

Synchrotron X-ray Absorption and Diffraction Studies on $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ perovskite catalyst in bifunctional oxygen electrodes

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1 INTRODUCTION

$\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ perovskite is used as an electrocatalyst in bifunctional oxygen-diffusion electrodes of Zn/air batteries[1]. We investigated $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ perovskite catalysed electrodes with *in situ* and *ex situ* XANES, EXAFS and XRD measurements to pursue valence state changes and structural changes during oxygen evolution and oxygen reduction. and during preparation of these electrodes.

2 RESULTS AND DISCUSSION

Electrochemical investigation of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ perovskite catalysed electrodes. Figure 1 shows the cyclic voltammogram of a perovskite-loaded electrode. The onset of oxygen evolution and reduction at 2.0 V and 0.9 V, respectively, is easily recognized from the faradaic currents. Between these two potentials, rather high capacitive and faradaic currents are observed which arise on account of the high-surface-area of the carbon/catalyst mixture.

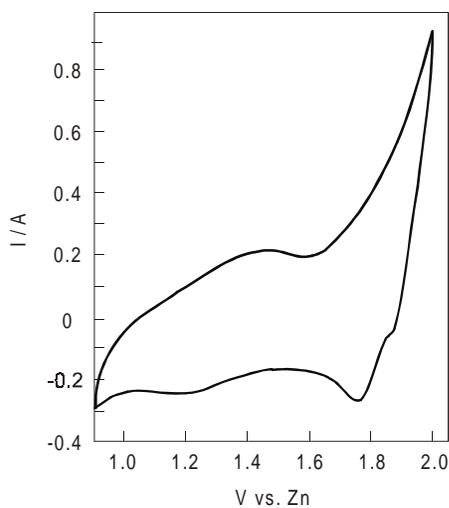


Fig. 1: Cyclic voltammogram of a $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ -loaded electrode.

XANES investigation. The edge in the XANES spectrum is expected to shift when the valence state of cobalt is altered. In the higher valence state, electrons are more strongly bound to the Co nucleus, hence the absorption edge where the X-rays start to knock out electrons will be shifted to a higher energy.

Figure 2 shows the near-edge X-ray absorption spectra of an electrode measured *in situ* at 0.9 V and 2.0 V vs. Zn, together with the XANES spectra recorded at samples of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ incorporated into an electrode (ELa06) or as powder diluted with BN (1 : 5) (PLa06).

The EXAFS spectrum of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ powder diluted with BN (1 : 5) has also been measured and then analyzed using the multiple-shell data analysis program XDAP [2]. The Fourier transforms (Figure 3) show peaks

at 1.57 and 3.25 Å. The peak at 1.57 Å can safely be assigned to the oxygen shell, and constitutes an indication for the distance between Co and oxygen in this compound. Corrections for phase shifts leads to a Co-O distance of 1.9 Å. The second peak most probably is due to the strong X-ray scattering properties of Lanthanum

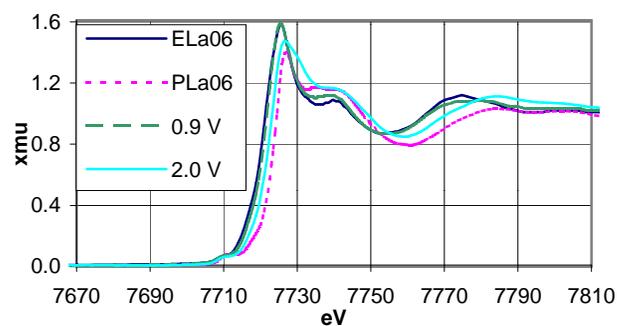


Fig. 2: XANES spectra of a sample of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ incorporated into an electrode (ELa06), of a sample of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ powder diluted with BN (1 : 5) (PLa06), and XANES spectra recorded *In situ* in an electrochemical cell at $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ -catalysed electrodes at 0.9 V and 2.0 V vs. Zn, respectively.

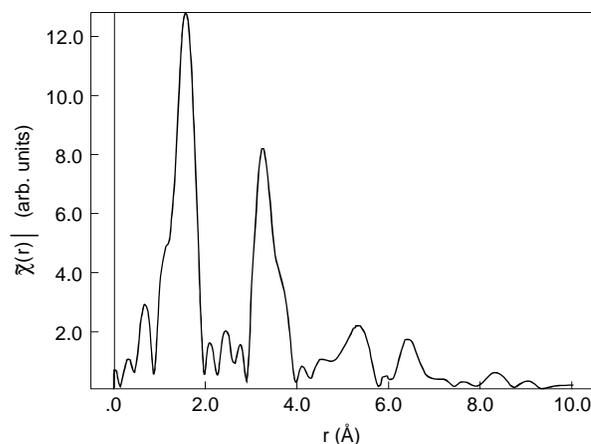


Fig. 3: Fourier transform function of the EXAFS signal obtained from the $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ -powder sample. This representation shows distinct peaks which indicate neighbor distances.

The XANES spectra show that the valence state of Co in the $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ perovskite is already slightly changing during the sintering process at 340°C. Valence state changes of cobalt could also be observed *in situ* when the electrode potential was varied over the potential range typically encountered in the Zn/air batteries during charge and discharge.

X-ray diffraction data showed that this valence state change has only a small influence on the molecular structure of the perovskite. They also revealed no significant changes within the first 160 hours of electrode operation at either the oxygen evolution or oxygen reduction potential. Some weak additional peaks were occurring at electrodes used for 1300 hours. We conclude that $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ perovskite is very stable under conditions encountered in alkaline Zn/air battery.

3 REFERENCES

- [1] S. Müller, K. A. Striebel, O. Haas, *Electrochim. Acta*, 39, 1661 (1994)
- [2] M. Vaarkamp, I. Dring, R.J. Stern, Koningsberger, D.C. *Phys. Rev. B* 50, 7872 (1994).

