Two-dimensional metal oxide pseudocapacitors are promising candidates for size-sensitive applications. However, they exhibit limited energy densities and inferior power densities. Here, we present an electrodeposition technique by which ultrathin CeO$_{2-x}$ films with controllable volumetric oxygen vacancy concentrations can be produced. This technique offers a layer-by-layer fabrication route for ultrathin CeO$_{2-x}$ films that render Ce$^{3+}$ concentrations as high as ~60 at% and a volumetric capacitance of 1873 F cm$^{-3}$, which is among the highest reported to the best of our knowledge. This exceptional behaviour originates from both volumetric oxygen vacancies, which enhance electron conduction, and intercrystallite water, which promotes proton conduction. Consequently, simultaneous charging on the surface and in the bulk occur, leading to the observation of redox pseudocapacitive behaviour in CeO$_{2-x}$. Thermodynamic investigations reveal that the energy required for oxygen vacancy formation can be reduced significantly by proton-assisted reactions. This cyclic deposition technique represents an efficient method to fabricate metal oxides of precisely controlled defect concentrations and thicknesses.
Increasing demands for energy-efficient portable electronic devices of minimal size have led to the development of two-dimensional (2D) electrochemical pseudocapacitors (EPCs)\textsuperscript{3–4}. Fabrication of 2D EPC materials of adequate transparency and electrical conductivity can extend the potential applications to optoelectronic devices, such as touch screens and solar cells\textsuperscript{3,4}. Generally, the two-dimensionality of the structures provides ultrafast electron transferability across the films and high-charge carrier accessibility to the active sites, resulting in desirable energy and power densities. Among the different types of energy storage devices, metal oxide (MO) pseudocapacitors have shown superiority owing to their greater energy densities and higher power densities compared to those of electrical double-layer capacitors (EDLCs) and batteries, respectively\textsuperscript{2}. However, conventional synthesis methods, which involve assembly of 2D MO nanosheets, lead to tight stacking of the sheets in the film, thereby hindering charge carrier diffusion through the interlayer spaces, impacting negatively on performance\textsuperscript{2,10}. As an alternative, MOs with intercalation pseudocapacitive behaviour (e.g., RuO\textsubscript{2} and Nb\textsubscript{2}O\textsubscript{5}) can be used since charge/discharge occurs not only at the electrode/electrolyte interface but also within the bulk of the 2D films\textsuperscript{11–13}. Nonetheless, high costs and toxicity in the case of RuO\textsubscript{2} and poor electron transfer rates in the case of Nb\textsubscript{2}O\textsubscript{5} limit their applicability\textsuperscript{14–16}. Further, limitations in achieving reproducible film thicknesses have resulted in inconsistent performance. To the best of our knowledge, intercalation pseudocapacitance has not been observed to date in CeO\textsubscript{2}, although very high specific capacitances of this material have been reported previously\textsuperscript{17,18}, indicating its promise for energy storage applications.

Here, we show a novel cyclic electrodeposition method to synthesise ultrathin films of CeO\textsubscript{2-x} (9–70 nm) comprised of ultrathin crystallites (3–8 nm). These films exhibit high oxygen vacancy concentrations ([\textit{V}\textsubscript{O}\textsuperscript{\textast}]) of ~4–15 at\% and intercrystallite H\textsubscript{2}O, where the former enhance the electron conduction and the latter promotes the proton conduction. These CeO\textsubscript{2-x} ultrathin films demonstrate proton insertion/disinsertion pseudocapacitive behaviour. They exhibit the outstanding volumetric capacitance of 1873 F cm\textsuperscript{-3}, which considerably exceeds the highest value yet reported (1160 F cm\textsuperscript{-3}) for ultrathin MnO\textsubscript{2}/Au\textsuperscript{19} to the best of our knowledge. This work reports a simplified, scalable and controllable method that can be extended to the fabrication of other MO thin films that are being used increasingly for electronic, energy storage and photoelectrochemical applications.

