

# CeO<sub>2</sub>-based materials as electrocatalysts for CO<sub>2</sub> electrochemical reduction in Solid Oxide Electrolysis Cells

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## Introduction

Ceria-based materials form a very promising class of electrocatalysts for CO<sub>2</sub> reduction reaction in high temperature solid oxide electrolysis cells (SOECs). The present project will be focused on exploring the underlying relationship between the reaction mechanism of CO<sub>2</sub> reduction and ceria electrocatalysts with varying dopant type and concentration, varying surface orientation and at special step and kink sites, analyzing the role of oxygen vacancies and electron defects in the surface reaction pathways. Determining the rate of CO<sub>2</sub> reduction and its response to the electrochemical polarization at the ceria–gas interface is crucial in order to achieve a rational optimization of the catalyst and oxide electrode.

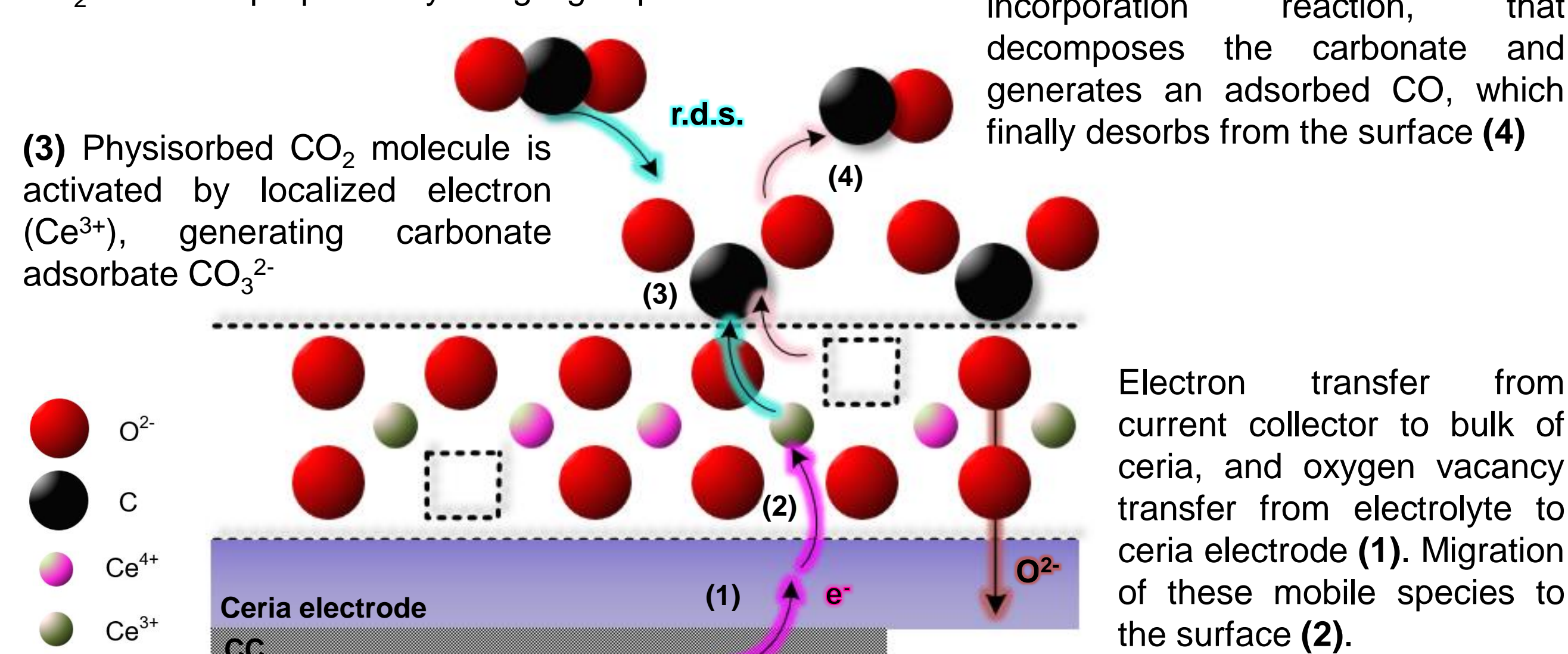
## Ceria as electrocatalyst

- Ceria is able to enhance the catalytic performance due to its ability to store and release oxygen via **reversible oxygen-vacancy formation** and **partial reduction to CeO<sub>2-x</sub>**;
- Ceria structure tolerate a considerable reduction **without phase change**, showing stability in its bulk form over a range of reducing conditions and elevated temperatures;
- In high-temperature SOCs, the mixed valence states of ceria facilitate **mixed ionic-electronic conductivity** (MIEC) behavior and surface activity for oxidation/reduction reactions;
- Recently, doped ceria was found to exhibit **remarkable activity** towards hydrogen oxidation and water splitting reactions (HOR and WSR, respectively), which **exceeds that of precious metal catalysts** [1].

## Reaction pathway

- Feng et al. [2] recently proposed a simplified electrochemical pathway for CO<sub>2</sub> reaction on ceria, schematically divided into four steps.

