

Framework Doping of Indium in Manganese Oxide Materials: Synthesis, Characterization, and Electrocatalytic Reduction of Oxygen

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The electrochemical reduction of oxygen is a reaction of prime importance in view of its practical application in clean energy generation systems, for example, fuel cells and metal–air batteries.¹ The electrocatalyst used to accelerate O₂ reduction in the cell is key in determining the electrical discharge, because O₂ reduction is the slower of the two half-reactions for the cell.² The noble metal Pt has excellent performance as an oxygen reduction electrocatalyst but is very expensive for large-scale applications and, in addition, experiences poisoning.² This leads to a need for cheaper materials with activity toward the oxygen reduction reaction (ORR).

Manganese oxide octahedral molecular sieves (OMS) have been widely used or proposed for possible use in catalysis, batteries, separations, chemical sensors, and other applications.³ The potassium form of the mineral hollandite⁴ is known as cryptomelane, has a chemical composition of KMn₈O₁₆, and is also denoted as K-OMS-2 in the literature.⁵ The crystal structure of cryptomelane is porous, including one-dimensional tunnels among a rigid MnO₂ framework composed of edge-shared and corner-shared MnO₆ octahedra. K⁺ is the predominant species in the tunnels besides water molecules.⁶ The tunnel size is 4.6 × 4.6 Å because of the 2 × 2 arrangement of the MnO₆ octahedra.

The mixed valency of manganese makes OMS-2 a good semiconductor and an oxidation catalyst. The average manganese oxidation state (AOS) in OMS-2 is around 3.8.⁶ The physical and chemical properties of doped manganese octahedral molecular sieves are significantly different from those of the undoped ones and are greatly influenced by the location of the doping ions.³ This motivated us to investigate chemical alteration of the manganese oxide framework. Previous work has been mostly concerned with the doping

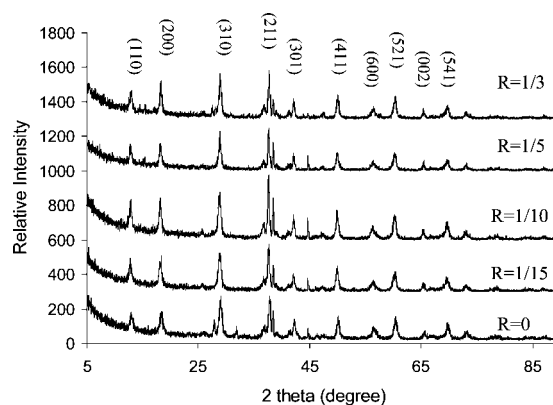


Figure 1. X-ray diffraction patterns for K-OMS-2 materials with different indium contents. R = molar ratio of In/Mn in the initial reaction mixture. The peak at 2θ of 44.7° is the Al (200) peak of the aluminum holder (JCPDS 4-787).

of different divalent metal cations into the tunnels of OMS-2,^{7,8} only a few studies have attempted to incorporate metal cations into the framework of OMS-2.^{3,9}

Indium tin oxide (ITO) and other indium doped materials are currently of great interest as electrode and sensor materials and have been extensively studied for potential applications.^{10–12} Herein we report the hydrothermal synthesis of a novel nanocrystalline material by doping indium into the manganese oxide matrix.

A typical synthesis of indium-doped K-OMS-2 material, denoted as K-In-OMS-2, involves the hydrothermal treatment of a suspension which is composed of 14.3 mmol of MnSO₄, 21.45 mmol of K₂S₂O₈, and 21.45 mmol of K₂SO₄. Indium nitrate was added such that the Mn/In molar ratio varied from 3 to 15. The entire mixture was autoclaved at 200 °C for 2 days. The slurry formed was filtered, washed with deionized water, and dried at 120 °C overnight. Indium free K-OMS-2 was prepared under the same conditions.

An XRD pattern for indium-free K-OMS-2 is shown in Figure 1, corresponding to synthetic cryptomelane (KMn₈O₁₆, JCPDS 29-1020). All other synthesized K-In-OMS-2 samples have XRD patterns similar to those of K-OMS-2. There are no significant changes in the XRD peak intensities and line widths. These indicate that all synthesized K-In-OMS-2 materials in this work have a cryptomelane type structure.