**Results**

**Characterisation of thin films.** The thermodynamics of the Ce\textsuperscript{3+–4+}–CH\textsubscript{3}COOH–H\textsubscript{2}O system, which was used to fabricate the thin films, were investigated (details in Supplementary Note 1). The resultant data were analysed to understand the electrochemical behaviour of the system and subsequently to determine the optimal conditions for the electrodeposition of Ce(OH)\textsubscript{4}, which forms readily to CeO\textsubscript{2} in aqueous solutions\textsuperscript{20} (details in Supplementary Note 2). By varying the cyclic voltammetry scan rate and number of cycles, CeO\textsubscript{2-x} films of different thicknesses and Ce\textsuperscript{3+} concentrations ([Ce\textsuperscript{3+}] of ~18–60 at\% (equivalent to 4.5–15\% of [\textit{V}\textsubscript{O}\textsuperscript{\textast}]) were deposited on fluorine-doped tin oxide (FTO) glass substrates. Figure 1a shows a representative X-ray diffraction (XRD) pattern of a CeO\textsubscript{2-x} thin film. The nanostructure and elemental composition of the film was studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) (Supplementary Note 3). Figure 1b shows an X-ray photoelectron spectroscopy (XPS) spectrum for the 3d orbital of Ce. The [Ce\textsuperscript{3+}], which was calculated from the areas of the Ce\textsuperscript{3+} doublet peaks (purple) at the binding energies of ~800 and ~805 eV, was high at 43.6 at\% ([\textit{V}\textsubscript{O}\textsuperscript{\textast}] = 10.9\%). Details of the quantitative analyses of the spectra are provided in Supplementary Note 4. These calculations were correlated with the XPS data for the 1s orbital of the O peaks, as shown in Fig. 1c. These were fit using Gaussian functions at 529.21 eV (peak 1, blue), 531.23 eV (peak 2, purple) and 532.96 eV (peak 3, black). Peaks 1 and 2 are for oxygen bound to Ce\textsuperscript{4+} ([O(Ce\textsuperscript{4+})]) and Ce\textsuperscript{3+} ([O(Ce\textsuperscript{3+})]), respectively, and peak 3 is for adsorbed water molecules ([H\textsubscript{2}O])\textsuperscript{21}. The area of the peak for oxygen bound to Ce\textsuperscript{3+} is ~56.0 at\% of the total oxygen concentration ([O]), which is even greater than the equivalent value of 43.6 at\% for Ce\textsuperscript{3+}. The difference in values is attributed to the effect of the sensitivity of the XPS beam: For the Ce 3d peak, the penetration depth extends to ~1.0 nm but, for the O 1s peak, it extends to ~1.5 nm\textsuperscript{22}. Figure 1d shows a representative high-angle annular dark-field (HAADF) image, which reveals a film thickness of ~18 nm and crystallites in the size range 3–8 nm. Two [O] distributions across (Fig. 1e) and within (Fig. 1f) crystallites were observed by EDS line profiles. Sharp decreases at the crystallite interfaces (Fig. 1e) confirmed increasing [\textit{V}\textsubscript{O}\textsuperscript{\textast}] at these locations, as reported previously\textsuperscript{23}. In contrast, the EDS line profile of [O] along a single crystallite (Fig. 1f) showed much less variation. The formation of a highly oxygen-deficient CeO\textsubscript{2-x} structure is confirmed by analysing the relative change in the Ce\textsuperscript{3+}/Ce\textsuperscript{4+} ratio using electron energy loss spectroscopy (EELS). Two representative areas within the bulk were analysed (Supplementary Fig. 7), the spectra of which are shown in Fig. 1g, at the crystallite boundaries, and Fig. 1h, within the crystallite. Hojo et al\textsuperscript{23} showed that the [\textit{V}\textsubscript{O}\textsuperscript{\textast}] can be evaluated from the ratio of the intensity (height) of the M5 peak (orange) to that of the M4 peak (green), where the ratio is bounded by the minimal value of ~0.9 for stoichiometric CeO\textsubscript{2} (viz., [\textit{V}\textsubscript{O}\textsuperscript{\textast}] = 0) and the maximal value of ~1.25 for CeO\textsubscript{2-x} (viz., CeO\textsubscript{2-x} with the theoretically maximal [\textit{V}\textsubscript{O}\textsuperscript{\textast}] = 25\%). In this work, the M5/M4 ratios for boxes g and h were determined to be ~1.19 and ~1.10 and hence represent approximate [\textit{V}\textsubscript{O}\textsuperscript{\textast}] of 20.7\% and 14.2\%, respectively. The greater [\textit{V}\textsubscript{O}\textsuperscript{\textast}] at the crystallite boundary compared to that in the bulk is consistent with the results of others\textsuperscript{23–27}. However, the high [\textit{V}\textsubscript{O}\textsuperscript{\textast}] at intracrystallite regions and the sub-nanometre layer-by-layer deposition (discussed subsequently) reveal that \textit{V}_\textsubscript{O} are at the boundaries but also suggest a homogenous distribution through the film. These data demonstrate that relatively high [\textit{V}\textsubscript{O}\textsuperscript{\textast}] are accommodated at both intercrystallite and intracrystallite regions.

