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Study of the mixed conducting $\text{SrFeCo}_{0.5}\text{O}_y$ ceramic membrane material by in-situ neutron powder diffraction

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Abstract

Dense ceramic tubes of the multi-phase mixed ionic/electronic conductor $\text{SrFeCo}_{0.5}\text{O}_y$ have been synthesized by solid-state reaction, and the stability of its component phases studied using in-situ neutron diffraction over the oxygen partial pressure ($p\text{O}_2$) range $10^{-0.68}$ to $10^{-15.0}$ atm at 900°C . This being the likely conditions to which membranes are exposed in operational methane conversion reactors. This material is stable between air and $\log p\text{O}_2 = -2.3$, with $\text{Sr}_2(\text{Fe,Co})_3\text{O}_y$ (236) being the majority phase. When the oxygen partial pressure is lowered, 236 starts decomposing into perovskite and rocksalt phases. The small fraction of remaining 236 rapidly undergoes decomposition at $\log p\text{O}_2 = -12.2$, leaving only $\text{SrFeO}_{2.5}$ and CoO . Rietveld analysis indicates that the oxygen content of the perovskite phase does not drop below $\text{O} = 2.5$ when $\log p\text{O}_2 = -15.0$, while there is an indication that CoO is reduced to cobalt metal. This decomposition at low partial pressures may be reversed when the gas is switched back to air, i.e., $\text{SrFeO}_{2.5} + \text{CoO}$ re-form $\text{Sr}_2(\text{Fe,Co})_3\text{O}_y$, to an extent that is seemingly dependent on sample and thermal history. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Recently, the mixed-conducting oxide $\text{SrFeCo}_{0.5}\text{O}_y$ (SFC2) has been identified as a potential dense ceramic membrane that can be used to separate gas at elevated temperatures. Indeed, Balachandran et al. [1] demonstrated that extruded membrane tubes of SFC2 can be used for partial oxidation of methane to produce syngas ($\text{CO} + \text{H}_2$) in a methane conversion reactor operating at $\approx 850^\circ\text{C}$. The oxygen flux obtained from the separation of air in this reactor is commercially feasible, and the use of this technology can significantly reduce the cost of oxygen separation [2].

Typically, $\text{ABO}_{3-\delta}$ perovskites which, as synthesized are single-phase materials, have been extensively studied for oxygen diffusion properties or membrane applications [3–6]. SFC2 differs from the $\text{ABO}_{3-\delta}$ perovskites in that it is not a single-phase material under standard synthesis conditions and times. Four known phases, $\text{Sr}_2\text{Fe}_{3-a}\text{Co}_a\text{O}_{6.5-\delta}$ (236), $\text{SrFe}_{1-b}\text{Co}_b\text{O}_{3-\delta}$ (perovskite/brownmillerite), $\text{Co}_{3-c}\text{Fe}_c\text{O}_3$ (rocksalt), and $\text{Co}_{3-d}\text{Fe}_d\text{O}_4$ (spinel), are certainly identifiable; their presence depends upon synthesis conditions [7,8]. Guggilla and Manthiram [9] and Ma et al. [10] have shown that substitution of Co for Fe in $\text{SrFe}_{1.5-x}\text{Co}_x\text{O}_y$ produces single-phase materials over a limited Co range (with limiting composition $\approx \text{SrFe}_{1.2}\text{Co}_{0.3}\text{O}_y$). This finding suggests that Co^{3+} is not particularly stable within the 236 structure. The enhanced performance of SFC2 when compared with that of the individual phases is not understood and is the focus of continuing research.

The commonly accepted crystallographic representation for the layered structure $\text{Sr}_2(\text{Fe},\text{Co})_3\text{O}_{6.5-\delta}$ is shown in Fig. 1. This structure is formed from perovskite and double-layer intergrowths. The Fe/Co atoms are in a +3 oxidation state and occupy three distinct environments: octahedral (sixfold), trigonal bipyramidal (distorted fivefold), and square pyramidal (distorted fivefold). The orthorhombic structure of 236 (*Iba2* space group) is related to the basic perovskite cell by the relationships $a = 2\sqrt{2}a_p$, $b \approx 5a_p$, $c = \sqrt{2}a_p$.

