Threshold catalytic onset of carbon formation on CeO₂ during CO₂ electrolysis: mechanism and inhibition†

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Carbon deposition from CO and other carbon-containing fuels is a major cause of the performance degradation of catalysts and electrocatalysts in many energy conversion devices, including low-temperature solid oxide cells (LT-SOCs). In this work, we present direct observation of carbon deposition on thin-film CeO₂ electrodes at LT-SOC operating temperatures (450 °C) in a CO/CO₂ atmosphere by in operando X-ray photoelectron spectroscopy. In contrast to the general view that CeO₂ is a carbon tolerant material, significant carbon formation was observed on CeO₂ during CO₂ electrolysis, with no other catalyst present. Moreover, carbon deposition on CeO₂ demonstrated an intriguing threshold onset formation against surface Ce³⁺ concentration. With the aid of Monte Carlo simulations, we propose the neighboring Ce³⁺–Ce³⁺ pairs to be a critical catalytic structure that facilitates carbon deposition from CO. Finally, we propose mitigation of carbon deposition on CeO₂ by doping CeO₂ with non-redox-active cations, and proved this concept using 50% Gd- and 50% Zr-doped CeO₂ as an example system. These findings provide an in-depth understanding of the mechanism of carbon deposition on CeO₂ during electrochemical reactions and can guide the design of carbon-resistant CeO₂-based electrocatalysts.

Introduction

To produce carbon-neutral fuels,¹² environmentally friendly technologies, including electrolysis³ and thermochemical splitting⁴ of water and carbon dioxide, have attracted significant attention. In particular, low-temperature solid oxide cells (LT-SOC) that operate from 400 °C to 650 °C are believed to be the next generation technology.⁵ However, carbon poisoning, or “coking”, due to carbon deposition on the catalyst surface during operation, is an important issue for processes involving carbon-containing species.⁶,⁷ It this coking process can lead to irreversible catalyst deactivation and cause mechanical degradation.⁸ One major type of carbon poisoning is from CO,⁹ which has been reported as either CO dissociation¹⁰–¹⁴ (CO → C + O) or the Boudouard disproportionation¹⁵–¹⁷ (2CO → CO₂ + C). At operating temperatures below 700 °C, carbon deposition is thermodynamically more favorable and occurs mainly via the Boudouard reaction.¹⁵–¹⁷ Consequently, it is important to develop carbon-tolerant electrocatalysts that can operate under LT-SOC operating conditions, with both high catalytic activity and long-term stability.

Ceria (CeO₂) and ceria-based materials have been widely investigated as catalysts and catalyst supports towards a broad range of reactions.¹¹,¹² The catalytic performance of CeO₂ is due to its excellent redox activity,¹² which can be expressed with the Kröger–Vink notation¹⁸ as

\[ 2\text{Ce}_0 + \text{O}_0 \rightarrow 2\text{Ce}^{4+} + \text{V}_0^- + \frac{1}{2}\text{O}_2 \]  

where \( \text{Ce}_0 \) and \( \text{V}_0^- \) denote Ce³⁺ (small polaron)¹⁸ and doubly positive charged oxygen vacancy, respectively. With this oxygen storage capability, CeO₂-based catalysts are also known to be carbon-tolerant as they can oxidize the deposited carbon with lattice oxygen.²⁷

LT-SOC fuel electrodes combining ceria-based materials with Ni have yielded high performance but their stability in
carbon-containing fuels remains a big challenge.\textsuperscript{5,28} While carbon deposition has been extensively studied on the Ni surfaces, few studies focus on carbon deposition on CeO\textsubscript{2}. Despite the high carbon tolerance of CeO\textsubscript{2} as a catalyst, carbon deposition may not be negligible on CeO\textsubscript{2} in LT-SOCs since the oxygen ion current can greatly affect the carbon tolerance of electrode materials.\textsuperscript{29} In particular, in electrolysis conditions, O\textsuperscript{2−} are constantly removed from the fuel electrode, making carbon deposition more favorable.\textsuperscript{29} As an example, recent studies have demonstrated that infiltrating Ni-YSZ with Gd-doped CeO\textsubscript{2} did not improve the carbon tolerance during CO\textsubscript{2} electrolysis.\textsuperscript{31-32} Therefore, to obtain a more complete picture of carbon deposition over Ni/CeO\textsubscript{2} electrodes, it is important to investigate the onset of carbon formation and carbon deposition mechanism on CeO\textsubscript{2} during electrochemical reactions. Moreover, besides Ni/CeO\textsubscript{2} electrodes, there has been considerable development of CeO\textsubscript{2}/perovskite fuel electrodes in LT-SOCs, as a means to improve the electrodes ability to work with carbon-containing fuels without carbon deposition.\textsuperscript{3,33} Hence a fundamental study of carbon deposition on CeO\textsubscript{2} surface would also benefit the design of these conducting-oxide electrodes.