**Mechanism of thin-film deposition.** In order to clarify the mechanism of formation of such ultrathin CeO\textsubscript{2-x} films, electrodeposition data were deconvoluted in terms of the reactions over cycling (the pH effect analysis is in Supplementary Note 5). Figure 2 shows the voltammograms obtained for cycle numbers 1, 25 and 50 at a scan rate of 300 mV s\textsuperscript{-1}. As shown in Fig. 2a, during the forward scan of the 1st cycle, Ce(OH)\textsubscript{4} precipitation occurs at E = 0.47 V vs. Ag/AgCl (Ox). This is followed by partial transformation of Ce(OH)\textsubscript{4} to CeO\textsubscript{2}, which is a nonfaradaic reaction and thus has no corresponding peak. The cathodic reaction for Ce(OH)\textsubscript{4} involves reductive dissolution to Ce(III) at E = –0.02 V vs. Ag/AgCl (Re\textsubscript{0}) and its return to the electrolyte. The lower peak current density of Re\textsubscript{0} relative to that of Ox\textsubscript{1} indicates only partial reduction of Ce(OH)\textsubscript{4}, since some of this already is transformed to CeO\textsubscript{2}. The cathodic reaction for CeO\textsubscript{2} involves the generation of Ce\textsuperscript{3+} and \textit{V}_\textsubscript{O} at E = –0.13 V vs. Ag/AgCl (Re\textsubscript{0}). As Fig. 2b (25th cycle) shows, the as-formed \textit{V}_\textsubscript{O} are annihilated partially during the forward scan at E = + 0.07 V vs. Ag/AgCl (Ox\textsubscript{2}), so there remain some residual [\textit{V}\textsubscript{O}] in the film (discussed in next paragraph). This is confirmed
the voltammogram area with cycling is indicative of continuous growth of the "cytary Fig. 9a, b and c, d, respectively. Also, the increasing growth of the volumetric results in the emergence of another pair of peak potentials (blue) in Fig. 2b at $E = -0.3 \text{ V vs. Ag/AgCl (Ox3)}$ and $E = -0.4 \text{ V vs. Ag/AgCl (Re3)}$, which correspond to proton insertion in and exclusion from, respectively, the Ce$^{4+}$-rich nanostructure. These data suggest that $V_{\text{O}^{*}}^{\text{O}^{*}}$ plays a critical role as a trapping site for proton diffusion during charging, so increasing the volumetric $[V_{\text{O}^{*}}^{\text{O}^{*}}]$ should enhance proton insertion/disinsertion and consequently increase the proton-related peak intensities. Thus, expansion in the sum of the peak areas shown in Fig. 2c (at the 50th cycle) can be ascribed to both the increasing thickness and the volumetric $[V_{\text{O}^{*}}^{\text{O}^{*}}]$ of the thin films. Simulated nanostructures corresponding to Ce(OH)$_4$ formation, Ce(OH)$_4$ to CeO$_2$ transformation and CeO$_2$-x formation are shown in Fig. 2d-f, respectively. Also, comprehensive discussion regarding the peak identification, chemical reactions involved and calculation of the peak areas is provided in Supplementary Note 6.