Fig. 2 shows the crystal structure of the $\text{Sr}(\text{Fe},\text{Co})\text{O}_{3-\delta}$ perovskite (*Pm3m* space group) and the defect ordered $\text{Sr}_2(\text{Fe},\text{Co})_2\text{O}_5$ (*Ibm2* space group shown) brownmillerite. In the perovskite structure, six oxygen atoms that form regular octahedra surround the Fe/Co atoms. The structure can readily adopt substoichiometry in the oxygen sub lattice and oxygen vacancies are usually formed randomly. Brownmillerite has a supercell ordering of vacancies in the perovskite structure $a = \sqrt{2}a_p$, $b = 4a_p$, $c = \sqrt{2}a_p$, where layers of corner sharing $(\text{Fe},\text{Co})\text{O}_6$ octahedra alternate along *b* with $(\text{Fe},\text{Co})\text{O}_4$ distorted tetrahedra. The ordered vacancies can be disordered at high temperature, where the material adopts the disordered perovskite structure.

Because any operational membrane is subject to a wide range of $p\text{O}_2$'s with air at one side ($p\text{O}_2 \approx 10^{-0.7}$ atm) and at the methane side ($p\text{O}_2 \approx 10^{-18}$ atm), there must be a gradient across the tube. How the $p\text{O}_2$ and oxygen diffusion actually varies from point to point across an operating membrane is outside the scope of this paper; Bouwmeester et al. [11] and Kim et al. [12] address this matter in more detail. Instead, we will focus on the phase compositions that are present at some $p\text{O}_2$ values. The stabilities of the aforementioned phases in SFC2 under the probable $p\text{O}_2$'s, which have until now been unknown, can be measured using in-situ diffraction techniques. Neutrons offer advantages over X-rays for studying $\text{Sr}(\text{Fe},\text{Co})_{1.5}\text{O}_y$ membrane materials since the coherent scattering lengths are not related to

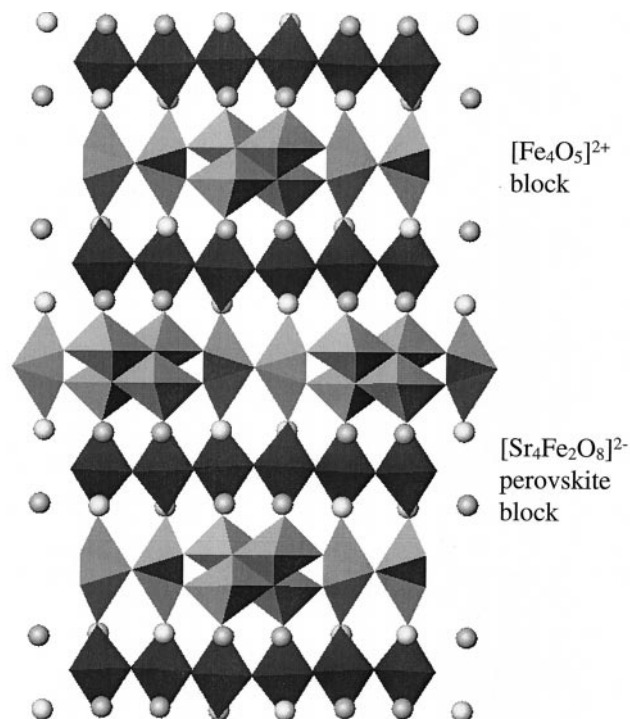


Fig. 1. Crystal structure of $\text{Sr}_2\text{Fe}_3\text{O}_{6.5-8}$, showing the layered structure comprised of perovskite and double-layer blocks.

atomic weight of the particular element. In fact, they are significantly different for each element here, and oxygen may readily be detected within the structures. Neutrons, with their penetrating power, allow the use of standard thickness tubes. At a pulsed spallation neutron source, the entire diffraction pattern is detected simultaneously and the special environment furnace sample holder (made of alumina) is not seen by the detectors in 90° scattering geometry.

In this experiment, we studied the stability of the individual phases in SFC2 at a several points covering a broad $p\text{O}_2$ range. Measurements were made at 900°C in various gas environments ($p\text{O}_2$ $10^{-0.7}$ to 10^{-15} atm), where the exact values were measured with an oxygen probe close to the sample.