Fig 1: Schematic diagram of the reaction pathway for CO<sub>2</sub> reduction proposed by Feng's group



- Solid–solid charge-transfer reactions and bulk and near-surface migration of localized electrons and oxygen vacancies (step 1, 2 in Fig. 1) are suggested to be not rate-determining. Thus, the rate determining steps are those occurring **at the ceria–gas interface** (step 3, 4 in Fig. 1).
- Efforts should focus on **lowering the barrier height for the electron transfer between Ce<sup>3+</sup> and surface CO<sub>3</sub><sup>2-</sup>**, namely decreasing the misalignment of the Ce 4f electronic state and the valence electrons in the adsorbate.
- Furthermore, reaction barriers might change with Ce<sup>3+</sup> and vacancy concentration. In the case of CO<sub>2</sub> adsorption, increasing adsorbate concentration upon cathodic bias has been predicted by DFT calculations to lead to **adsorbate–adsorbate interaction** [3].

## Outcome

The storage of energy by converting electricity into chemical bonds involves electrocatalysis as an essential ingredient, that is, solid nanostructured materials whose surfaces accelerate the reaction of interest. The ultimate goal of this project is to identify a ceria-based electrocatalyst for CO<sub>2</sub> reduction with superior performance than the state of the art materials used today, gathering further knowledge on the different aspects playing a role in the cell operation.

## Project approach

- The model electrode consists of an highly tailored **ceria thin film** deposited on yttria-stabilized zirconia (YSZ) single crystal substrate through **Pulsed Laser Deposition** (PLD). A high-performance noble metal porous electrode infiltrated with doped-ceria nanoparticles will be applied as counter electrode, in order to make use of it as a pseudo-reference electrode, enabling the determination of the working electrode behavior under polarization.