Energy Dispersive X-ray (EDX) analysis was used to determine the amount of indium in the samples (Table 1). The actual In/Mn atomic ratios of the samples are much lower than the initial ratios of reactants added, suggesting that there is limited solubility of indium oxide in K-OMS-2.

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Table 1. Chemical Composition and AOS of Manganese in Indium Doped Materials

nominal ratio ^a In/Mn	actual ratio ^b In/Mn	AOS of Mn
0	0	3.70
1/15	0.004	3.73
1/10	0.007	3.78
1/5	0.011	3.76
1/3	0.019	3.61

^a Molar ratio in the initial reaction mixture. ^b Atomic ratios in K-OMS-2 and K-In-OMS-2 materials, determined by EDX. AOS: average oxidation state.

A potentiometric titration method was used to measure the average oxidation state of manganese in all of the samples.^{13,14} Indium doping caused a change in the average oxidation state (AOS) of Mn (Table 1). The AOS for the indium-free cryptomelane is 3.70, confirming that both Mn³⁺ and Mn⁴⁺ are present in the structure, with Mn⁴⁺ being the predominant species, as addressed in ref 9. When the nominal indium doping was less than 1/5 of the manganese in cryptomelane, the AOS of manganese increased with increasing amount of doping, reaching the highest at 3.78. The AOS of manganese dropped when the nominal ion doping was 1/5 of the manganese or higher, showing similar trends as that found for Fe-doped K-OMS-2.³ When the nominal ion doping was less than 1/5 of the manganese, In³⁺ was more likely to substitute for Mn³⁺ in the framework. When the nominal ion doping was 1/5 of the manganese or higher, more Mn⁴⁺ was replaced by In³⁺, resulting in a decrease of AOS.

Yellow In₂O₃ is only known in a single form.¹⁵ The strongest XRD peak of In₂O₃ powders occurs near 2θ of 31° (JCPDS 22-336). The XRD pattern for the physical mixture of K-OMS-2 and In₂O₃ (atomic ratio of In/Mn = 0.019) clearly shows a peak around 2θ of 31°, as shown in Figure 1 of Supporting Information. The presence of out-of-framework In₂O₃ was ruled out by XRD patterns.

Synthesized K-In-OMS-2 samples have Raman spectra similar to those of K-OMS-2 (Figure 2). Bands at 570–580 cm⁻¹ and 630–640 cm⁻¹ can be attributed to Mn–O lattice vibrations in MnO₂.^{16,17} The band around 380 cm⁻¹ is associated with Mn–O–Mn in the MnO₂ octahedral lattice.¹⁶ Raman intensities are usually directly proportional to the concentration of the active species.¹⁸ Generally, the bands at 384, 578, and 635 cm⁻¹ have slightly decreasing trends with increasing amounts of indium doping. This indicates that manganese was gradually substituted by indium with increasing amounts of doping.

IR spectra of cryptomelane samples are shown in Figure 3. Two additional bands gradually showed up and shifted toward lower wavenumbers with increasing indium content.

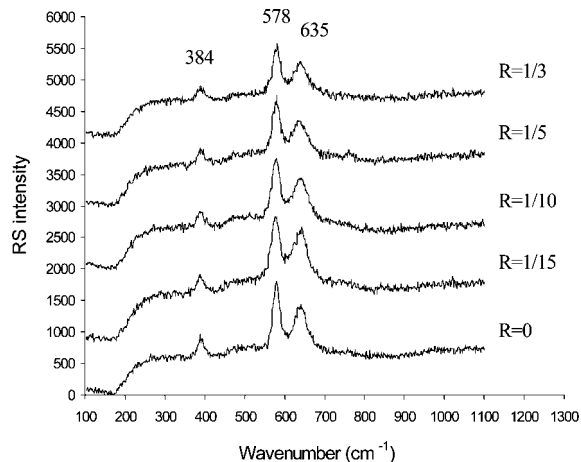


Figure 2. Raman spectra for In-free and In-substituted K-OMS-2. The same amount of samples was used in Raman studies. *R* = molar ratio of In/Mn in the initial reaction mixture.