In this work, we systematically studied carbon deposition in CO/CO\textsubscript{2} mixture on four types of fluorite-type ceria thin films: undoped ceria (CeO\textsubscript{2}), 20\% Gd-doped ceria \( \text{Gd}_0.2\text{Ce}_{0.8}\text{O}_{1.9} \), 50\% Gd-doped and 50\% Zr-doped ceria \( \text{Gd}_0.5\text{Ce}_{0.5}\text{O}_{2.75}, \text{Zr}_0.5\text{Ce}_{0.5}\text{O}_2 \). Despite the general opinion that CeO\textsubscript{2} is a carbon-tolerant material, we demonstrated for the first time with \textit{in operando} ambient pressure X-ray photoelectron spectroscopy (APXPS) that carbon is readily deposited on the CeO\textsubscript{2} surface within half an hour, under LT-SOC operating conditions (450 °C, CO/CO\textsubscript{2} atmosphere, \( \sim 1 \) V polarization). Moreover, with quantification of both \([\text{Ce}^{3+}]\) and the amount of deposited carbon, we demonstrate an intriguing threshold \([\text{Ce}^{3+}]\)-carbon relation for the onset of carbon formation on CeO\textsubscript{2}. Combining APXPS data with Monte Carlo simulation, we propose the most likely catalytic reaction for carbon deposition from CO on CeO\textsubscript{2} to be the neighboring Ce\textsuperscript{3+}–Ce\textsuperscript{3+} pair. Finally, we propose doping CeO\textsubscript{2} with non-redox-active cations can effectively mitigate the carbon deposition on CeO\textsubscript{2} in the LT-

![Fig. 1 Schematics of the experimental configuration and sample characterization. (a) The electrochemical cell consists of a thin-film ceria working electrode, a buried Pt grid, an 8\% yttria-stabilized zirconia (YSZ) solid electrolyte, and a porous Pt counter electrode. (b) SEM image showing the patterned Pt grid; scale bar, 100 µm. (c) High-resolution X-ray diffraction data of symmetric 2θ−θ scan of the ceria thin-films on the electrochemical cell. (d) Low-energy electron diffraction patterns for the ceria thin films on YSZ (001) without Pt grids, collected at 450 °C in UHV using 110.6 eV electrons (color legends in (c)). A fourfold symmetry is present on all ceria electrodes, highlighted by the dashed square.](https://doi.org/10.1039/C9TA04504G)
SOCs operating conditions, as exemplified in the case of Gd0.5Ce0.5O1.75 and Zr0.5Ce0.5O2.

**Results**

The experimental setup is shown in Fig. 1a and b, which depicts the electrochemical cell consisting of a ceria thin film electrode, an 8% yttria-stabilized zirconia (YSZ) (001) single crystal electrolyte, a Pt grid buried under the ceria electrodes, and a porous Pt counter electrode. The out-of-plane symmetric X-ray diffraction scan for the ceria films on the electrochemical cell is shown in Fig. 1c. The ceria films demonstrated both (001) and (111) orientations: the films grown epitaxially on YSZ are in the (001) direction while the polycrystalline regions grown on Pt grids follow a mixed (001) and (111) texture. Verification of this assignment is shown in ESI Fig. S2.† As explained in ESI Note 1,† all the ceria films have cubic fluorite structure (space group Fm3m). To reveal the surface structure, low-energy electron diffraction (LEED) patterns were collected on ceria films epitaxially grown on YSZ (001) without Pt grids at 450 °C, i.e., the same temperature where carbon deposition was studied. As shown in Fig. 1d, the surface of all the ceria thin films on YSZ (001) had a four-fold symmetry, in agreement with the (001) fluorite-type ceria surface structure.24,34 On the other hand, the polycrystalline regions on the Pt grids have yielded no LEED pattern, consistent with previous reports.24