2. Experimental

$\text{SrFeCo}_{0.5}\text{O}_y$ powder was prepared by a solid-state reaction of appropriate amounts of SrCO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and Fe_2O_3 . Mixing and grinding were conducted for 10 h in isopropanol with zirconia media. After drying, the mixture was calcined in air at 850°C for 16 h, with intermittent grinding. After the final calcination, the powders were ground to an average particle size of $\approx 7 \mu\text{m}$. The resulting finely divided powder was packed into a mold

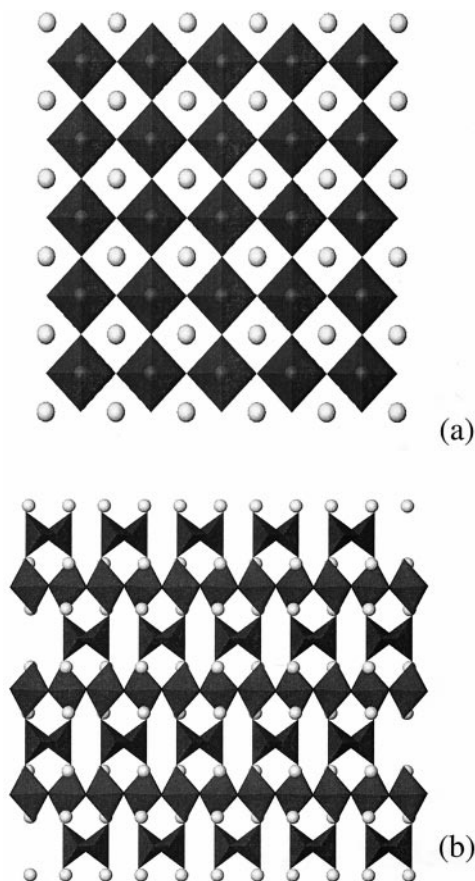


Fig. 2. Crystal structures of (a) $\text{Sr}(\text{Fe,Co})\text{O}_{3-\delta}$ perovskite and (b) $\text{Sr}_2(\text{Fe,Co})_2\text{O}_5$ brownmillerite.

and isostatically pressed with a 30,000 psi load. The green-body tube was removed from the mold and sintered in air for 5 h at 1200°C at a heating rate of $120^\circ\text{C}\cdot\text{h}^{-1}$ and cooling rate $\approx 90^\circ\text{C}\cdot\text{h}^{-1}$. These sintered tubes have a wall thickness ≈ 0.9 mm and their bulk density is $>90\%$ of theoretical density.

Neutron diffraction measurements were carried out on the General Purpose Powder Diffractometer (GPPD) at IPNS Argonne. Variable temperature and gas environment measurements were performed in a “Miller” furnace with a solid zirconia electrolyte oxygen sensor (Ceramic Oxide Fabricators SIRO2). Several gases were used in varying combinations to achieve the desired range of partial pressures; air (AGA < 10 ppm H_2O), argon (AGA 99.996%), 5.12% $\text{O}_2/\text{bal. Ar}$ (AGA), 1% $\text{CO}/\text{bal. Ar}$ (AGA) and carbon dioxide (AGA). The furnace was heated/cooled at $240^\circ\text{C}\cdot\text{h}^{-1}$, with a 20-min equilibration period at temperature. Gas flows were controlled with Brooks Series 5820 mass flow controllers before they entered a mixing loop and were delivered to the furnace. Data were collected at 15-, 30-, or 60-min intervals on the 90° banks and Rietveld [13] analysis was performed with GSAS [14]. The data were fitted to a model that assumed the presence of 236, perovskite and rocksalt phases, or perovskite and rocksalt phases when the 236 had decomposed. Peak

