Experimental report

08/09/2021

Proposal:	**5-21-1132**	**Council:**	10/2019

Title: Relation of phase fields and structural transitions to oxygen loss inreversible solid oxide cell electrodes based on SrFeO3-d

Research area: Materials

This proposal is a new proposal

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Samples:
SrFeO3-d
SrFe0.9Mo0.1O3-d

Instrument	Requested days	Allocated days	From	To
D2B	3	3	14/09/2020	17/09/2020

Abstract:

Perovskites based on SrFeO3-d (SF) are the focus of considerable recent attention as both positive and negative electrodes in symmetrical and reversible solid oxide fuel cells. Substitution of Fe for Mo in SrFeO3-d (SFM) stabilizes the cubic XRD phase at room temperature and improves electron-hole conductivity. Encouragingly, little difference in polarization resistance is observed under dc bias and operating temperature between the SF and SFM phases and the well-known Co-based perovskites with higher thermal expansion, as we recently demonstrated (J. Power Sources 437 (2019) 226895). We propose to study the phase fields and transition temperatures of the SF and SFM phases under air in the temperature range 25-900 °C and relate oxygen content with the phase transitions and oxide-ionic and electronic conductivity. The excellent resolution and data quality at D2B will reveal structural features of the oxygen sublattice which are not accessible by other means.

Structural transitions and oxygen loss in reversible solid oxide cell electrodes based on $SrFeO_{3-\delta}$

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Cobalt-free perovskites based on $SrFeO_{3-\delta}$ have been gaining attention as both positive and negative electrodes in symmetrical and reversible SOFCs since high efficiency is exhibited in both fuel-cell and electrolysis modes [3,4]. Different performances of similar systems for reduction and oxidation reactions in the two modes indicates that oxygen content at the working temperature may be critical to many currently unknown aspects of the electrochemical process. We recently showed that substitution of Fe for Mo in $SrFeO_{3-\delta}$ stabilises the cubic phase at room temperature and considerably improves electron-hole conductivity [5]. Although the polarisation resistance is much lower for Co-based $SrCoO_{3-\delta}$ compositions under conditions of no bias, there is little difference in performance under dc bias at higher current densities in the intermediate temperature range for the Fe-based systems with the added benefit that the thermal expansion is lower than the Co-based perovskites. Here, we studied the phase fields in air of the highly promising SOFC electrode materials $SrFeO_{3-\delta}$ and $SrFe_{0.9}Mo_{0.1}O_{3-\delta}$ as a function of temperature to reveal the role of oxygen content and phase field on electrode performance.

Neutron Powder Diffraction (NPD) as a function of temperature was employed for detailed structural analysis of $SrFeO_{3-\delta}$ (SFO) and $SrFe_{0.9}Mo_{0.1}O_{3-\delta}$ (SFM) using the high-resolution D2B diffractometer at the Institut Laue-Langevin (ILL, Grenoble, France). Diffraction patterns were collected in air, using an open quartz tube, in the 2θ range RT-900 °C working at a wavelength $\lambda = 1.046531$ Å. The background from the quartz tube recorded at each temperature was subtracted from the corresponding pattern, prior to analysis by Rietveld refinement using the Fullprof software. The refinements were performed fixing the Fe/Mo ratio and using isotropic thermal parameters for all atoms. Figure 1 shows the temperature evolution of NPD patterns for SFO (Figure 1(a)) and SFM (Figure 1(b)); a limited zone of the NPD patterns is plotted for the sake of clarity. At RT, SFO exhibits a tetragonal structure (S.G. I4/mcm) due to ordering of oxygen vacancies, which was previously observed at RT for an oxygen content of 2.85 per formula unit [6].

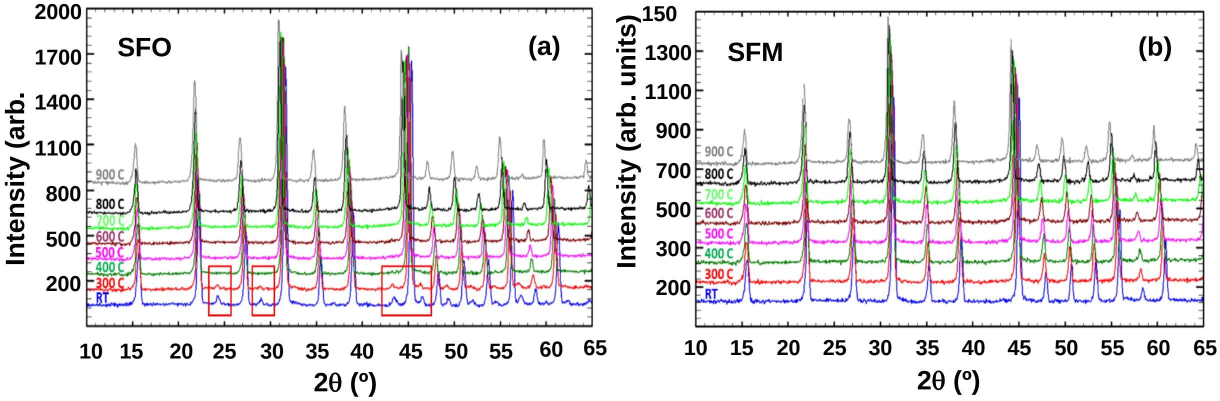

Figure 1. NPD patterns of (a) SFO and (b) SFM in the range RT- 900ºC. Note that some peaks of SFO indicated in (a) disappear at 400 ºC corresponding to the tetragonal-to-cubic phase transition.