The formation of $V_{\text{O}^{*}}^{\text{O}^{*}}$ was confirmed further by thermodynamic calculations (Supplementary Note 7). Typically, the $V_{\text{O}^{*}}^{\text{O}^{*}}$ formation energy is highly positive and can be varied in the range 1.20–2.25 eV, which is subject to the crystal size and exposed facets. However, integration of protons (H$^+$) during reaction in an aqueous solution can shift dramatically the required energy toward low values of ~0.1 eV (Supplementary Table 9). In our experiments, local protons are provided at the working electrode/electrolyte interface upon OH$^-$ consumption during the formation of Ce(OH)$_4$ (Ox1). Although the durability of as-synthesised $V_{\text{O}^{*}}^{\text{O}^{*}}$ is affected by the Ox2 reaction, during the forward scan, high OH$^-$ consumption by the Ox3 reaction limits the availability of OH$^-$ for the Ox4 reaction. Thus, the annihilation of $V_{\text{O}^{*}}^{\text{O}^{*}}$ occurs partially, leaving the remaining $V_{\text{O}^{*}}^{\text{O}^{*}}$ in the structure. This is confirmed by increasing the peak current density for the proton intercalation reaction (Re3) as a function of cycling. Therefore, both experimental and theoretical evidence confirm a proton-assisted oxygen vacancy creation (PAOVC) mechanism, in which a high content of volumetric $V_{\text{O}^{*}}^{\text{O}^{*}}$ in the CeO$_2$-x nanostructure can be obtained. There appears to be only one work on the creation of $V_{\text{O}^{*}}^{\text{O}^{*}}$ using PAOVC. In that work, a constant reduction potential was applied to as-synthesised nanotubes of TiO$_2$ (~40 nm wall thickness), leading to the creation of a high $[V_{\text{O}^{*}}^{\text{O}^{*}}]$. Although that work followed the same principle as ours, applying an excessively high constant potential to as-synthesised samples results in a situation of highly unstable $V_{\text{O}^{*}}^{\text{O}^{*}}$, which are in a non-equilibrium condition. Therefore, the $[V_{\text{O}^{*}}^{\text{O}^{*}}]$ reduces very quickly (over a few hours) in ambient conditions, making such nanostructures unsuitable for applications where long-term exposure is required. In contrast, in our work, there is only a one-step process comprised of cyclic deposition, followed by PAOVC, to yield a high density of volumetric $[V_{\text{O}^{*}}^{\text{O}^{*}}]$. Additionally,
due to equilibration (production/annihilation) of $V_{\text{Ce}}^{\bullet}$ over the cycling, the resultant CeO$_2$ exhibits great chemical stability after long-term exposure to aqueous solutions (Supplementary Fig. 10).