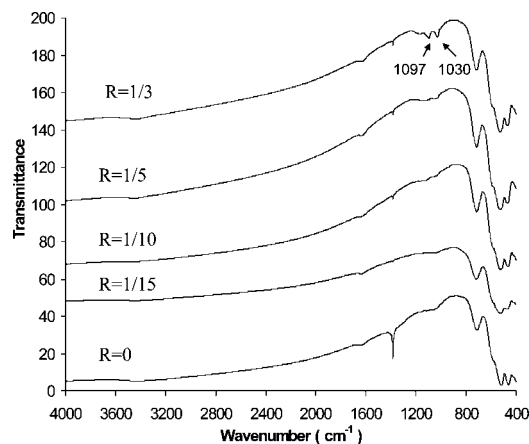


Figure 3. IR spectra for In-free and In-substituted K-OMS-2. *R* = molar ratio of In/Mn in the initial reaction mixture.

They become very clear at 1097 cm⁻¹ and 1030 cm⁻¹ in K-In-OMS-2 (*R* = 1/3). Similar phenomena were observed in the framework doping of indium into the MFI structure and beta zeolite.¹⁹ The peak at 1097 cm⁻¹ is attributed to the T–O–T (In–O–Mn) lattice vibration whereas the attribution of the band at 1030 cm⁻¹ is unclear at present. The band around 1097 cm⁻¹, which was attributed to the T–O–T lattice vibration of indium-doped oxide materials, together with the shifting toward lower values indicates that indium was incorporated into the framework.¹⁹ The reason why a band shift was observed in IR but not in Raman remains unclear.

DeGuzman et al. examined the electroactivity of manganese oxides using cyclic voltammetry (CV) and found that K-OMS-2 is not electroactive.⁴ Here, cyclic voltammetry was used to test the electrocatalytic activity in the oxygen reduction of indium-free and indium-doped (*R* = 1/5) K-OMS-2. A gas-diffusion electrode was prepared to check the ability of these samples to reduce oxygen. The cell setup

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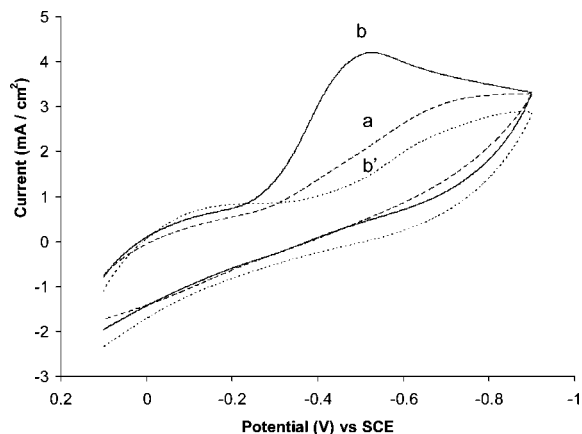


Figure 4. Cyclic voltammograms obtained at a rate of 50 mV/s using samples (a) indium-free K-OMS-2 and (b) In-substituted K-In-OMS-2 ($R = 1/5$) in carbon powder. Curves a and b were recorded in an O_2 -saturated 1.0 M KOH solution while curve b' was obtained in N_2 -purged 1.0 M KOH solution.

consisted of a working electrode containing the sample powder/carbon powder mixture on carbon paper, a SCE reference electrode, a Pt counter electrode, and a 1.0 M KOH solution as the electrolyte. The process for the preparation of the working electrodes was shown in the literature.²⁰ A computer controlled CHI 430 electrochemical workstation was used to obtain cyclic voltammograms, and a scan rate of 50 mV/s was used. In a typical experiment, the cell was first purged with $N_2(g)$ for 30 min followed by an initial scan, and then the cell was purged with $O_2(g)$ for 30 min and scanned again. All experiments were done at ambient temperature (22 ± 2 °C).

