

Manganese Oxide Thin Films with Fast Ion-Exchange Properties

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Confinement of inorganic and organic species into microporous materials such as zeolites and layered compounds is an important and growing field of research.^{1,2} Introduction of guest species into host structures can be done by intercalation or ion-exchange reactions.¹ The resulting nanocomposite systems may have physical and chemical properties drastically different from those of the original components.^{3,4} Recent developments of interesting systems are the fabrication of a new class of solid-state microlasers based on zeolite-dye crystals⁵ and the synthesis of a selective and highly active biomimetic catalyst based on tungstate-exchanged layered double hydroxides which have been used for oxidative bromination reactions.⁶

Polycrystalline microporous materials are widely used for adsorption, separation processes, and catalysis.⁷ On the other hand, thin films are the desirable form of molecular sieves for use in electronic, magnetic, optical, or molecular recognition studies and applications.^{8,9} However, the preparation of multiple samples having the same host structure and different guest species is often a long and difficult process.¹ Ion-exchangeable thin films of microporous materials can allow production of a large number of organic and inorganic intercalates in a simple manner. Such films¹⁰ have been used in ion-exchange reactions that occur over a period of a few minutes to several days. In this work we report the preparation of lamellar manganese oxide thin films that can

undergo fast ion-exchange reactions in solution with inorganic and organic cations.

Thin films (~1 μm thick by SEM) supported on glass or quartz substrates were prepared from a solution of tetraethylammonium manganese oxide (TEAMnO_x) colloids.¹¹ The preparation, characterization, and self-assembly processes on flat surfaces of these novel manganese oxide sols have been previously described in detail.^{12–14} TEM and small-angle neutron scattering data show that the TEAMnO_x colloidal particles are on the order of 20–80 Å in diameter.¹² X-ray absorption spectroscopy indicates that the particles have a layered structure consisting of edge-shared MnO₆ octahedra with an average oxidation state of 3.7.¹³ XRD data for TEAMnO_x films show structures consistent with CdI₂-type layers of MnO_x negatively charged with TEA⁺ counterions and water molecules between these anionic layers.^{11,12}

Cation exchange of the film was carried out in aqueous solutions of Cd(NO₃)₂ and Methylene Blue [3,7-bis(dimethylamine)phenothiazonium, MB]. To achieve ion-exchange, the films were immersed in the desired solution (1 × 10⁻² M)¹⁴ for 3 s and immediately were taken out from the dipping solution and rinsed twice with deionized water and then dried at room temperature. The ion-exchange of the film was confirmed by depth profiling measurements using X-ray photoelectron spectroscopy,¹⁵ UV-visible spectroscopy,¹⁵ XRD,¹⁵ and chemical analyses (vide infra).

The XPS depth profile for the film ion-exchanged with Cd²⁺ (Cd–MnO_x film) coated on glass is shown in Figure 1. The XPS data show a surface containing oxygen, manganese, cadmium, and carbon. During the first 5 min of sputtering, the oxygen, cadmium, and carbon signals rapidly decrease while the manganese signals increase. As the surface is further penetrated, a steady state is reached with a uniform concentration over 50 min of sputtering. The etching process was continued until an increase of the silicon signal (Si 2p) was obtained.¹⁶ The concentration of cadmium from the data is approximately 9% near the surface and 7% in the steady-state region (bulk). Nitrogen from TEA⁺ or NO₃⁻ was not detected in the film, which indicates that Cd²⁺ quantitatively replaced the TEA⁺ cation and that most of the carbon present in the film is due to contamination. The O/Mn atomic ratio gradually decreases from its initial value of 2.2 at the surface to about 1.3 in the bulk. This effect is due to chemical reduction and loss of oxygen via ion sputtering.^{17b} The XRD

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(11) A volume of 600 μL of a solution of 13 mM tetraethylammonium manganese oxide colloid was spread onto a glass substrate (1.5 cm × 1.5 cm). After evaporation of the solvent at room temperature a uniform film was formed. The film was annealed at 70 °C for 5 min. The XRD pattern¹² for TEA–MnO_x film gives seven reflections: 17.06 (001), 8.54 (002), 5.70 (003), 4.26 (004), 3.41 (005), 2.50 (100), and 1.44 Å. (110), with an interlayer spacing of $d_{001} = 17$ Å.