Fig. 2 summarizes the surface chemistry evolution during carbon deposition reaction. In the experiment, cathodic (CO₂...
reduction) and anodic (CO oxidation) biases were applied on the electrochemical cell. Since the width of Pt stripes (~20 μm) is much smaller than the X-ray spot size (~1 mm in diameter), the APXPS results reveal an average surface chemistry of the epitaxial and polycrystalline ceria regions. Fig. 2a shows the normalized C 1s, Ce 4d and valence band (VB) photoelectron spectra on Gd$_{0.2}$Ce$_{0.8}$O$_{1.5}$ as a representative case. All the spectra were calibrated by aligning the Ce 4d$_{5/2}$ peaks at 122 eV$^{35,36}$ and then normalized to the Ce 4d intensity. Three main features were observed in the C 1s spectra. First, the pronounced rising peak at around 285 eV corresponds to the deposited graphitic carbon, in agreement with previous studies on carbon deposition on ceria.\textsuperscript{37-38} Secondly, the peak at around 290 eV is an adsorbate peak, which has been commonly attributed to a carbonate species on the ceria surface.\textsuperscript{36-38,39} Since a detailed investigation of the CO/CO$_2$ adsorption structure on ceria is beyond the scope of this paper, we leave this peak assigned as an adsorbate. Studies on this topic can be found in the ref. 40 and 41. Finally, the two peaks at around 292 eV and 293.5 eV originate from CO and CO$_2$ gas phase.\textsuperscript{34,45} The assignment of the two gas peaks has been verified by collecting the C 1s spectra while the sample was extracted (ESI Fig. S6†).

The components with the two highest binding energies (shaded region in the plot) in the Ce 4d spectrum arise purely from Ce$^{4+}$ species.\textsuperscript{36,44} Note the Ce$^{4+}$ features decreased under increasing cathodic polarization, indicating the reduction of ceria surface. In the valence band spectra, the feature at about 1.5 eV corresponds to the Ce 4f peak, whose normalized intensity reflects the concentration of Ce$^{3+}$ at the surface.\textsuperscript{36,45} Consistent with Ce 4d spectra, the valence band Ce 4f peak intensity increased with increased reduction state at the surface under cathodic polarization. As shown in Fig. 2a and ESI Fig. S7a,\textsuperscript{1} surface [Ce$^{3+}$] increased monotonically with cathodic polarization for all the ceria samples. At open circuit, both Gd$_{0.2}$Ce$_{0.8}$O$_{1.9}$ and Zr$_{0.5}$Ce$_{0.5}$O$_{2}$ were more reduced than CeO$_2$, indicating a higher reducibility, consistent with previous studies.\textsuperscript{16-18} On the other hand, 50% Gd-doped CeO$_2$ was less reducible. This could originate from defect–defect interactions in ceria – a high concentration of extrinsic oxygen vacancies and large Gd$^{3+}$ ions increase the formation energy of additional oxygen vacancy (and Ce$^{3+}$).\textsuperscript{49,50}

The amount of the deposited carbon under different biases is shown in ESI Fig. S7b.\textsuperscript{1} Due to voltage loss at the electrolyte and the counter electrode, the applied electrical bias was not entirely converted into an electrochemical potential at the ceria electrodes. Therefore, it is not possible to compare the carbon deposition behavior across samples as a function of bias. Instead, we use the surface reduction state, [Ce$^{3+}$], as a metric in carbon deposition at the ceria surface. This is reasonable, because [Ce$^{3+}$] depends on the effective oxygen chemical potential determined by the gas composition and the electrochemical potential at the ceria electrodes.\textsuperscript{21} Carbon deposition as a function of [Ce$^{3+}$] is plotted in Fig. 2b. There are two important features in the [Ce$^{3+}$]–carbon relation: firstly, there is a clear threshold of [Ce$^{3+}$] for the onset of carbon deposition. As shown on CeO$_2$ and Gd$_{0.2}$Ce$_{0.8}$O$_{1.9}$, significant carbon deposition was only observed when [Ce$^{3+}$] reached a critical value of around 50%. Secondly, the carbon deposition was suppressed on Gd$_{0.3}$Ce$_{0.5}$O$_{1.75}$ and Zr$_{0.3}$Ce$_{0.5}$O$_{2}$. As illustrated, negligible amount of carbon was observed on Zr$_{0.3}$Ce$_{0.5}$O$_{2}$ throughout the entire polarization range even though [Ce$^{3+}$] exceeded 50%. Although carbon was also observed on Gd$_{0.3}$Ce$_{0.5}$O$_{1.75}$ when polarizing the sample to almost 100% [Ce$^{3+}$], the deposited carbon intensity was much smaller than that on Gd$_{0.2}$Ce$_{0.8}$O$_{1.9}$.

Fig. 2c shows the cation fraction of dopants as a function of [Ce$^{3+}$] during the polarization and carbon deposition process. The surface dopant concentration remained relatively constant before the threshold carbon deposition, but there is an apparent increase after that. For example, the surface Gd concentration in Gd$_{0.2}$Ce$_{0.8}$O$_{1.9}$ and Gd$_{0.3}$Ce$_{0.5}$O$_{1.75}$ increased at high [Ce$^{3+}$]. The increase of measured cation fraction originates from the fact the XPS signal from Ce gets attenuated more by the deposited carbon, while the dopant are less affected. The observed apparent increase of dopant/Ce ratio thus indicates that more carbon was deposited onto Ce sites than on the dopants (ESI Fig. S12†).