Figure 4 shows the cyclic voltammograms (CVs) for the oxygen reduction for indium-free and indium-doped ($R = 1/5$) K-OMS-2 electrodes in an O_2 -saturated 1.0 M KOH electrolyte with a scan rate of 50 mV/s. The voltammogram obtained in a N_2 atmosphere showed that K-In-OMS-2 ($R = 1/5$) was electrochemically inactive in this potential range and for the scan rate used in this study, as shown in curve b'. Curve a shows that oxygen reduction did not occur in indium-free K-OMS-2. However, oxygen reduction potentials and peak currents were obtained at the K-In-OMS-2 ($R = 1/5$) electrode, as shown in curve b, indicating that K-In-OMS-2 ($R = 1/5$) is electrochemically active in the electrocatalytic reduction of O_2 . When the electrolyte was repurged with O_2 , K-In-OMS-2 ($R = 1/5$) showed a restoration of the O_2 reduction peak, which means that K-In-OMS-2 was stable toward O_2 reduction. A slower scan rate of 25 mV/s was also used to test the electrochemical activity toward ORR of indium-free K-OMS-2 and K-In-OMS-2 ($R = 1/5$). The results have no significant differences from those collected using a scan rate of 50 mV/s, as shown in Figure 2 of Supporting Information. On the basis of electrocatalytic activity results obtained from CVs, K-In-OMS-2 is a promising electrode material for O_2 reduction.

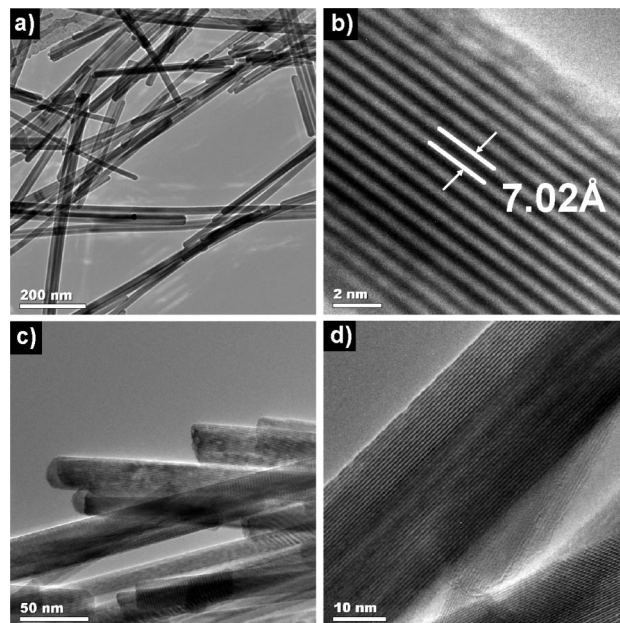


Figure 5. (a) TEM image of indium-free K-OMS-2. (b) HRTEM image of indium-free K-OMS-2 single nanorod. (c) TEM image of K-In-OMS-2 ($R = 1/5$). (d) HRTEM image of K-In-OMS-2 ($R = 1/5$). R = molar ratio of In/Mn in the initial reaction mixture.

The products of indium-free and indium-doped ($R = 1/5$) OMS-2 were further characterized by transmission electron microscopy (TEM), as shown in Figure 5. Figure 5a shows the morphology of indium-free K-OMS-2. This image shows the typical nanorod shapes of cryptomelane with an average diameter of 19 nm. The lattice fringes were clearly observed from high-resolution TEM (HRTEM) images, as shown in Figure 5b. The distance between the neighboring lattice fringes corresponds to the d -spacing of the (110) planes. Indium-doped ($R = 1/5$) K-OMS-2 also has a nanorod shape with an average diameter of around 18 nm (Figure 5c,d).

In summary, manganese oxide materials with novel chemical compositions have been hydrothermally synthesized. Doped indium was found to be in framework sites in synthetic cryptomelane, based on the results of XRD, AOS of manganese, Raman, and IR. CV results show that manganese oxide doped with indium generates electrocatalytic activity for the O_2 reduction reaction. Further studies using other non-Pt materials, including In_2O_3 and other indium-doped oxides, are planned in our laboratory.

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Supporting Information Available: X-ray diffraction patterns for the physical mixture of K-OMS-2 and In_2O_3 (atomic ratio of In/Mn = 0.019) and cyclic voltammograms obtained at a rate of 25 mV/s using indium-free K-OMS-2 and In-substituted K-In-OMS-2 ($R = 1/5$) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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