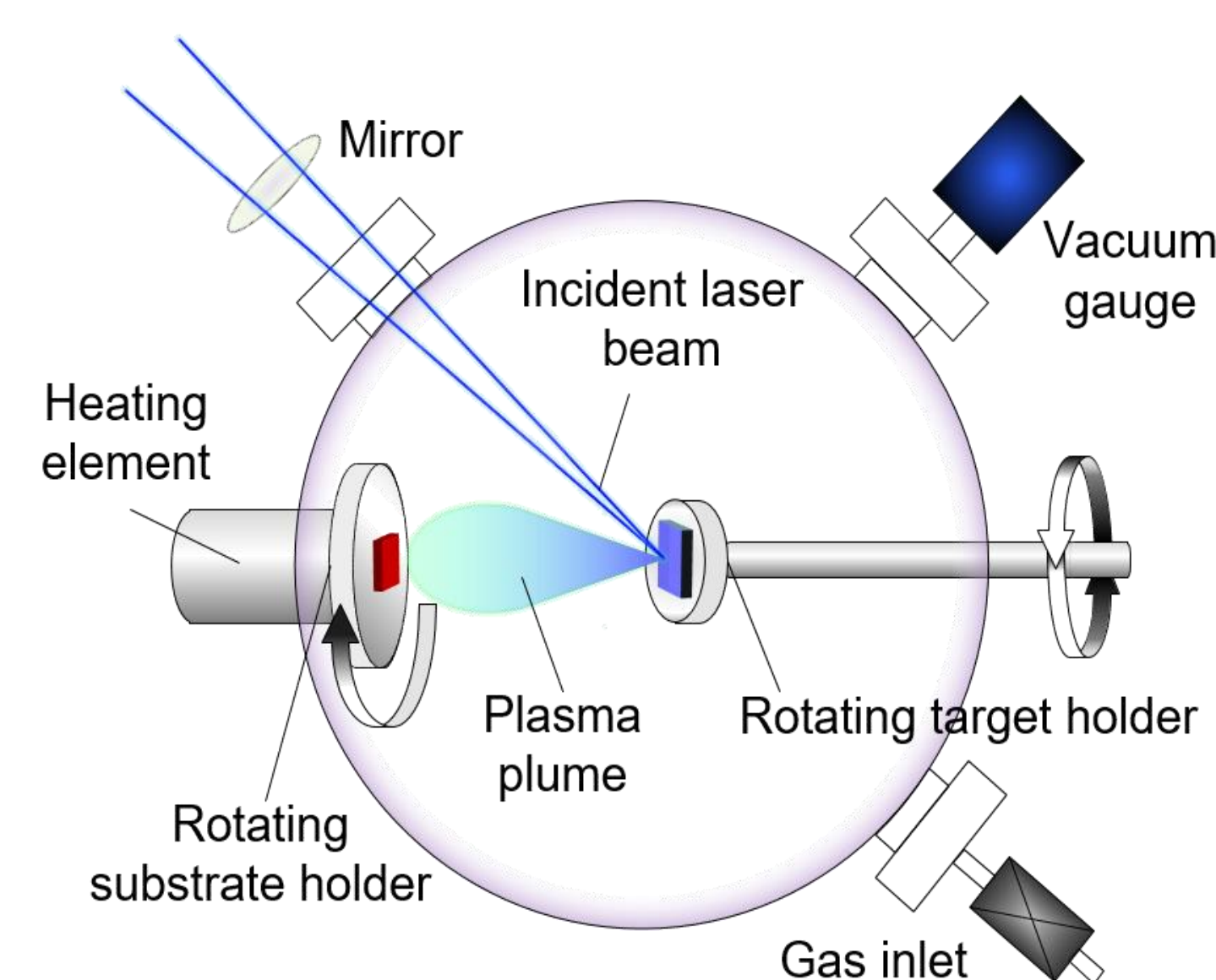


Fig 2: Schematic view of the PLD working principle

- Investigation of the **activity dependence on surface orientation** will be pursued, by employing epitaxial gadolinium-doped ceria (GDC) monolayers of fixed composition deposited on YSZ single crystals of varying orientation: (100), (110), (111).