To confirm and better demonstrate the threshold [Ce$^{3+}$], carbon relation, we monitored carbon deposition on Gd$_{0.2}$Ce$_{0.8}$O$_{1.9}$ at different biases (i.e., different [Ce$^{3+}$]) as a function of time. The Ce 4d and C 1s spectra collected during the 1.5 hour measurement at open circuit are shown in Fig. 3a and b respectively. As can be seen, the spectra remained stable throughout the measurement, indicating neither carbon formation nor oxidation state change. Then, a cathodic bias (−0.7 V) was applied to reduce the surface further, but still below the threshold [Ce$^{3+}$]. The spectra collected immediately after polarization, after 0.5 hours and after 1.5 hours are shown in Fig. 3c and d. A small graphitic carbon peak appeared and the surface Ce became more reduced due to cathodic polarization. Nonetheless, no further change of the surface chemistry took place, with no increase in the carbon peak intensity during the 1.5 hours of measurement time. Upon increasing the applied cathode bias to −1.2 V to reduce the surface beyond the [Ce$^{3+}$] threshold, significant amount of carbon accumulated already within the first 0.5 hours and the carbon intensity continued to increase during the measurement (Fig. 3f). Meanwhile, a new broad peak appeared at about 125 eV, originating from the carbon KV Auger peak\textsuperscript{21} (Fig. 3e). This time-dependent measurement clearly indicates that significant carbon deposition only occurs when the ceria surface reaches a threshold [Ce$^{3+}$]. After the onset of carbon deposition when [Ce$^{3+}$] was greater than the threshold, the carbon growth exhibited a self-limiting behavior. The carbon intensity at the surface saturated and stopped growing when the thickness of the deposited carbon reached 1–2 monolayers (ESI Note 7†).

Along with the carbon deposition, the adsorbate peak vanished. If indeed this adsorbate is the carbonate precursor in CO$_2$ electrolysis reaction,\textsuperscript{36,38} its suppression indicates loss of catalytic activity for CO$_2$ electrolysis because of the surface being covered by deposited carbon. In addition, the gas peak shifted to a lower binding energy, possibly due to a change in the gas adsorption behavior on the carbon-covered surface.\textsuperscript{21}
Threshold, despite the considerable amount of Ce³⁺ and V
threshold/C⁰ remained stable during our measurement. Upon reaching the carbon deposition was observed at OCV and the Ce 4d spectra by comparing the three spectra in Fig. 3e.

deposition started and increased sharply. Spectra are normalized to clearly visualized from the decreasing intensity of Ce⁴⁺ peaks in 9 : 1 CO/CO₂ atmosphere at (a and b) open circuit (OCV), (c and d) −0.7 V, and (e and f) −1.2 V electrical bias in sequence. No significant carbon deposition was observed at OCV and −0.7 V, and the surface remained stable during our measurement. Upon reaching the threshold −1.2 V polarization (i.e., threshold [Ce³⁺]), the carbon deposition started and increased sharply. Spectra are normalized to the corresponding CO gas peak.

The change of Ce 4d spectra during carbon deposition is twofold (Fig. 3e): first, the total intensity of the normalized Ce peak decreased as a result of carbon deposition. Second, and more interestingly, the surface became more enriched with Ce⁴⁺ during carbon deposition. The increase of surface [Ce⁴⁺] can be clearly visualized from the decreasing intensity of Ce⁴⁺ peaks in the Ce 4d spectra by comparing the three spectra in Fig. 3e. Possible reasons for this carbon-induced Ce⁴⁺ enrichment are discussed in ESI Note 10.

To summarize, rapid carbon formation from CO only occurred when the surface [Ce³⁺] exceeded a threshold value of about 50%. This threshold relation is intriguing since the carbon intensity remained negligible prior to the [Ce³⁺] threshold, despite the considerable amount of Ce⁴⁺ and V₀ in the near-surface region. In addition, we found the carbon deposition was almost completely suppressed on both Gd₀.5Ce₀.5O₁.₇₅ and Zr₀.₅Ce₀.₅O₂ throughout the entire polarization range, even after [Ce³⁺] well exceeded the threshold concentration (50%).