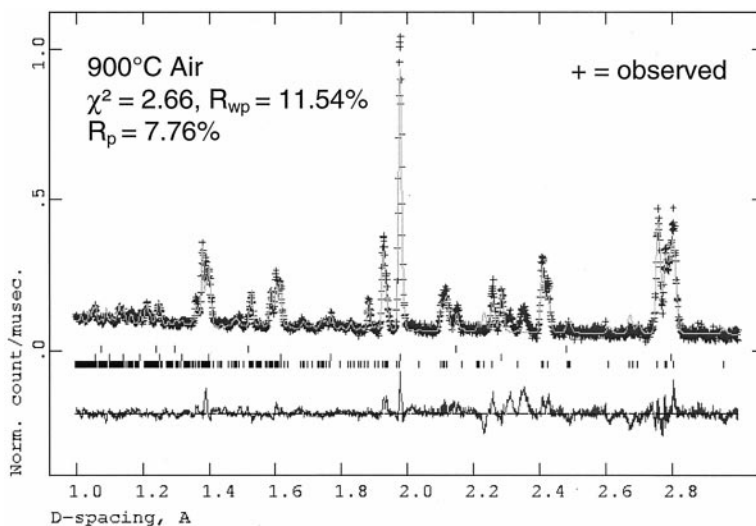


Fig. 3. Rietveld profile fit to powder neutron diffraction data of SFC2 sample obtained at 900°C in air. Reflection markers represent rocksalt, perovskite, and 236 phases from top to bottom, respectively.

widths of individual phases were obtained from a summed 1050°C data set (6 h); no evidence of broadening was detected. For individual short runs, in addition to background and histogram scale factors, only lattice parameters and phase fractions were allowed to vary. Fe/Co and O fractions of phases were set at values obtained from other measurements. On the other hand, when data sets were summed to improve counting statistics, it was possible to vary the above-mentioned parameters. However, it should be noted that summing of data sets would yield valid results only when there is relative stability between each data set.

The fabricated membrane tube was initially heated to 1050°C for 8 h to ensure removal of any spinel phase that may have been formed during the cooling phase of tube synthesis. This time period also allows the phases to reach reasonably stable levels, before cooling to the appropriate temperature.

As with any experiment of this type, the system can never really be considered to have attained a thermodynamic equilibrium because the assigned measurement period is limited. We make no claims to have reached or be studying absolute equilibrium.

3. Results and discussion

The structure of $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ (cobalt-free 236) described by Yoshiasa et al. [15] is not correct in detail [16]. The reported structure for Co-doped 236 is also not correct, although the imperfections are less dramatic. Rietveld refinement shows instabilities, in particular, the fivefold irons and oxygen atoms within the double-layer block. Until the correct cell and space group are correctly determined, the *Iba2* space group is still sufficient for studying of the multiple-phase $\text{SrFeCo}_{1.5}\text{O}_y$, as demonstrated by Fjellvåg et al. [17]. We have used the Yoshiasa structure as our model to fit the 236 phase in SFC2.