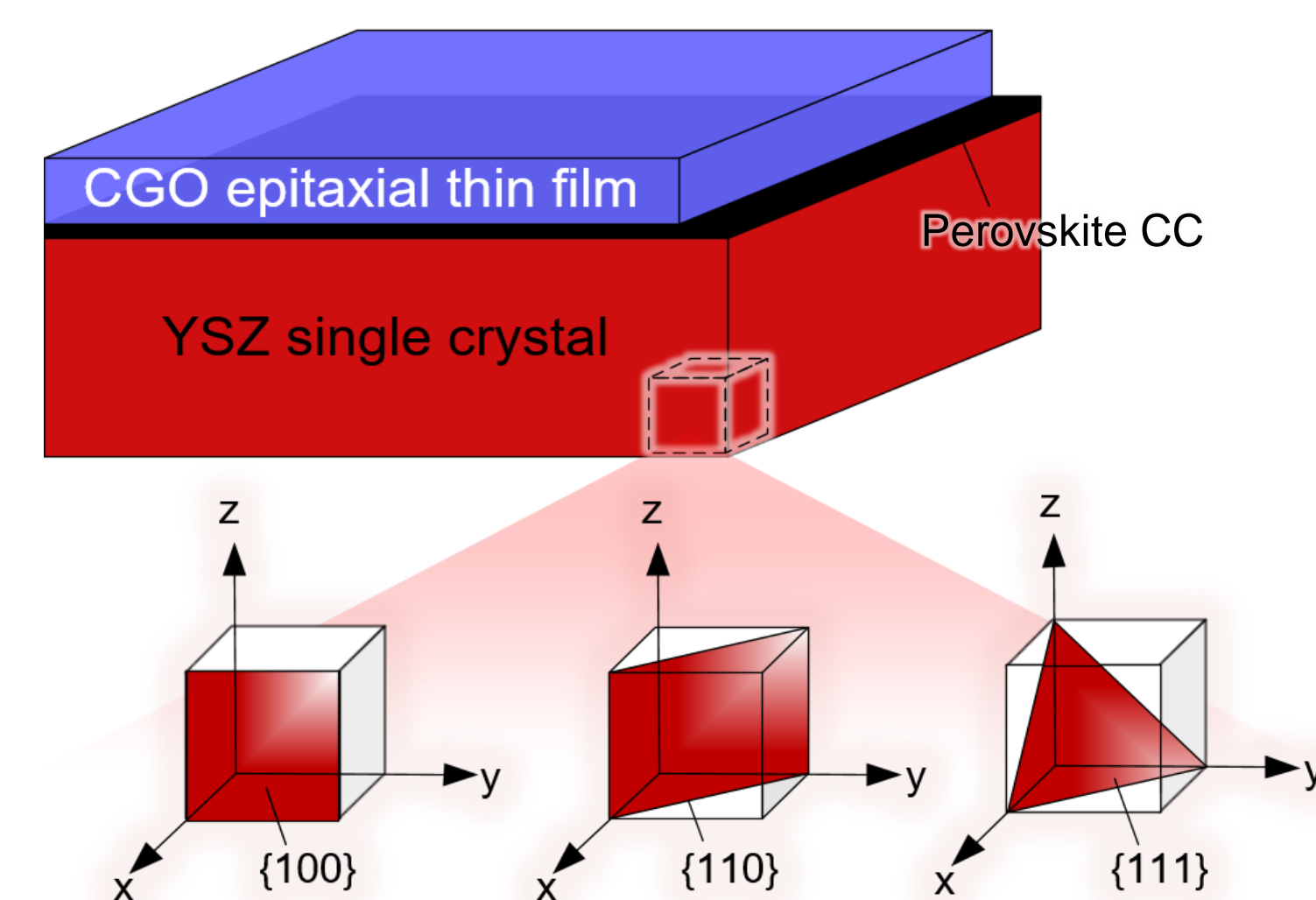


Fig 3: Schematic representation of the lattice planes orientations under investigation in the single crystal substrate

- The **influence of different dopant cations** in the CeO<sub>2-x</sub> fluorite structure will be analyzed, by keeping as baseline the above described cell structure and progressively changing the composition of the targets used in the PLD process.