Discussions

We propose that the threshold [Ce³⁺]-carbon relation can have three origins, which may act individually or synergistically. First, the threshold may arise from the thermodynamics aspects ("thermodynamic threshold"), where the carbon deposition reaction is only thermodynamically favorable beyond a threshold cathodic polarization (i.e., threshold [Ce³⁺]). Secondly, the threshold can arise from the formation of catalytic sites for carbon deposition ("catalytic threshold"), where the dominant catalytic sites are only formed in significant numbers beyond a threshold [Ce³⁺]. Thirdly, the threshold may come from the stability of the deposited carbon on the ceria surface ("stability threshold"). For the last case, carbon can be produced at low [Ce³⁺], but the reaction products stay stably at the ceria surface beyond the threshold of [Ce³⁺]. In the following paragraphs, we discuss all three possibilities and show the threshold [Ce³⁺]-carbon relation must be most likely due to a threshold in the formation of the catalytic structure (Ce³⁺–Ce⁴⁺ pair) at the surface ("catalytic threshold").

We first examine the “stability threshold”. Ceria is known for its ability to catalyze the combustion of carbon;³⁴ it may remove (oxidize) the deposited carbon on the surface. As an example, Zr-doped ceria can oxidize the surface carbon with lattice oxygen even at 200 °C.⁷ Therefore, it is possible that the deposited carbon can only be stabilized on an oxygen-deficient surface, where no O²⁻ species being available to oxidize the deposited carbon. In this scenario, the observed threshold of [Ce³⁺] should reflect a threshold of V₀, where a sufficiently oxygen depleted CeO₂ surface is unable to inhibit carbon deposition. However, this is in contrast to our observation that carbon deposition was suppressed on Gd₀.₅Ce₀.₅O₁.₇₅, the most oxygen-deficient ceria surface at a given [Ce³⁺]. Therefore, we view this scenario to be unlikely.

In addition, the “stability threshold” can originate from a threshold carbon cluster size. Carbon dimers (C₂) have been observed to have higher stability than monomers (C₁) and are the key intermediates in the growth of graphene on Au surfaces.⁵⁵ Similarly here, carbon cluster formation may also be a key step in the carbon deposition reaction on ceria. Carbon deposition has been found more favorable near defect sites.⁵⁶ Therefore, carbon atoms deposited on the surface with a higher defect concentration are more likely to be located closer to each other, promoting the “clustering” process. In this scenario, the observed threshold [Ce³⁺]-carbon relation should be associated with a threshold surface defect density to ensure that the deposited carbon forms clusters. Clustering of single carbon atoms to form pairs of carbon atoms induces a peak shift in the C 1s spectra as reported by Xu et al.⁵⁶ We did not find such a peak shift, and therefore we deem this scenario to be unlikely.

We then examine the “thermodynamic threshold”. The reaction environment is already thermodynamically favorable for the Boudouard reaction even without polarization.²² In this
case, a thermodynamic threshold can only arise from the CO dissociation reaction. As the surface [Ce3+] depends directly on the overpotential at the electrode, a threshold [Ce3+]–carbon relation indicates that a threshold of overpotential is required to split the adsorbed CO. Had this scenario been the case, we would expect the surface overpotential to be a good descriptor for the carbon deposition reaction on ceria. In this case, all the samples reported in Fig. 2c should merge into one common threshold overpotential–carbon relation. However, as illustrated in ESI Fig. S17, this overpotential–carbon relation cannot explain our observation. In particular, this “thermodynamic threshold” cannot resolve the paradox that at similar surface overpotentials, significant amount of carbon deposition was observed on Gd0.2Ce0.8O1.9; and between Zr0.5Ce0.5O2 and Gd0.5Ce0.5O1.75, indicating that both the oxygen sites and the V_o play a minor role, if any, in catalyzing carbon deposition. Consequently, only the Ce pairs (Ce3+-Ce4+ or Ce3+-Ce3+) may act as the catalytic structure.

To resolve the most likely catalytic structure, we conducted a model Metropolis Monte Carlo simulation to quantify Ce pair formation on the ceria surface as a function of [Ce3+]. In principle, one would need to consider all the possible surface terminations to model site-by-site the pairing of reduced ceria cations. Here, we model the Ce3+ pair formation on the (001)-type ceria surface, i.e., the majority surface structure of the electrochemical cell. As will be presented later, the insights drawn from the (001) surface model can be extended to other types of ceria facets as well. Different energies of defect–defect interactions between the nearest-neighbor Ce3+ sites (E>Ce-Ce) were tested, ranging from 0 to 0.2 eV, with positive values representing repulsion. The energies were chosen from a previous calculation, indicating the interaction energy between the nearest-neighbor Ce3+-Ce3+ pair in the bulk of ceria is 0.1 eV. As a result, Fig. 4a shows the concentration of Ce3+-Ce4+ and Ce3+-Ce3+ pairs on the equilibrated undoped lattice at different

![Image](https://example.com/image.png)