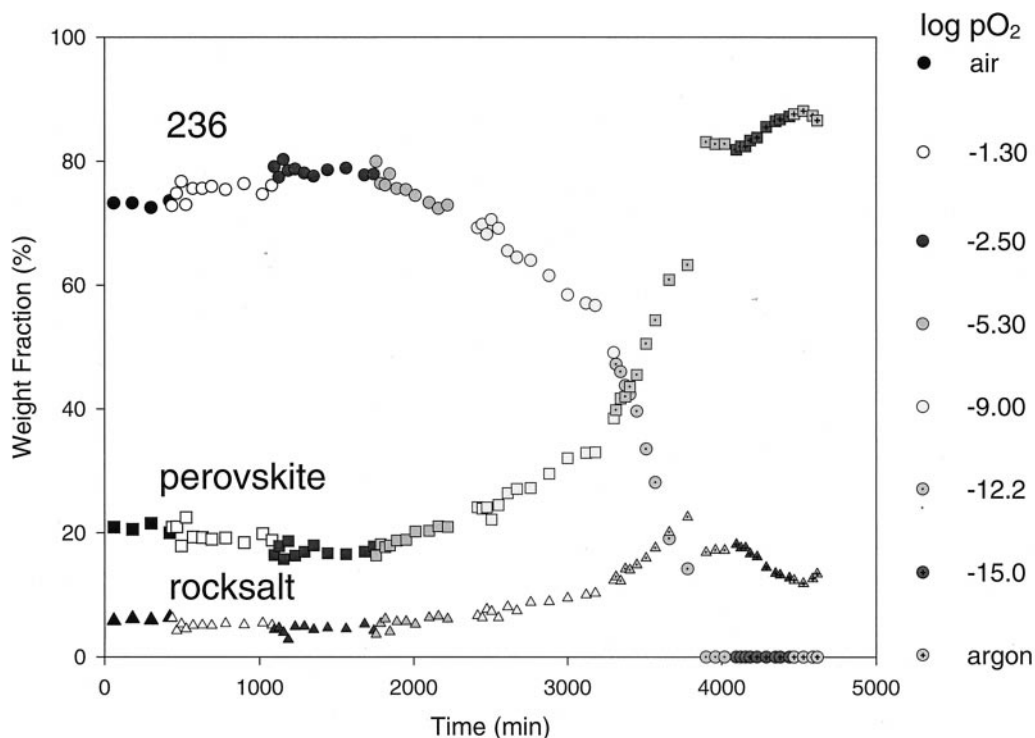


Fig. 4. Calculated weight fractions for phases present in SFC2 at various pO_2 values. Circles = 236, squares = perovskite, triangles = rocksalt.

Fig. 3 shows the observed and calculated patterns that were obtained from the Rietveld refinement on SFC2 (neutron diffraction) data at 900°C in air. Three phases are easily identified and the resulting fit is acceptable. Two unassigned reflections at $\approx 2.3 \text{ \AA}$ are probably from an Fe-rich impurity (presumably an atypical polymorph of Fe_2O_3), that is not evident in data collected at ambient temperature because these peaks overlap with those of other phases. The model of Yoshiasa is adequate, although it is not possible to refine the oxygen, thermal, and positional parameters individually in a stable fashion. Positional parameters for oxygen atoms were fixed and thermal parameters were restrained together. The thermal parameters of the fivefold Fe/Co were also restrained. For this sample, the Rietveld analysis at 900°C in air gives the approximate Fe:Co ratio of the perovskite phase as $\text{SrFe}_{0.75}\text{Co}_{0.25}\text{O}_y$. The 236 phase composition is $\approx \text{SrFe}_{1.2}\text{Co}_{0.3}\text{O}_y$, and some Fe is on the Co site in the CoO phase.

Plotted in Fig. 4 are the weight fractions obtained from the Rietveld refinements performed on the SFC2 material for the entire experiment. The data points are not randomly distributed and the trends may be confirmed by visual inspection of the raw data. In air and down to a $\log pO_2$ of -2.5 , there is no indication that any phases are unstable. Below this pO_2 , the 236 phase decomposes into perovskite and rocksalt phases. Diffraction patterns taken at differing partial pressures, Fig. 5, serve to show how the 236 phase decomposes and the corresponding diffraction patterns are simplified.

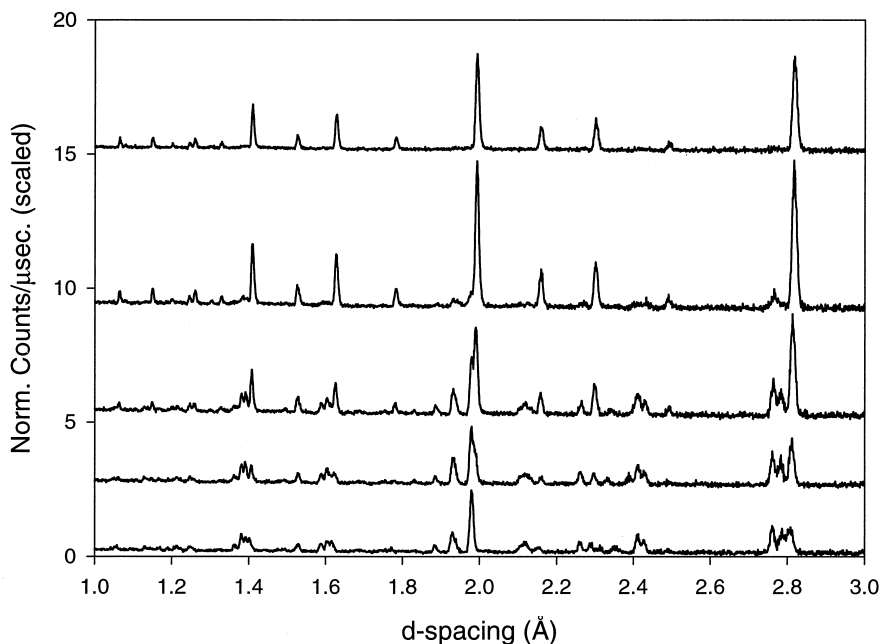


Fig. 5. Diffraction patterns obtained from SFC2 material at 900°C under decreasing partial pressure, from bottom to top of figure.

