Chemical Oxidation of $SrCoO_{3-\delta}$

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Various chemical oxidants were investigated for their capability to oxidize brownmillerite $SrCoO_{2.5}$ to perovskite $SrCoO_{3-\delta}$. Among the oxidants tested, $KMnO_4$/HCl was found to be the strongest to yield $SrCoO_{3-\delta}$ with $\delta \approx 0.06$.

The perovskite $SrCoO_{3-\delta}$ system is known for its wide range of oxygen nonstoichiometry. Hence, it serves as a kind of prototype for the recently highlighted functional oxides of mixed-valent (III/IV) cobalt. With the proper choice of process parameters it can be obtained as different types of metastable single phases with orthorhombic ($0.5 < \delta < 0.6$),[1,2] tetragonal ($0.1 < \delta < 0.25$)[2,3] or cubic ($\delta \approx 0$)[3–5] symmetry. Synthesis of the oxidized phases usually goes through the orthorhombic brownmillerite phase $SrCoO_{2.5}$,[1] which has ordered oxygen vacancies such that the structure is composed of alternately stacked layers of corner-sharing CoO_4 tetrahedra and CoO_6 octahedra. For the oxidation of $SrCoO_{2.5}$, electrochemical[3–5] and high-pressure[2,6] techniques have been employed. Possibility to utilize chemical ways for the control of oxygen content was brought up by Nemudry et al.[3] who oxidized $SrCoO_{2.5}$ by immersing the sample into an aqueous solution of Br_2 and NaOH. Compared to the other methods chemical oxidation requires only a very simple experimental set up. In the present work, several other chemical oxidizing agents are utilized.

The $SrCoO_{2.5}$ precursor was prepared from Co and $SrCO_3$ powders, dissolved in stoichiometric amounts in 3 M HNO_3 solution and then chelated by EDTA/NH_3 solution containing EDTA in 50% excess. The solution was dried, burned and then calcined at 900 °C. The calcination product was ground and pressed into pellets for the final heat treatment in air at 1000 °C for 40 h, followed by quenching to room temperature. The X-ray diffraction pattern for the product revealed a single-phase brownmillerite with an oxygen content of 2.50 per formula unit, as determined by iodometric titration.

For the oxidation experiments, the $SrCoO_{2.5}$ pellets were crushed and ground. Four different oxidizing media were employed: (1) aqueous solution of 0.2 M $KMnO_4$ and HCl in various concentrations, (2) aqueous solution of $Na_2S_2O_8$ saturated at room temperature, (3) 1:1 dispersion of Br_2 and H_2O, and (4) aqueous solution of 0.3 M Br_2 and 5 M NaOH. The experiments were carried out for 50-mg samples in 2-mL plastic vials except for experiment (4), which was carried out for a 200-mg sample in a 20-mL glass tube. Immersion time varied from 1 to 24 h. Temperature was controlled using a water or an ice bath and a thermometer. After the oxidation treatment, the sample powder was washed with deionized water plus ethanol [(1) and (2)] or CH_3CN plus ethanol [(3) and (4)] and subsequently dried in air at room temperature.

X-ray diffraction (XRD) patterns were collected for the samples with a Rigaku RINT2550 diffractometer equipped with a rotating Cu anode. Software JANA 2000 was used in the profile-fitting mode for the lattice-parameter refinements [in space groups, *I*4/*mmm* ($SrCoO_{3-\delta}$) and *Pnma* ($SrCoO_{2.5}$)].[5] The XRD-pure samples were additionally characterized for the precise oxygen content by means of iodometric titration:[7] sample powder of ca. 20 mg was dry-mixed with ca. 200-mg KI and dissolved in 30-mL oxygen-freed 1 M HCl solution. The amount of iodine produced from iodide through oxidation by Co^{III} and/or Co^{IV} was instantly determined by titrating with 0.015 M $Na_2S_2O_3$ solution using starch as an indicator. Each titration analysis was repeated several times with reproducibility better than ±0.01 for the oxygen content, $3 - \delta$.