**Fig. 4** Quantification of Ce pair formation on the (001) ceria surface with Monte Carlo simulation. (a) The response of Ce pair formation to the interaction energy between neighboring Ce3+ cations, with positive energies representing repulsion. Note a threshold behavior was observed in the Ce3+-Ce3+ pair formation at repulsive interaction energies, and no threshold is found for the formation of Ce3+-Ce4+ pairs, as expected. (b) Effect of doping on the Ce pair concentration, with the interaction energy fixed at 0.1 eV. Note that doping suppresses Ce pair formation. The error bar for the simulation is smaller than the line width. (c–e) Exemplify three scenario, with schematic lattices showing the effect of repulsive interaction and doping on the Ce3+ pair formation: (c) undoped ceria surface without neighboring Ce3+ pair interaction, where Ce3+ and Ce4+ arrange randomly. (d) Undoped ceria surface with repulsive Ce3+-Ce3+ interaction. Since Ce3+ and Ce4+ arrange alternately, no Ce3+-Ce3+ pair is formed up to 50% [Ce3+]. (e) Ceria lattice with 50% of its sites occupied by the dopant. Since Ce sites are isolated from each other by the dopants, the Ce3+-Ce3+ pair formation is suppressed.
interaction energies. When \( E_{\text{Ce}^3-\text{Ce}^3} = 0 \) eV (no interaction), the concentration of \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pairs progressively increased with \( [\text{Ce}^{3+}] \). However, when considering the repulsive interactions \( (E_{\text{Ce}^3-\text{Ce}^3} = 0.1, 0.2 \) eV), a threshold formation of \( \text{Ce}^{3+}-\text{Ce}^{4+} \) pair appeared. On the other hand, no threshold relation was found in the formation of \( \text{Ce}^{3+}-\text{Ce}^{4+} \) pairs, as expected.

The effect of doping on \( \text{Ce} \) pair formation is shown in Fig. 4b, with the interaction energy between neighboring \( \text{Ce}^{3+} \) sites fixed at 0.1 eV. As described in more detail in the Methods section, the dopant sites are randomly distributed and are treated as immobile during the simulation. Lattices with three different doping ratios were calculated: 0%, 20%, and 50%, which is in accord with the surface composition measured with APXPS (Fig. 2c). As a result, lattices with higher doping ratio exhibited a smaller concentration of \( \text{Ce}^{3+}-\text{Ce}^{4+} \) and \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pairs.

The dependence of \( \text{Ce} \) pair concentrations on the interaction energy and doping concentration is explained as follows. Due to the repulsive interactions between adjacent \( \text{Ce}^{3+} \) sites, it is energetically more favorable for \( \text{Ce}^{3+} \) to be surrounded by \( \text{Ce}^{4+} \) (Fig. 4d). As a result, the \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pair is difficult to form at low \( [\text{Ce}^{3+}] \). However, once \( [\text{Ce}^{3+}] \) exceeds 50%, any increase in \( [\text{Ce}^{3+}] \) results in additional \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pair formation because of site unavailability, regardless of the interaction strength. Consequently, the \( \text{Ce}^{4+}-\text{Ce}^{3+} \) pair concentration exhibits a threshold formation against \( \text{Ce}^{3+} \). Regarding the doping effect: since dopants were treated as immobile sites between Ce atoms in the lattice, they impede \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pair formation by “isolating” Ce sites from each other (Fig. 4e). Note each lattice structure shown in Fig. 4c–e only represents one possible configuration at a given \( [\text{Ce}^{3+}] \) and dopant concentration. In the real simulation process, a 50 by 50 2D cubic lattice was employed and the simulation results in Fig. 4a and b reflect the average values obtained from energy minimization of different lattice configurations.

As demonstrated in the Monte Carlo simulations, the catalysis of carbon deposition reaction is very likely linked to the \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pair formation. To better verify this idea, Fig. 5 presents the comparison of the carbon deposition measured by APXPS and the calculated \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pair concentration. The simulated \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pair formation exhibits a very similar behavior as the deposited carbon intensity as a function of \( [\text{Ce}^{3+}] \): the model not only captures the absolute value of the onset threshold (\(~50\% [\text{Ce}^{3+}]\)) but also correctly reflects the relative carbon intensity between ceria surfaces at different doping concentrations. As a result, we conclude that our model qualitatively delivers a strong evidence that the neighboring \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pair is the corresponding catalytic structure for carbon deposition from CO. Even though we modeled the pairing effect on the (001) surface, we believe that the same argument can be also applicable to other major surface terminations. This is because, regardless of the surface termination, two CO molecules must be dissociated nearby to each other, to enable the C-C bond formation during the growth of graphitic carbon. In other words, it is the formation of adjacent catalytic sites for carbon deposition, i.e., the formation of a nearest neighbor “\( \text{Ce}^{3+}-\text{Ce}^{3+} \)” pair, that is critical for the coking reaction. Since the distance between the nearest Ce–Ce pairs is the same on the (001), (011), and (111) fluorite-type surfaces, we would expect a similar catalytic behavior for carbon deposition on these low-index surface terminations of ceria. Nevertheless, future studies are needed to confirm this.