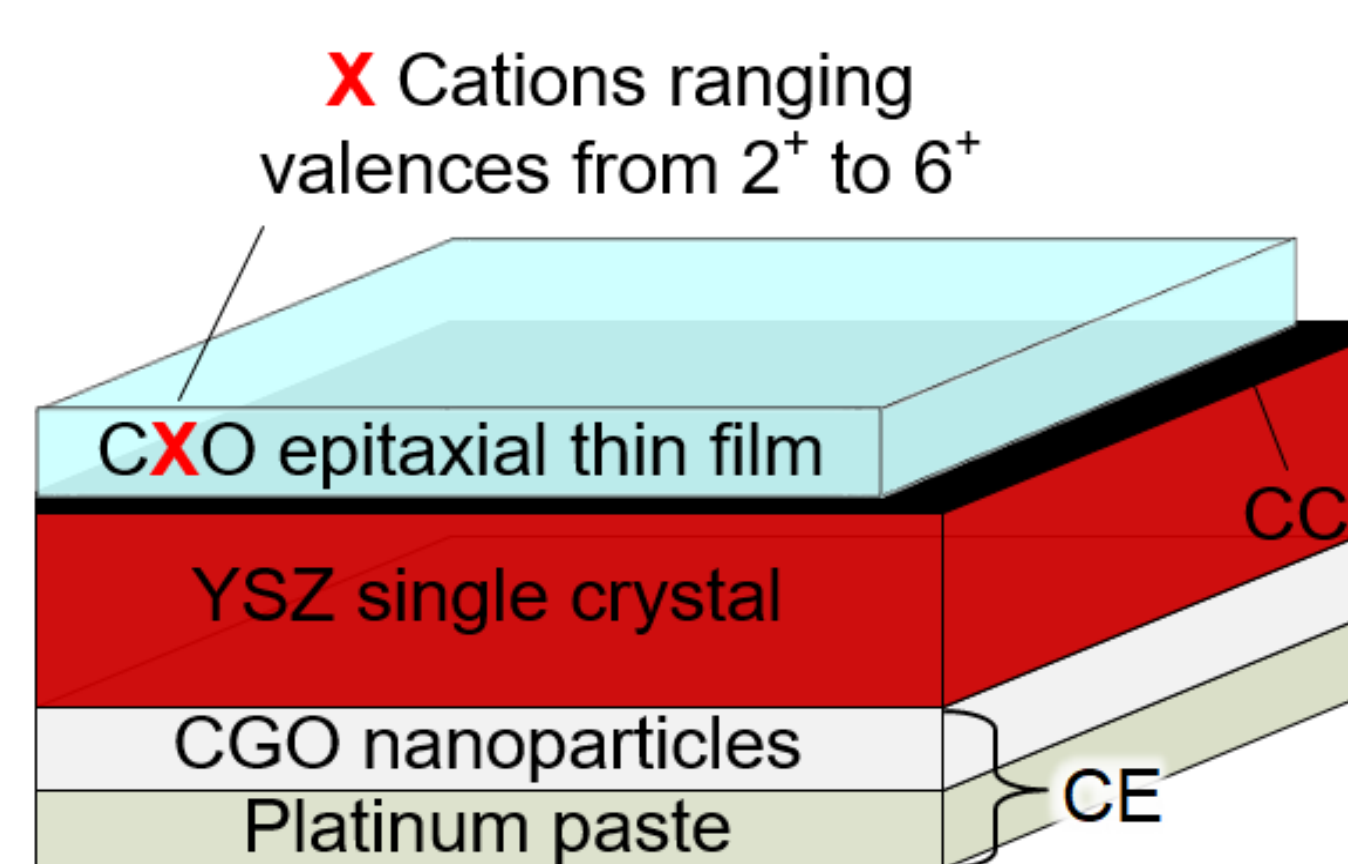


Fig 4: Schematic representation of the complete cell

- The analysis of the **effect on catalytic activity of tensile and compressive isotropic strain** introduced in the lattice will be pursued.

- Size/shape-dependent properties in size-tunable CeO<sub>2</sub> nanocrystals** will be studied by adopting shape-selective synthesis approaches, in order to analyze whether edge/step and corner/kink sites offer enhanced reactivity.

## Combination with DFT-based modelling

- Strong efforts will be devoted to combine the in-situ studies and the experimental data obtained within the project with density-functional theory based modelling and ab-initio calculations pursued on the same system in a parallel PhD project.