In the $Na_2S_2O_8$ medium the oxidation reaction was very aggressive being accompanied with vigorous gas evolution. Moreover, the color of the solution turned pink apparently due to dissolved $Co(H_2O)_6{}^{2+}$, and at the end of experiment the sample grains were coated with $SrSO_4$ (visible even in the XRD patterns) as a consequence of reductive decomposition of $S_2O_8{}^{2-}$. With the other oxidation media employed neither color change nor significant gas evolution was observed. However, after the $KMnO_4$/HCl oxidation at 80 °C, the sample powder was slightly brownish, indicating the presence of small amount of a MnO_2 impurity. Moreover, once the HCl concentra-

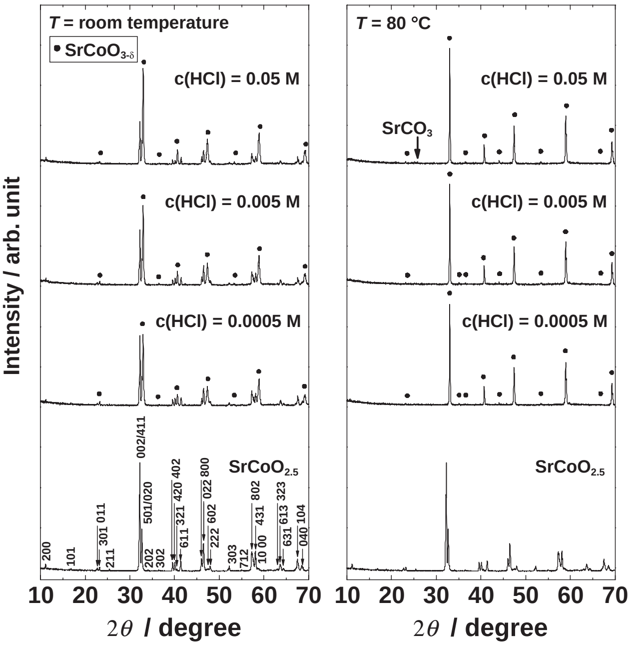

Figure 1. XRD patterns for the $SrCoO_{3-\delta}$ samples obtained from the $KMnO_4$/HCl oxidation treatments under various experimental conditions. Indices given in the bottom-left pattern are for the orthorhombic (*Pnma*) $SrCoO_{2.5}$ precursor phase.

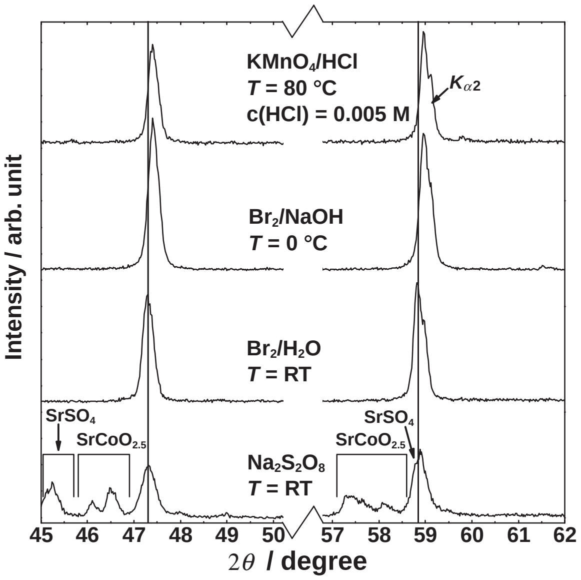

Figure 2. Portions of the XRD patterns for the products from various oxidation experiments showing the exact positions of the 440, 004, 622, and 404 reflections due to the tetragonal ($I4/mmm$) $SrCoO_{3-\delta}$ cell. A positive shift in the peak position reflects the higher oxygen content. RT = room temperature.