**Electrochemical performances of thin films.** The electrochemical behaviour of the CeO$_{2-x}$ films was investigated in 1 M NaCl aqueous electrolyte (pH = 7) using a three-electrode configuration system, in which Ag/AgCl, Pt coil and deposited film on FTO were used as reference, counter and working electrodes, respectively. Figure 3a shows typical voltammograms of the CeO$_{2-x}$ films with ~4 at% Ce$^{3+}$ (scan rate: 5–500 mV s$^{-1}$). At a scan rate of 5 mV s$^{-1}$, an exceptional volumetric capacitance of 1873 F cm$^{-3}$ and an areal capacitance of 4.56 mF cm$^{-2}$ were achieved (the calculation method is given in Supplementary Note 8). The high capacitances of the thin films are attributed to the optimal crystallite sizes (3–8 nm; Supplementary Fig. 11), which are identical to the experimental particle size range reported (3–8 nm) to exhibit the greatest surface Ce/O ratio and consequent high oxygen storage capacity. In contrast, a subnanometre particle size has been projected by calculation to exhibit optimal oxygen storage capacity. The rapid kinetics of the charge/discharge reactions were assessed by measuring the overpotential values, which did not vary significantly in the range 0.05–0.3 V for all of the scan rates. The rate-controlling mechanism during the charge/discharge is determined by Eq. 1:

$$i = a v^b$$

where $i$ is the peak current, $a$ is a constant, $v$ is the scan rate and the exponent $b$ indicates the predominant kinetics mechanism. A $b$ value of 0.5 indicates a slow semi-infinite current while a value of 1 indicates rapid surface-confined capacitive behaviour (i.e., high power density). The $b$ values were calculated to be 0.86 and 0.80 for the charge and discharge reactions, respectively, at scan rates of 5–500 mV s$^{-1}$, demonstrating that the high power density of the CeO$_{2-x}$ films originated from unique surface-controlled kinetics. Examination of the $b$ values for the well-known intercalation pseudocapacitor Nb$_2$O$_5$ (0.80 and 0.70 for the charge and discharge reactions, respectively, at scan rates $\leq$50 mV s$^{-1}$) indicates that the power densities are comparable.

Additionally, the contribution of different charge/discharge mechanisms (surface $k_1v$; bulk diffusion: $k_2v^{0.5}$) of the CeO$_{2-x}$ film is considered using Eq. 2:

$$i(V) = k_1 v + k_2 v^{0.5}$$

where $i(V)$ is the instantaneous current and $k_1$ and $k_2$ are obtained from the slope and ordinate intercept ($v \rightarrow \infty$), respectively, of the $i(V)/v^{0.5}$ vs. $v^{0.5}$ plot. Figure 3c shows that the relative contributions of the two mechanisms change at different scan rates, although the surface capacitive mechanism is dominant at all scan rates (Fig. 3c).

Figure 3d illustrates the excellent stability of the charge-storage performance, where the capacitance retention of ~94% after 1000 cycles is achieved. As expected, the efficiency of the film changes slightly during the first 500 cycles and then the efficiency becomes constant. In order to evaluate the stability of the film, XPS analysis was conducted after 1000 cycles, the results of which reveal that there is insignificant change in the [Ce$^{3+}$] while the [Ce$^{4+}$] decreased and the $[\text{O}_2\text{H}_2\text{O}]$ increased, as shown in Supplementary Fig. 10. Figure 3e compares the volumetric and areal capacitances of the CeO$_{2-x}$ film, as a function of thickness, in comparison to other films reported in recent publications. These data reveal that the CeO$_{2-x}$ film exhibits the highest volumetric capacitance and that the value is eight times greater than that of carbon nanotube-MnO$_2$ hybrid ultrathin films. This extraordinary performance can be attributed to the coexistence of (1) effective intracrystallite electron conduction owing to the $V_{\text{Ce}}^{\bullet}$ in CeO$_{2-x}$ and (2) rapid intercrystallite proton transfer activated by the adsorbed water molecules (H$_2$O peak in Fig. 1c). The latter is supported by the symmetry of the
voltagograms, particularly the peak potentials of the redox reactions, revealing unique redox pseudocapacitive behaviour that is characteristic of redox pseudocapacitors, such as hydrous RuO2. The most commonly cited possible charge/discharge redox reactions are as follows:

\[
\begin{align*}
\text{Cathodic charge reaction:} & \quad \text{Ce}^{4+} + x\text{O}_2 + y\text{e}^- + \beta\text{H}^+ \rightarrow \text{Ce}^{3+} + x\text{O}^{2-} + y\text{OH}^{\beta^-} + \beta\text{H}^+ \\
\text{Anodic discharge reaction:} & \quad \text{Ce}^{3+} + x\text{O}^{2-} + y\text{e}^- + \beta\text{H}^+ \rightarrow \text{Ce}^{4+} + x\text{O}_2 + y\text{OH}^{\beta^-}
\end{align*}
\]

