state values. In addition, we want to point out that much of literature relies on reporting proton conductivity under constant "relative humidity". Reporting relative humidity instead of water partial pressure leads to the following complication: relative humidity is a derived quantity that contains both the water partial pressure and the temperature. Relative humidity can be changed by

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changing water concentration, temperature, or both. In order to differentiate between the two competing thermodynamic driving forces of temperature and water vapor concentration (i.e., the water chemical potential), it is paramount to report those two values, instead of relative humidity. In particular, from literature it is unclear whether measurements carried out at constant relative humidity and varying temperature mean that relative humidity was fixed at a reference temperature (which would mean that the water vapor concentration was in fact constant) or whether the actual relative humidity was kept constant, which means that both the temperature and the water vapor concentration were changed at the same time. The latter would make it impossible to separate the effects of temperature and water chemical potential, two competing driving forces which, as we indicated before, both strongly contribute to the total ionic conductivity in hydrated oxides.

2.4. The Influence of Thermal Annealing on Conductivity

We now turn to investigate more deeply the effect that thermal annealing has on the observed proton conductivity. From the data reported in Figures 4 and 5, it appears that the electrochemical impedance of as-deposited films stabilized after 5 h of exposure to moist air at 25 °C, prior to the thermal treatment of the sample. However, these data at least qualitatively also agree with the trend observed after the heat treatment, implying an equilibration time of up to 100 h. This yields the question whether the total equilibration time was in fact that long, and the observed apparent equilibration after 5 h was only an artifact of measurement noise, or whether the heat treatment affected the sample response by increasing total conductivity through microstructural changes and the measurement observing the relaxation into this higher conductivity state.

To further elucidate this, we compared the electrochemical impedance data of the sample as it was deposited to a film that was deposited simultaneously, but subsequently post-annealed at 500 °C. This was motivated by previous studies of the crystallization and grain growth kinetics of sprayed ceria thin films: Given the deposition temperature of 305 °C, the heating step to 400 °C likely led to further crystallization in the film, modifying the microstructure. However, this was impossible to verify on the same sample via XRD, since electrodes were already deposited on the sample for the electrochemical impedance study. Thus, a more controlled model experiment with a post-annealed sample was carried out to further investigate this.

Figure 6 compares the Nyquist plots of the post-annealed and as-deposited films under moist air, at 25 °C (Figure 6a) and at 400 °C (Figure 6b), respectively. We find that the total conductivity is about one order of magnitude higher for the post-annealed film, when compared to the as-deposited one ($\sigma_{annealed} = 3.3 \times 10^{-5}$ S cm⁻¹ and $\sigma_{deposited} = 9.5 \times 10^{-6}$ S cm⁻¹ at 25 °C, $\sigma_{annealed} = 1.1 \times 10^{-4}$ S cm⁻¹, and $\sigma_{deposited} = 4.0 \times 10^{-5}$ S cm⁻¹ at 400 °C).

We ascribe this stark difference in protonic conductivity at 25 °C, Figure 6a, to the difference in amorphous-to-crystalline ratio between the as-deposited and post-annealed films, which was observed by XRD in this study and has been extensively





Figure 6. Nyquist plot with maximum frequencies of as-deposited and post-annealed films at a) 25 °C under moist air and b) at 400 °C under moist air with peak frequencies labeled. Annealing increases both the proton conductivity at low temperatures and the overall oxygen ion conductivity at high temperatures by approximately one order of magnitude which is explained by a change in interface density and amorphous-to-crystalline ratio caused by annealing the film.

studied in the past. Importantly, the discussion presented here does not serve to recreate previous thorough crystallinity studies on ceria deposited via spray pyrolysis,^[33–37] but rather to investigate the impact of the known structural properties of sprayed ceria films and of processing parameters in general on proton conduction. This model is schematically depicted in **Figure 7** and explained in the following. The amorphous phase of ceria is expected to generally have a lower overall conductivity than the crystalline phase, as in the free-volume model of amorphous solids, deep potential wells trap secondary charge carriers such as protons.^[43,44] On the other hand, in crystalline fluorites, grain boundaries have been observed as the dominant transport pathway for proton conduction,^[16,27] and in a similar fashion, the interface between crystalline grains and

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Figure 7. Room temperature proton conduction pathways for biphasic films a) as-deposited and b) annealed at 500 °C. The lower conductivity pathway is through the amorphous phase (red) and the higher conductivity is along the amorphous-crystalline interface and grain boundaries (green). As films are annealed, grain size increases and the amorphous phase fraction decreases, increasing the amount of high conductivity paths and explaining the increase in the overall proton conductivity of annealed films.