tion was too high (≥0.05 M at 80 °C), the sample partly dissolved and small amounts of a $SrCO_3$ impurity were detected in the XRD patterns. On the other hand, some of the grains after the $KMnO_4/HCl$ and $Br_2/NaOH$ oxidations appeared in metallic golden color, which was taken as an indication of the fully oxidized $SrCoO_{3.0}$ phase.[3]

All the oxidizing agents employed were found to oxidize the $SrCoO_{2.5}$ brownmillerite; $KMnO_4/HCl$ turned out to be the most efficient oxidant. The extent of oxidation was followed by inspecting the evolution of the XRD pattern: progress in oxidation results in changes in the lattice symmetry and contraction in the lattice dimension. In Figure 1, shown are representative XRD patterns for samples treated in the $KMnO_4/HCl$ medium under different conditions. The sample treated with 0.2 M $KMnO_4$/0.005 M HCl at 80 °C was single-phase tetragonal $SrCoO_{3-\delta}$ with the oxygen content determined at $\delta = 0.06$. Oxidation with Br_2/H_2O resulted in a less-oxidized end phase with $\delta = 0.21$, apparently due to the lower oxidation power of Br_2 compared to that of MnO_4^-. Oxygen-content analysis was not feasible for the $Na_2S_2O_8$ treated samples because of the $SrCO_3$ impurity. However, comparison of the XRD patterns for the differently oxidized samples (see Figure 2) revealed that the $Na_2S_2O_8$ treated samples were close to the Br_2/H_2O treated samples in terms of the peak positions (and hence also in terms of the oxygen content). Also seen was that the $Br_2/NaOH$ treated samples resembled those for the $KMnO_4/HCl$ treated samples. The fact that the $Br_2/NaOH$ treatment resulted in higher oxygen contents than the Br_2/H_2O treatment indicates that the oxidation power of Br_2 depends on pH. Finally in Figure 3, we show the relationship between the lattice volume (as calculated per $SrCoO_{3-\delta}$ formula unit) and the oxygen content, $3 - \delta$, (as determined with iodometric titration) for the present samples together with relevant literature data for comparison.

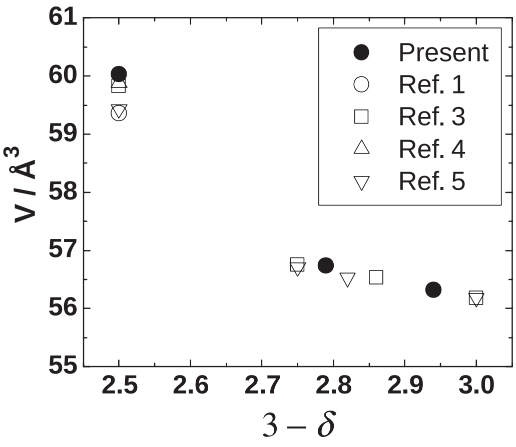

Figure 3. Lattice volume per $SrCoO_{3-\delta}$ formula unit (V) plotted against the oxygen content ($3 - \delta$) for the present samples for which iodometric titration was performed. Relevant literature data are included for comparison.

In the $KMnO_4/HCl$ and the $Na_2S_2O_8$ treatments, an increase in the concentration of HCl and $Na_2S_2O_8$, respectively, was found to speed up the oxidation reaction but not to affect the oxygen content of the end product. Very similar effects were observed upon increasing the reaction temperature. In terms of the reaction speed, the Br_2/H_2O dispersion was found the best among the oxidizing media investigated.

In conclusion, we developed novel wet-chemical routes to efficiently oxidize the $SrCoO_{3-\delta}$ system. The oxidation power of the oxidizing agent employed affects the oxidation rate and propably also the final oxygen content. The highest oxygen content of $\delta \approx 0.06$ was attained with an aqueous $KMnO_4$/HCl solution.

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