First-principles calculations of effect of oxygen vacancies on thin films. The mechanism of electron conduction has been investigated with spin-polarised density functional theory (DFT) calculations (for details, see Methods). In accordance with recent work and DFT calculations, the Ce electrons in orbitals 5s, 5p, 6s, 5d and 4f and the O electrons in orbitals 2s and 2p were considered to be the valence electrons. First, we determined the most energetically favourable configurations for \( V_{O}^{\alpha} \). We found that the interactions between oxygen vacancies are attractive and so they tend to form clusters. According to our DFT calculations, during the transformation from stoichiometric CeO2 (Fig. 4a) to non-stoichiometric CeO2-\( \alpha \) (Fig. 4b), the vacancy clusters form one-dimensional tunnel-like structures along the [001] direction. As shown in Fig. 4c, an increase in \( V_{O}^{\alpha} \) from 0% to 25% results in a substantial decrease in the energy band gap \( E_g \) of 38%, namely, from 3.2 eV to 1.9 eV. Consequently, an increase in \( \delta \) may yield significant enhancements in the electronic transport of CeO2-\( \alpha \), as has been suggested previously by other researchers. The origin of the decrease in the band gap stems from the two electrons left by the vacancy formation, which fills the localised 4f orbitals in the two surrounding Ce ions (mostly forming the bottom of the conduction band). Figure 4d illustrates the electronic charge density redistribution that occurs during the change from stoichiometric CeO2 to non-stoichiometric CeO2-\( \alpha \), which leads to a charge density increase around the Ce ions (see surface denoted by blue colour). In addition, we checked how possible nano-size effects influence the estimation of the \( E_g \) in stoichiometric and non-stoichiometric ceria and the results, which are given in Supplementary Note 9, reveal insignificant nano-size effects.

Controllability of thickness and oxygen vacancy concentration of thin films. In this section, we show that our method can be used for precision engineering of both the \( V_{O}^{\alpha} \) and the film thicknesses. Figure 5a–d show the voltammograms of four films at scan rates of 50, 300, 1000 and 3000 mV s\(^{-1}\), respectively. The characterisation data (XRD, laser Raman microspectroscopy (Raman), TEM, atomic force microscopy (AFM) and time-of-flight secondary ion mass spectrometry (TOF SIMS)) of the films are provided in Supplementary Note 10. As expected, increasing the scan rate results in increasing peak area owing to the greater current density and resultant deposition of CeO2. However, owing to the faster kinetics at higher scan rates, there is insufficient time for the Ce(OH)\(_{2}\) → CeO2 transformation to occur immediately before the reverse scan (Fig. 2), which results in the
Fig. 4 First-principles calculations performed on stoichiometric CeO\textsubscript{2} and non-stoichiometric CeO\textsubscript{1.5}. a Structural projections along the [100] and [110] directions for stoichiometric CeO\textsubscript{2}. b Structural projections along the [100] and [110] directions for non-stoichiometric CeO\textsubscript{1.5}, where the V\textsubscript{O} are self-organised into clustered one-dimensional tunnels oriented in the [001] direction. c Effect of V\textsubscript{O} on calculated spin-polarised total density of electronic states, showing spin-up (positive) and spin-down (negative) regions (Fermi energy levels shifted to zero). d Structural projections along the [100] direction for stoichiometric CeO\textsubscript{2} and non-stoichiometric CeO\textsubscript{1.5}; surfaces of identical electronic charge are highlighted with blue colour; the electronic density increases around the Ce ions, which are located near the oxygen vacancies, compared to the stoichiometric system. Large yellow and small red spheres represent Ce and O ions, respectively.