amorphous ceria is expected to have an increased protonic conductivity. In Figure 7, the red paths exemplify low-conductivity pathways through the amorphous fraction, and the green paths exemplify the higher conductivity paths along grain edges and grain boundaries. The as-deposited film is largely amorphous and therefore has a low fraction of crystalline material, as well as a low and disconnected fraction of grain boundaries and amorphous-crystalline interface, Figure 7a. In contrast, the annealed film is mostly crystalline, with larger nano-sized grains. Both higher crystallinity and larger grain size enhance the density of developed grain boundaries and amorphouscrystalline interfaces, Figure 7b. From this, it can be inferred that for the post-annealed film, the higher fraction of crystalline material, with larger grains, increases the fraction of highlyconducting paths of the overall system, and therefore increases the total protonic conductivity of the ceria. If proton conductivity were purely dominated by a water film on the surface, and conduction within ceria were to play no role, we would not expect to see a significant difference in conductivity between the post-annealed and as-deposited films: the water film formation on the surface should remain unaltered by the annealing process. Therefore, enhanced conductivity along grain boundaries and similarly, along the interfaces of amorphous-crystalline ceria explains the enhanced conductivity in the post annealed film and supports previous reports that assign proton conductivity not just to a surface effect, but also to highly conducting grain boundaries within fluorites.

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Furthermore, the high temperature behavior in Figure 6b supports this explanation: the two samples show largely identical behavior in the high frequency regime of the impedance spectrum. In contrast, the low frequency component of the as-deposited film has about a four-fold higher resistance. This data is in very good agreement with previous studies from Avila-Paredes et al.^[16] and Kim et al.^[27] In those studies, the high frequency arc is assigned to bulk transport and the low frequency component is assigned to transport across grain boundaries. The noteworthy difference to these previous studies is that samples investigated here contain a significant fraction of amorphous ceria, whereas previous studies investigated fully crystalline samples. However, a largely analogous explanation can be employed: The high frequency arc is associated with oxygen ion conductivity through the bulk, and the low frequency arc is associated with oxygen diffusion across grain boundaries, or more generally interfaces. The post-annealed film has a larger crystalline-to-amorphous ratio as well as larger grains than the as-deposited film. Interestingly, the ratio of crystalline to amorphous ceria does not influence the bulk contribution of the conductivity. On the other hand, this ratio largely affects the low frequency regime, that is, interface-governed conductivity. Here, the post-annealed film shows much higher conductivity, which is due to a lower density of interfaces (grain boundaries and amorphous-crystalline interfaces) across any given cross-section. Assuming that no new grains are nucleated, which is in agreement with previous JMAK analyses,^[33] grain growth reduces the number of interfaces through which a charge carrier would need to pass. For fully isolated grains in an amorphous matrix, which can be expected for the as-deposited sample, each grain contributes two amorphous-to-crystalline interfaces. For connected grains such as in the post-annealed sample, two adjacent grains share an interface, and therefore, each grain contributes only one interface. This means that for the post-annealed film the total grain boundary resistance, that is, the sum of all grain boundary resistances encountered by a charge carrier, is reduced. Lastly, we reason that the lower overall conductivity compared to literature can be attributed to the at least partially amorphous nature of the ceria thin films characterized here.

Collectively, we show that ceria films processed via a wetchemical processing route such as spray pyrolysis at low temperatures exhibit proton conductivity under moist air at temperatures of 150 °C and below. This proton conductivity occurs along interfaces (grain boundaries and amorphous-tocrystalline interfaces) within the ceramic as well as along the surface, and we have successfully manipulated the conduction pathway through thermal annealing. In addition, the overall equilibration times observed in this study are much longer than previously reported, indicating that slow kinetics may have SCIENCE NEWS _____ www.advancedsciencenews.com

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suppressed the observation of grain boundary conductivity in previous studies.

3. Conclusions

This work presents new insights into the proton conductivity of ceria, deposited via the wet chemical route spray pyrolysis. Our results shed new light onto the large fluctuation of observed proton conductivities in ceria and the role of a biphasic amorphous and crystalline configuration. This discrepancy of proton conductivities reported in literature may be explained by long stabilization times and slow sample evolution, since we observe equilibration times of up to three days. This can explain why some previous studies did not observe interior or crossplane proton conductivity, while others did: proton conduction may have been kinetically suppressed due to the slow hydration kinetics uncovered here. In addition, our data shows that low temperature proton conductivity is dependent on crystallinity and grain size. This demonstrates that proton conductivity at low temperatures does not solely rely on a water layer adsorbed to the surface but includes grain boundary and amorphous-tocrystalline interface contributions.

Ceria served as the model system due to its single-phase nature and unusually high proton conductivity at low temperatures, in addition to the ability to control its microstructure through rational processing. Thin films of ceria were successfully deposited by spray pyrolysis as model systems to investigate the influence of hydration kinetics on proton conductivity in ceria. We purposefully selected a wet-chemical processing route to design the ceramics, being spray pyrolysis, in an effort to reach high hydration levels compared to more traditional processing techniques such as sintering of pellets or pulsed laser deposition. Through electrochemical impedance spectroscopy we detect increasing proton conductivity at decreasing temperatures of 125 °C and below in moist atmospheres, agreeing with what has been presented in literature on hydrated ceria.