To summarize, in this section we discussed three possible origins of the onset of carbon deposition at a threshold \( [\text{Ce}^{3+}] \) at ceria surfaces. We deduce that this behavior arises mostly likely because of the formation of \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pairs after exceeding a threshold of \( [\text{Ce}^{3+}] \) at the surface. From this, we also deduce that the \( \text{Ce}^{3+}-\text{Ce}^{3+} \) pair serves as the catalytic structure for carbon deposition from CO. Consistent with this argument, the enhanced
carbon resistance on 50% Zr-doped and 50% Gd-doped ceria originates from a suppressed Ce\(^{3+}\)-Ce\(^{3+}\) pair formation. In this work, the proposed catalytic structure does not define a specific reaction pathway, and further studies are needed to reveal the atomistic reaction steps enabled by this catalytic structure.

**Conclusions**

In this work, we systematically studied the carbon deposition reaction during CO\(_2\) electrolysis on four fluoride-type ceria thin films: CeO\(_2\), Gd\(_{0.5}\)Ce\(_{0.5}\)O\(_{1.75}\), and Zr\(_{0.5}\)Ce\(_{0.5}\)O\(_2\). By performing in operando APXPS measurements, we revealed that, despite the general opinion that CeO\(_2\) is a carbon-tolerant catalyst, carbon deposition can readily occur on CeO\(_2\) surfaces to mitigate carbon poisoning in LT-SOCs. Moreover, carbon deposition exhibits an onset at a threshold value of 50% Ce\(^{3+}\) concentration when dopant concentration is relatively low or zero. This intriguing threshold [Ce\(^{3+}\)]-carbon relation deepens the understanding of the carbon deposition reaction mechanism: combining APXPS data with Monte Carlo simulation, we propose the most likely catalytic structure for carbon deposition to be the neighboring Ce\(^{3+}\)-Ce\(^{3+}\) pair. Inspired by this mechanism, we propose that doping CeO\(_2\) with non-redox-active cations can effectively mitigate the carbon deposition on CeO\(_2\) under LT-SOC operating conditions. This idea has been verified with in operando APXPS on 50% Gd and 50% Zr-doped CeO\(_2\), where carbon formation has been effectively suppressed.

Since Ce\(^{3+}\) is a key enabler in a wide range of electrocatalytic reactions,\(^{24,36}\) suppressing carbon deposition while maintaining a high [Ce\(^{3+}\)] is required for developing carbon-tolerant ceria-based electrocatalysts. Our results indicate that suppressing Ce\(^{3+}\)-Ce\(^{3+}\) pair formation at high [Ce\(^{3+}\)] can be the key to alleviate carbon deposition from CO. This includes ways to isolate Ce\(^{3+}\) cations from each other, for example by doping ceria with non-redox-active cations (such as 50% Zr- and 50% Gd-doped CeO\(_2\) in this work). When used as fuel cell electrodes, it has been suggested that higher Gd concentrations in Gd-doped ceria can improve electrode's electrical conductivity as well as dimensional stability.\(^{44-46}\) Previous studies have also shown that heavily Zr-doped ceria benefits oxygen surface exchange\(^{42}\) as well as bulk diffusivity.\(^{63}\) Therefore, both enhanced carbon resistance and electrocatalytic performance could be realized simultaneously on heavily doped ceria surfaces. In addition, as the number of Ce\(^{3+}\) sites per unit surface area of doped ceria is lower than the undoped case, one may also consider increasing the total surface area of the doped ceria by employing nanoparticles.\(^{64,65}\)

**Methods**

**Film fabrication**

The electrochemical cells were fabricated on 10 mm × 10 mm × 0.5 mm 8% yttria-stabilized zirconia (YSZ) (001) single crystal substrates (MTI Corporation), which served as the solid electrolyte. Pt paste (SPI Supplies) was applied on the back of the YSZ substrate and then sintered in air at 800 °C for 1 hour as the counter electrode (CE). Buried, micro-patterned Pt grids were fabricated through photolithography on the front side of the substrate as the current collector (ESI Fig. S1†). The thin film working electrode (WE) was deposited on top of YSZ and Pt grids using pulsed laser deposition (PLD), where a KrF excimer laser with 248 nm wavelength was used. During deposition, the substrate temperature was kept at 750 °C in an oxygen pressure of 10 mTorr.