Fig. 5 Proton-assisted control of oxygen vacancy formation during cyclic voltammetry. Cyclic voltammograms at scan rates: a 50 mV s\textsuperscript{-1}. b 300 mV s\textsuperscript{-1}. c 1000 mV s\textsuperscript{-1}. d 3000 mV s\textsuperscript{-1}. e-h Corresponding XPS Ce 3d spectra. i-l Corresponding XPS O 1s spectra.
creation of a thinner layer of CeO$_2$–x. The application of a large reduction current to the layer during each reverse scan leads to the creation of high [$V_o^{**}$] effectively throughout the entire film. These conclusions are supported experimentally by the Ce 3d XPS results in Fig. 5e–h, which show increasing [Ce$^{3+}$] from 18 at% to 44 at% at scan rates of 50 mV s$^{-1}$ to 3000 mV s$^{-1}$, respectively; the film thicknesses for 100 cycles were in the range ~25 nm to ~70 nm (i.e., ~1–3 atomic layers per cycle). Further, the XPS results for the O 1s XPS spectra in Fig. 5i–l show that the fractional [O/ Ce$^{2+}$] increases from 18 at% to 56 at% at scan rates of 50 to 3000 mV s$^{-1}$, respectively, which also confirms that higher scan rates lead to the generation of higher [$V_o^{**}$]. Additionally, the XPS results are confirmed by photoluminescence (PL) spectroscopy of the thin films, the results of which are given in Supplementary Fig. 18.

Figure 6a shows increasing areas of the pseudocapacitance-related cyclic voltammograms as a function of [Ce$^{3+}$] at the associated scan rates (electrochemical performances are given in Supplementary Fig. 17). The electrochemical performance data are summarised in Fig. 6b, which shows that increasing the [Ce$^{3+}$] (and corresponding [$V_o^{**}$]) by ~2.5 times results in an eightfold increase in the volumetric capacitance.

The effects of variation of the cycle number at a constant scan rate on the change in film thickness also were considered (XPS, TEM, AFM and TOFSIMS results are in Supplementary Note 11). The data show that the film thickness is directly proportional to the cycle number. In contrast, increasing the cycle number decreased the [$V_o^{**}$], as reflected by the [Ce$^{3+}$] (and corresponding [$V_o^{**}$]) by ~2.5 times results in an eightfold increase in the volumetric capacitance. 

Discussion
In summary, the present work reports a straightforward approach to fabricate ultrathin films with high [$V_o^{**}$] and precisely controlled thickness using near-room-temperature cyclic voltammetry at large cycle numbers and high scan rates. Critically, by leveraging the slow kinetics of the cerium redox reactions and the PAOVC mechanism, layer-by-layer deposition of highly reduced CeO$_2$–x with homogeneous volumetric distributions of $V_o^{**}$ was achieved. Further, rapid cyclic deposition was shown to create volumetric $V_o^{**}$ with long-term stability, which has led to the observation of pseudocapacitive behaviour in CeO$_2$–x. This behaviour is attributed to simultaneous intracrystallite electron conduction owing to high volumetric [$V_o^{**}$] and rapid intercrystallite proton transfer activated by adsorbed water molecules. These nanostructures, which can be engineered for superior performance using scan rates up to two orders of magnitude greater than those used in the present work, exhibit the highest volumetric capacitance of any ultrathin film to date (Supplementary Table 12). The present work shows that the PAOVC method has the potential to be applied to other MOs for a range of applications in energy and the environment, e.g., gas sensing, oxygen storage and energy storage.