On heating, the tetragonal structure remains up to 300 ºC, above which cubic perovskite forms (S.G. Pm-3m) due to disordering of oxygen vacancies. The phase transition occurs around 400 ºC and the cubic structure is stable up to 900 ºC. In contrast, SFM is cubic in the entire studied range, RT-900 ºC, and possesses a significantly larger oxygen content, as reported previously [5], attributable to the high oxidation state of Mo (VI). The random distribution of Mo and Fe ions in the perovskite B site most likely leads to a random distribution of oxygen vacancies associated with cubic symmetry. The much higher concentration of vacancies in the anionic substructure of SFO may result in poor long-term material stability. The thermal evolution of the unit-cell volume of SFO determined from NPD refinement, Fig. 2, exhibits a linear increase with increasing temperature in the range RT-300 ºC (Fig. 3(a)). The cell volume undergoes a contraction in the range 300-400 ºC associated to the tetragonal-to-cubic transition, then increases linearly once more as temperature increases further (400-900 ºC). The linear expansion is greater in the high-temperature range in comparison to that at low-temperature, corresponding to rapid oxygen loss at about 400 ºC, previously determined by thermogravimetry [5], thereby reducing the B-site cations which adopt a higher average ionic radii. Although the Mo-doped composition exhibits cubic symmetry in the entire range RT-900 ºC, the volume expansion as a function of temperature also exhibits a greater slope for temperatures higher than ~400 ºC (Fig. 2(b)), again ascribed to abrupt oxygen loss and the concomitant reduction of B-site cations. The volume expansions determined by NPD are consistent with the thermal-expansion behaviour previously determined by dilatometry and confirm lower values of thermal expansion coefficients for SFM in comparison to SFO (Fig. 2), due to the lower content of the larger Fe^{3+} ions in SFM and the stronger Mo-O bond in comparison to that of Fe-O, which is apparent from the lower oxygen loss on heating obtained for SFM (data not shown).

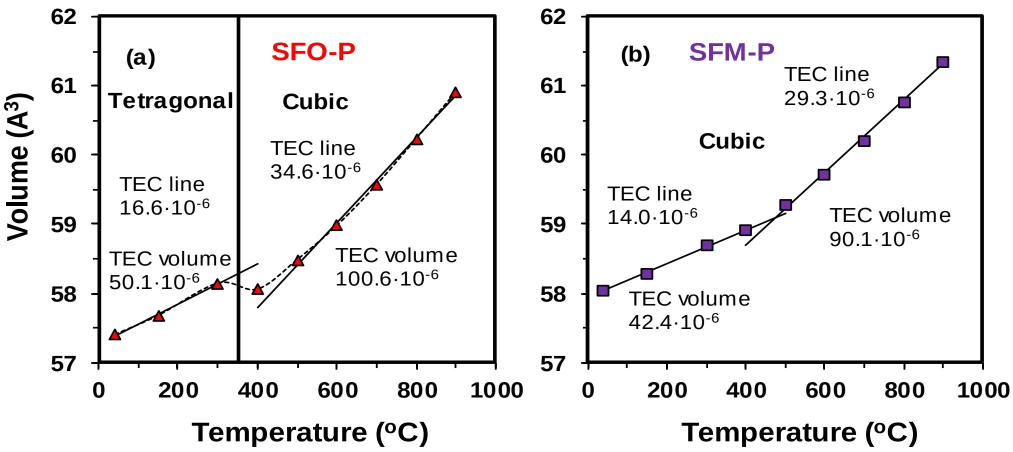

Figure 3. Temperature dependence of unit-cell volume for SFO (a) and SFM (b), determined from NPD data.

Molybdenum was confirmed as an efficient dopant for phase stabilisation and electrochemical enhancement of $SrFeO_{3-\delta}$ cathodes. Electrochemical performance of the compositions and fuel-cell tests are rationalised in terms of the phase symmetry and oxygen content in an upcoming paper [7].

References

[1] A. Hauch, S.D. Ebbesen, S.H. Jensen, M. Mogensen, J. Mater. Chem. 18 (2008) 2331–2340.
[2] M.A. Laguna-Bercero, J. Power Sources. 203 (2012) 4–16.
[3] A. Aguadero, D. Pérez-Coll, J.A. Alonso, S.J. Skinner, J. Kilner, Chem. Mater. 24 (2012) 2655–2663.
[4] Q. Liu, X. Dong, G. Xiao, F. Zhao, F. ChenAdv. Mater. 22 (2010) 5478–5482.
[5] V. Zapata-Ramírez, G.C. Mather, M.T.M.T. Azcondo, U. Amador, D. Pérez-Coll, J. Power Sources. 437 (2019) 226895.
[6] J.P. Hodges, S. Short, J.D. Jorgensen, X. Xiong, B. Dabrowski, S.M. Mini, C.W. Kimball, J. Solid State Chem. 151 (2000) 190–209.
[7] V. Zapata-Ramírez, P. Rosendo-Santos, U. Amador, C. Ritter, G.C. Mather, D. Pérez-Coll, submitted to *Renewable Energy*