An important finding is that film conductivity equilibration times under moist air at room temperature are up to three days long, indicating extremely slow hydration kinetics. This is even more surprising since ceria was present here in thin film form and one may even expect longer hydration equilibration times for bulk processed sintered pellets. To our knowledge, such results have not been reported, and we recommend future studies on the protonation of ceria and other metal oxides to consider the long equilibration times to ensure steady-state measurements.

Our work additionally demonstrates that thermal history plays a major role in sample conductivity. After heating films to 400 °C under moist air, conductivity significantly increased, which may be a result of the long equilibration times previously discussed or of microstructural changes in the sample caused by heating. To further study the effect of thermal treatment on conductivity, impedance measurements were taken for a 500 °C post-annealed and as-deposited film. The conductivity for the post-annealed film was higher than the as-deposited and likely can be explained by the increase in degree of crystallinity and grain size with annealing.

One interesting observation from studies so far is that there are conflicting reports on the cross-plane conductivity of protons through dense ceria. Some studies have detected such conductivity, and even used it for concentration cells.^[14] while in others, no proton conductivity through dense ceria was observed.^[18] Our results can help explain this inconsistency in literature so far: hydration of ceria is a slow process, that can take days even for thin films, as we show here. In contrast, surface adsorption is a fast process which allows protonic conductivity along surfaces and through porous samples to occur quickly. This implies that cross-plane conductivity through sufficiently thick dense samples may be kinetically suppressed, explaining why some studies did not observe such conductivity through thick samples. Besides the slow kinetics observed in our measurements, this hypothesis is supported by a second observation: We observe that proton conductivity is significantly increased by the post-annealing process, meaning that modifications to the film itself (grain size, degree of crystallinity) in fact modified the proton conductivity. If proton conductivity were purely dominated by a water film on top of the ceria surface, and conduction within ceria were to play no role, we would not expect to see a significant difference in conductivity between the post-annealed and not annealed films: the water film formation on the surface should remain largely unaltered by annealing process. Since this is not the case, we conclude that we observe protonic conductivity through the film itself, which is dominated by grain boundary and amorphouscrystalline interface conductivity.

By showing that both thermal history and the slow kinetics of hydration play a significant role in the low temperature protonic conductivity of ceria, we have shed some light in the large scatter among conductivity data of ceria existent among earlier reports in literature. We have shown that equilibration even for thin films can be extremely slow, beyond reported experimental durations thus far and that the thermal history of the sample has to be taken into account when interpreting conductivity data. This expanded understanding is of relevance for the further development of technology based on the proton conductivity in ceria, such as implantable glucose fuel cells, and also adds to the understanding of systems where fast response and controlled behavior is key, such as sensors or resistive switching memory.

4. Experimental Section

Sample Preparation: Cerium oxide thin films were prepared via spray pyrolysis with a precursor solution made up of 0.01 mol L⁻¹ cerium nitrate (III) hexahydrate (99.9% purity, VWR international, USA) dissolved in 33:33:33 volume percent diethylene glycol monobutyl ether, 1- methoxy 2-propanol, and ethanol (all reagent grade chemicals with >98% purity from Sigma Aldrich, USA). The precursor solution was then fed into a spray gun (AG361, DeVILBISS, USA) at a 5.4 mL h⁻¹ flow rate and atomized into droplets with a 0.6 bar air pressure. Droplets were sprayed onto a heated Si₃N₄ coated (100) silicon substrate (1 cm × 1 cm, supplier: Sil'tronix, France) for 287 min at a working distance of 30 cm between the spray gun nozzle and the substrate. The substrate was placed on a steel plate heated by a hotplate (VWR, USA) set to 350 °C. The surface temperature immediately before spraying, measured by a thermocouple placed on the substrate surface, was 305 °C. Where indicated, samples were post-annealed at 500 °C for 6 h with a 10 °C min⁻¹ heating rate



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purity, ACI Alloys, USA). Characterization: Electrochemical impedance spectroscopy measurements were taken with a Zahner IM6 potentiostat (Zahnerelektrik, Germany) at a frequency range of 1 MHz to 100 mHz at a 50 mV amplitude. Measurements were carried out in a temperature controlled Linkam heating stage (Linkam Scientific, UK) from 25 to 400 °C under either dry air (Ultra Zero grade, Airgas, USA) or moist air. Moist air measurements were executed by bubbling dry air through deionized water at room temperature to obtain a water partial pressure of 0.027 atm. Impedance data was subsequently analyzed and fit using an equivalent circuit model with 3 RC circuits in serial configuration, using the software ZView (Scribner Associates, USA). The cerium oxide film microstructure and thickness were analyzed by SEM (Zeiss Supra55VP Field Emission SEM). XRD measurements were carried out on ceria films using the Rigaku SmartLab diffractometer with Cu ${\rm K}_{\alpha}$ radiation at a 40 mA current and 40 kV voltage to characterize the microstructure and determine cerium oxide grain size. The film thickness was determined via profilometry (Dektak 150, Veeco, USA).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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