Methods

Electrochemical cell preparation. The electrodeposition was performed using a classical three-electrode configuration system$^{48,49}$. Fluorine-doped tin oxide on glass (FTO; Wuhan Geao Scientific Education Instrument, China; 2.0 cm × 1.5 cm) with a film resistivity of ~18 Ω. platinum (Basi Inc., Indiana, USA, coil L = 23 cm, wire D = 0.5 mm), and Ag/AgCl (Basi Inc., West Lafayette, IN, USA) were used as the working, counter and reference electrodes, respectively. All potentials were adjusted the pH to value of 6.

Synthesis of ultrathin films. Ultrathin films of CeO$_2$–x were deposited electrochemically on FTO substrates using cyclic voltammetry at scan rates in the range 50–3000 mV s$^{-1}$ and cycle numbers in the range 50–2000 using an aqueous electrolyte. The electrolyte was synthesised by mixing 0.05 M Ce(NO$_3$)$_3$·6H$_2$O and 0.05 M Ca(H$_2$O)$_2$ at DI water (resistance 18.2 MΩ cm); 1 M NaOH was used to adjust the pH to value of 6.

Characterisation. Mineralogical data for the films was obtained using a Philips X’Pert Multipurpose X-Ray Diffractometer (MPD; Almelo, Netherlands, CuKa radiation [0.15405 nm], 2$t^0$–80° 2θ, step size 0.02° 2θ, scanning speed 5.5° 2θ min$^{-1}$). The peaks were analysed using X’Pert High Score Plus software. These data were supplemented by laser Raman microspectra (Raman; Renishaw in Via Raman microscope, Gloucestershire, UK, beam diameter 1.5 µm), which was equipped with a 35 mW helium-neon green laser (514 nm), in the range 200–800 cm$^{-1}$. The spectra were fitted and calibrated using Renishaw WIRE 4.3 software. Electron micrographs of the thin-film nanostructures were obtained by high-resolution transmission electron microscopy (HRTEM; Philips CM 200, Eindhoven, the
was installed in the AFM holder and used for all measurements. The samples were microscopy (AFM; Bruker Dimension Icon SPM, PeakForce Tapping mode, Bill-

First-principles calculations. The PBEsol functional was used, as implemented in the VASP package. A 3×3×1 supercell scheme, with \( U = 3 \) eV, was employed for superior treatment of the localised Ce 4f electronic orbitals (the adopted PBEsol + U set-up was confirmed to reproduce the experimental lattice parameter and band-gap of bulk CeO\(_2\) as closely as possible). The "projector augmented wave" method was used to represent the ionic cores by considering the force on the atoms fell below 0.01 eV Å\(^{-1}\). These technical parameters yielded zero-temperature energies that converged to within 0.5 meV per formula unit. In order to estimate accurate energy band gaps, the hybrid HSE06 exchange-correlation functional was used. Our spin-polarised density functional theory calculations were performed on a supercell containing 24 atoms for the stoichiometric system. The non-stoichiometric geometries were generated by successively removing oxygen atoms from the simulation box.

Electrochemical measurements. The electrochemical performance of the ultra-thin films was studied using a three-electrode system by cyclic voltammetry as a component of one an electrochemical station (Estat Pro, Crown Point, IN, USA). The system included an Ag/AgCl electrode as reference electrode (Basi Inc., West Lafayette, IN, USA), Pt wire as described previously as counter electrode (Basi Inc., West Lafayette, IN, USA) and CeO\(_2\) film on FTO substrate as working electrode in 1 M NaCl aqueous electrolyte; the pH was adjusted to 7 using a 1 M NaOH solution. Cyclic voltammetry was measured using a negative potential window in the range \(-1.0\) to \(-0.2\) V vs. Ag/AgCl electrode at room temperature for scan rates in the range 5–500 mV s\(^{-1}\). In order to confirm that the total capacitances calculated could be attributed to the ultrathin CeO\(_2\) films, the volumetric capacitance of bare FTO was determined to be insignicant (\(\leq 10^{-9}\)\% of that of the CeO\(_2\) films).

Data availability

All data are available within the manuscript and supplementary information. Further information can be acquired from the corresponding authors upon reasonable request.

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