An important consideration in the study of $\text{SrFeCo}_{1.5}\text{O}_y$ is a detailed understanding of the crystallographic changes that occur during progressive reduction. Although uncertainty in the 236 structure limits our ability to determine the precise oxygen and Fe/Co content of the various phases, the diffraction data do provide important information about the lattice and phase fractions.

Because the data in Fig. 4 indicate significant changes in the phase distributions within the sample during the experiment, another point of interest is to see how the 236 and perovskite phases behave. Looking at the volumes of 236 and perovskite phases, Figs. 6 and 7, respectively, we can see that their behavior differs. This difference is represented more clearly in Fig. 8, where we have scaled the volume of the 236 phase relative to the perovskite at 900°C in air. From air to $\log p\text{O}_2 = -2.5$, the volume of 236 is essentially unchanged, and we see no effect on its weight fraction. When the 236 phase begins to decompose, its volume increases. Co loss and oxygen loss from the double-layer (there is no indication that Co is present on the octahedral site) appears to be responsible for the volume increase during decomposition. Although the perovskite phase becomes more Fe rich during decomposition of the 236 phase, its change in volume is initially driven by the progressive decrease in oxygen content as the value of $\log p\text{O}_2$ decreases between air and -9.00 . Below this, the change in oxygen content is small and the increase in volume is accounted for mostly by the replacement of Co (assuming 3+ oxidation state and octahedral coordination and high spin state the ionic radius is ≈ 75 pm) with Fe (assuming 3+ oxidation state and octahedral coordination and high spin state the ionic radius is ≈ 78.5 pm).

Upon complete decomposition of the 236 phase, the Rietveld refinement indicates that the

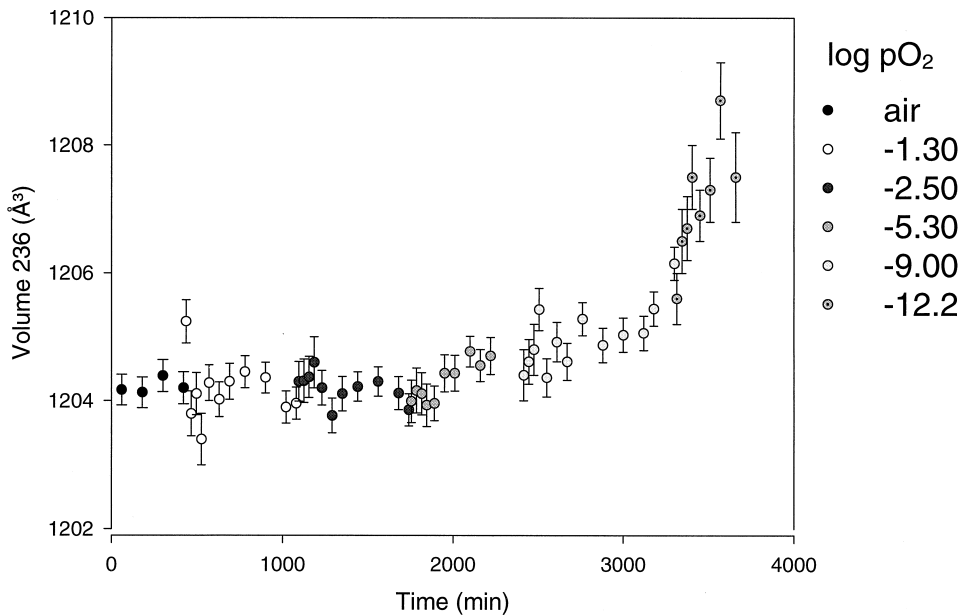


Fig. 6. Cell volume of 236 phase plotted as function of experimental time at various pO_2 values. Error bars shown on diagram.