**In operando APXPS**

The APXPS measurements were carried out at Beamline 9.3.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory (ALS); the NAP-XPS end station of the Pierre and Marie Curie University set on TEMPO beamline at Synchrotron SOL-EIL; and the IOS beamline 23-ID-2 of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Lab. The electrochemical cells described above were placed on a ceramic heater, with thermocouples mounted directly onto the surface for temperature measurements. The thermocouple along with a Pt wire was also used to apply electrochemical bias on the sample, where the Pt wire was welded to a Pt foil beneath the CE. During the experiment, cathodic (CO\(_2\) reduction) and anodic (CO oxidation) biases were applied on the electrochemical cell to drive surface redox reaction as well as to change the oxidation state of surface Ce cations.

Samples were preconditioned at 350 °C in 20 mTorr O\(_2\) at the beginning of the measurement to remove adventitious carbon. The operando environment studied in this work was 450 °C in 0.15 Torr (SOLEIL, NSLS-II) and 0.3 Torr (ALS) 9 : 1 CO/CO\(_2\) atmosphere, under cell bias ranging from +0.7 to −1.5 V. The APXPS spectra were collected at an incident photon energy of 370 eV (SOLEIL) and 400 eV (ALS, NSLS-II), CeO\(_2\), Gd\(_{0.5}\)Ce\(_{0.5}\)O\(_{1.75}\), and Zr\(_{0.5}\)Ce\(_{0.5}\)O\(_2\) were tested in ALS while Gd\(_{0.8}\)Ce\(_{0.2}\)O\(_{1.9}\) were tested in all of the three beamlines. All the XPS spectra were quantified with CasaXPS software. Carbon deposition intensity was calculated by integrating the graphitic carbon area in the C 1s spectra and then normalized to the CO gas peak intensity (ESI Note 4†). [Ce\(^{3+}\)] was calculated as the peak area ratio of Ce\(^{3+}\) features to the total area of Ce 4d (ESI Note 5†).

**Monte Carlo simulation**

A 50 × 50 2D square lattice with periodic boundary conditions was employed to simulate the ceria (001) surface. Since the aim of this simulation is to quantify Ce pair formation, the simulated lattice consists purely of Ce and dopant sites, and no oxygen sites were considered. In the simulated square 2D lattice, each atom has four nearest neighboring sites and represents either a Ce (Ce\(^{3+}\) or Ce\(^{4+}\)) or a dopant. Only the interaction between two nearest Ce\(^{3+}\) sites was considered, while all other interactions were ignored. Therefore, the system Hamiltonian can be expressed as $H = N_{\text{Ce}^3-\text{Ce}^3}E_{\text{Ce}^3-\text{Ce}^3}$, where $N_{\text{Ce}^3-\text{Ce}^3}$ and $E_{\text{Ce}^3-\text{Ce}^3}$ denote the Ce\(^{3+}\)-Ce\(^{3+}\) pair number and the interaction energy between them, respectively. In this model, Ce\(^{3+}\) and Ce\(^{4+}\) sites were set free to switch while dopant sites were considered immobile. This assumption is in agreement
with the significant lower mobility of cations compared to that of polarons in ceria. The Metropolis Monte Carlo simulation was conducted as follows:

(1) Randomly pick two Ce sites on the lattice and calculate the energy difference \( \Delta H \) of switching \( \text{Ce}^{3+} \) and \( \text{Ce}^{4+} \).

(2) If the switch results in a reduced system energy (\( \Delta H < 0 \)), accept it with a probability of 1. Otherwise, accept the switch with a probability of \( \exp \left( \frac{\Delta H}{k_B T} \right) \), where \( k_B \) and \( T \) denote the Boltzmann constant and temperature respectively.

In accord with the experimental environment, the simulation temperature was set to be 450 °C. 100 random configurations were generated as initial guesses at each \([\text{Ce}^{3+}]\) and doping ratio. Then each of the 100 initial lattices was evolved by switching sites according to the Metropolis scheme. Each Monte Carlo step (MCS) consisted of 2500 switching trials, and the ensemble average was estimated by averaging over the last 200 MCS after equilibrium. Finally, the concentration of Ce pairs (both \( \text{Ce}^{3+} - \text{Ce}^{3+} \) and \( \text{Ce}^{3+} - \text{Ce}^{4+} \)) were calculated as the mean value of the 100 thermodynamically equilibrated lattices (ESI Note 1†).

**Author contributions**

J. W., S. R. B., and B. Y. conceived the experiment design. J. W. and Q. L. prepared the samples and J. W. conducted the sample characterization. All authors carried out the APXPS experiments. J. W. performed the Monte Carlo simulations. All authors contributed to writing the manuscript. B. Y. supervised the project.

**Conflicts of interest**

The authors declare that they have no competing financial interests.

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