

## Electrodeposition of Ce-Zr Powder

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### Introduction

ZrO<sub>2</sub> addition to CeO<sub>2</sub> promotes the catalytic properties of ceria.<sup>1,2</sup> Ceria-zirconia mixtures are most commonly being synthesized by bulk co-precipitation<sup>3</sup>. To our knowledge there is no report of ceria-zirconia mixtures generated by electrochemistry. Switzer<sup>4</sup> and Yanchun *et al.*<sup>5</sup> have produced ceria from ammoniacal nitrate solutions by the production of hydroxyl ion at the electrode surface (generation of base method) under an applied current. The aim of this paper is to report our recent findings on the electrochemical synthesis of the mixed oxide CeO<sub>2</sub>-ZrO<sub>2</sub>.

### Experimental

A two-compartment electrochemical cell was used. The electrolyte consisted of 0.5 M ammonium nitrate and varying concentrations of zirconyl (IV) nitrate hydrate and cerium (III) nitrate hexahydrate. A platinum mesh was used as the anode and the reference electrode was a saturated calomel electrode (SCE). An inverted stationary stainless steel shaft-disc electrode<sup>6</sup> in a quiescent solution, which prevents hydrogen bubbles from getting trapped onto the surface, was used.

Potentiostatic experiments were carried out at room temperature of  $23 \pm 1^{\circ}$  C with a BAS-Zahner IM6(e) system. Deposit composition was analyzed using a Kevex Omicron X-ray fluorescence analyzer. Specimens were also analyzed for their structure under bright field high resolution transmission electron microscope, TEM (JEOL Model JEM 2010). X-ray diffraction analysis was carried out using a diffractometer, (Siemens, model D5000) with Cu-K<sub>α</sub> radiation.

### Results and discussion

The Figure 1 shows that the mole fraction of Zr measured in the powder increases with increasing molar ratio of Zr/Ce in the electrolytic solution. It was found that the applied potential didn't have any significant effect on the composition of the powder. The TEM micrograph, shown in Figure 2, is a representative, electrosynthesized powder, which exhibits an average grain size between 4-6 nm. The electron diffraction pattern suggests crystallinity. The XRD spectra of the powder indicates a single phase cubic solid solution.

The predominant electrochemical reactions are the reduction of water, molecular oxygen and nitrate ions that generate the hydroxyl ion. The surface pH thus rises sufficiently, to co-precipitate the powder directly onto the electrode surface. The presented electrochemical method gives us the advantage of producing CeO<sub>2</sub>-ZrO<sub>2</sub> powders with nanometric size crystallites and having a composition required for improved catalytic activity.

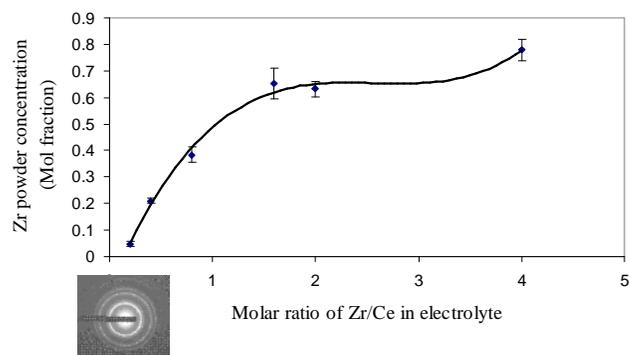


Figure 1. Effect of initial electrolyte composition on final powder concentration.

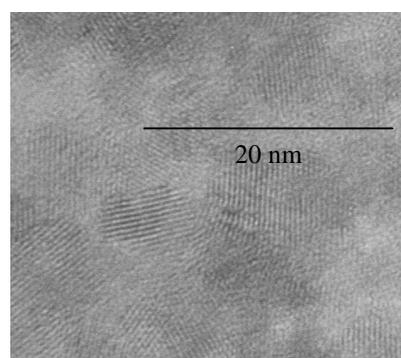


Figure 2. TEM micrograph and electron diffraction pattern of a Ce<sub>0.82</sub>Zr<sub>0.18</sub>O<sub>2</sub> sample.

### Conclusion

Nanocrystalline CeO<sub>2</sub>-ZrO<sub>2</sub> powders were prepared electrochemically by the cathodic electrogeneration of base method. The average particle size was in the range 4-6 nm. X-ray diffraction confirmed a solid solution when Zr(IV) was codeposited with Ce(IV).

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