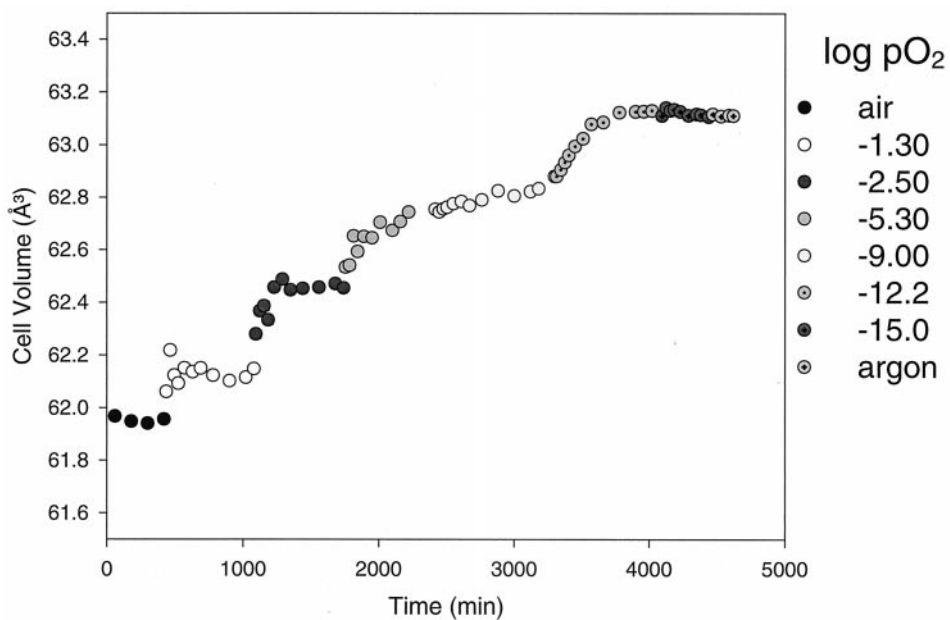


Fig. 7. Cell volume of perovskite phase plotted as function of experimental time at various pO_2 values. Error bars are smaller than point size.

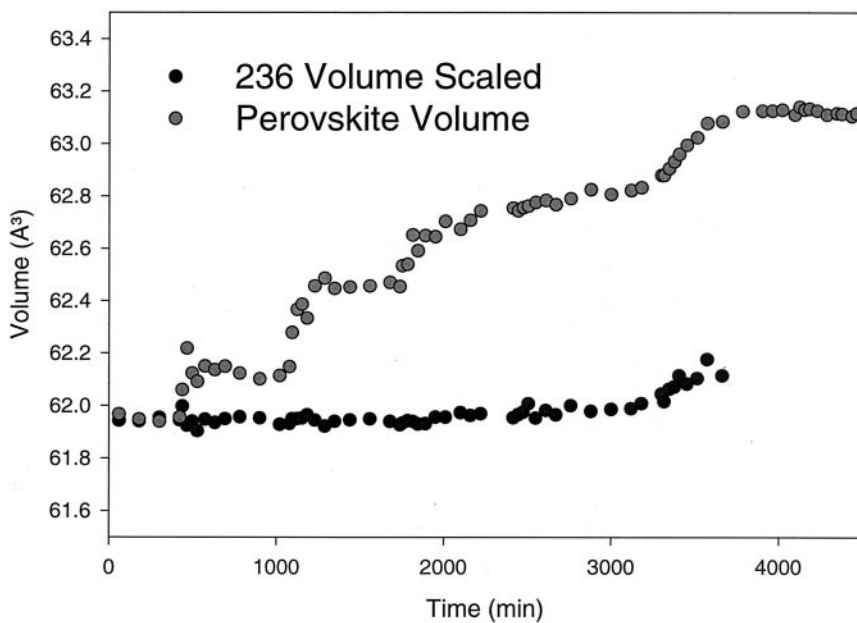


Fig. 8. Cell volume of perovskite phase and 236 phase (scaled) plotted as function of time at various pO_2 values.

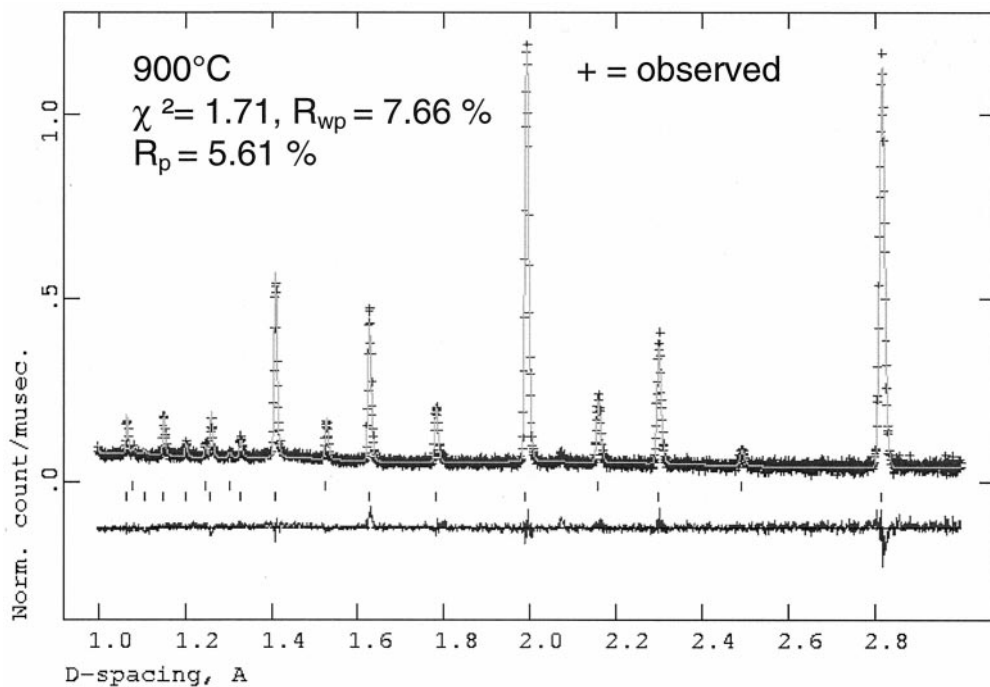


Fig. 9. Rietveld profile fit to powder neutron diffraction data from SFC2 sample obtained at 900°C. Reflection markers represent rocksalt and perovskite phases from top to bottom, respectively.

material consists of $\text{SrFeO}_{2.5}$ and CoO . Fig. 9 shows the fit obtained from the two-phase mixture at low $p\text{O}_2$. At $\log p\text{O}_2 = -15$, there is no evidence that the perovskite oxygen content drops below the value presented above. There is, however, an indication at this $p\text{O}_2$, that some CoO is being reduced to Co metal. Note that there is no direct evidence from the diffraction pattern that Co metal is present. Changing the carrier gas to Ar probably brings about some reversal of this reduction, although there does not appear to be any change to the perovskite phase.

Once the sample has been reduced to $\text{SrFeO}_{2.5} + \text{CoO}$ at 900°C , we are able to bring about the reverse process (re-form 236) when the carrier gas is switched back to air at this temperature. However, a wide variation that ranges from 25–65 wt%, is observed in the resultant weight fraction of 236. In these cases, samples were made from different batches of powder and had different thermal histories. Further investigation is ongoing.

4. Conclusions

We have successfully performed in-situ neutron diffraction experiments on a $\text{SrFeCo}_{0.5}\text{O}_y$ (SFC2) ceramic membrane tube at several $p\text{O}_2$ values. At the beginning of the experiment, the $\text{Sr}_2(\text{Fe,Co})_3\text{O}_y$ (236) phase is dominant, but begins a decomposition to perovskite and rocksalt phases when the $\log p\text{O}_2$ is below -2.5 . The remaining 236 phase fully decomposes by $\log p\text{O}_2 = -12.2$, whereupon only $\text{SrFeO}_{2.5}$ (perovskite) and CoO remain. It is possible to bring about a reversal of the decomposition when switching back to air at temperature, the extent of which varies significantly among samples. How these phases might be distributed across an operational membrane during oxygen permeation has not been determined, but this work does suggest that the tube might be rich in 236 on the air side and 236 deficient near the methane side. This requires further study since different phase distributions should clearly give rise to different electronic properties.

Acknowledgments

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