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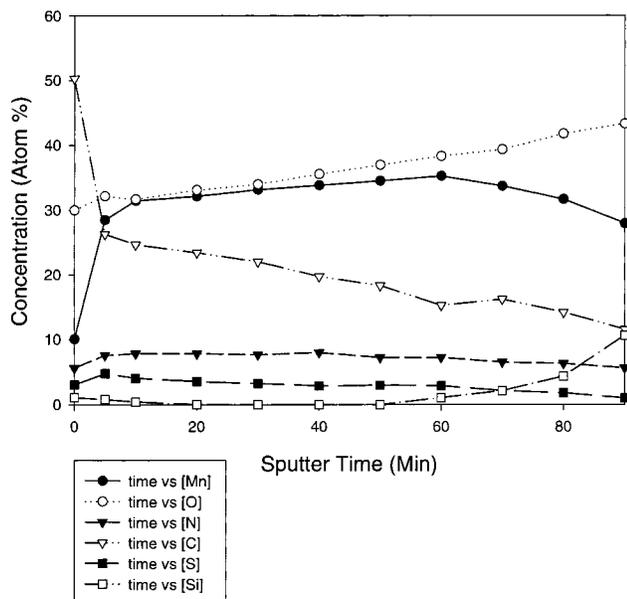
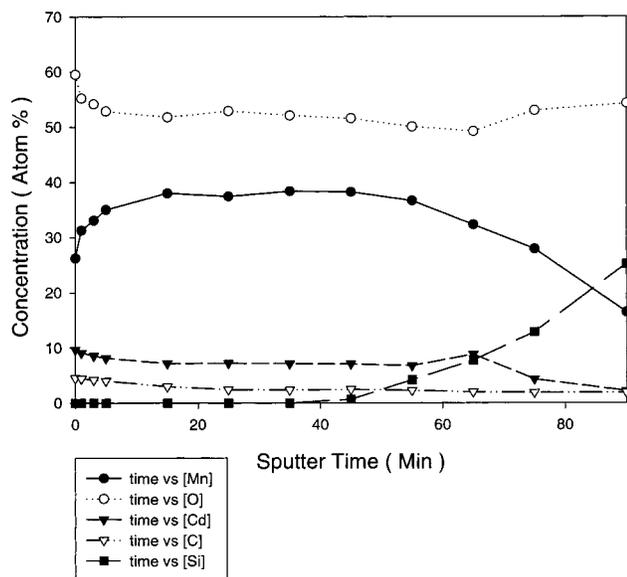
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(14) Concentrations lower than 1 × 10⁻² M result in incomplete exchange. In comparison to our films, ion exchangeable thin films from layered transition metal oxides^{10b,c} and zeolites^{10a} have been prepared with thickness ranging from 0.2 to 5 μm and zeolite particle sizes between 0.5 and 1.5 μm . Typical concentrations of aqueous solutions of metal cations used to exchange these films were 1 M during periods of time at least 30 min long up to several days.

(15) The XPS data were acquired using a Leybold-Heraeus LHS-10 instrument equipped with an Al K α X-ray source and a SPECS EA 10MCD energy analyzer. The sputtering conditions were $E_{\text{Ar}^+} = 5.0$ keV, $I_{\text{E}_{\text{miss}}} = 10$ mA, sputter area = 10 mm × 10 mm. The ion gun was oriented 30° above the sample plane. UV-visible transmission spectra were obtained on an HP8452A spectrophotometer. XRD data were obtained on a Scintag XDS-2000 diffractometer using Cu K α radiation.

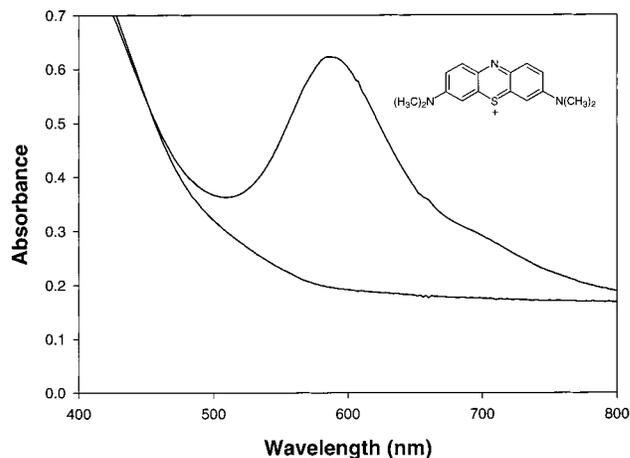
(16) Surface roughness increases due to Argon sputtering^{17a} give rise to the gradual rise in the Si 2p signal.

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 Figure 1. XPS depth profile of Cd-MnO_x film.

 Figure 2. XPS depth profile of MB-MnO_x film.

pattern for the Cd-MnO_x film consists of three broad reflections at 7.4 (001), 3.7 (002), and 2.5 Å (100). This indicates that the layered structure is compressed after replacement of the large TEA⁺ cations with Cd²⁺ ions. Elemental analyses suggest that the cadmium-exchanged material only contains trace levels of carbon after exchange.

The film ion-exchanged with MB⁺ (MB-MnO_x film) was also sputtered until the glass surface was reached, Figure 2. The time required for this operation was similar to that of the Cd-MnO_x film. The XPS data reveal a surface rich in carbon and oxygen with manganese, nitrogen, sulfur, and silicon present in concentrations less than 10%. The depth compositional measurements for this sample exhibit complicated variations within the surface region. A dramatic change in the concentration of carbon and manganese is observed after 5 min of sputtering. The carbon concentration decreases by half while the manganese concentration increases almost two times. Upon Ar⁺ bombardment, the O/Mn ratio changes and becomes close to unity. These data suggest that the organic molecule decomposes and enhances the reduction process of Mn under the ion beam. Although a steady state is not reached, the sulfur coming from MB is present at concentrations of 3 to 4% through the etching process. This observation


 Figure 3. Absorption spectra in the region of 400 to 800 nm for (A) TEA-MnO_x film and (B) MB-MnO_x film.

strongly suggests that the MB cations penetrated the whole film. Elemental analyses are also consistent with exchange of Methylene Blue throughout the bulk material.

The UV-visible spectra for the MB-MnO_x films exhibit two main broad absorption bands at 366 and 584 nm. The broad absorption at 366 nm tailing out to 600 nm is assigned to charge-transfer transitions of the manganese oxide layers.¹² This absorption band appears at a lower wavelength than that observed for bulk manganese oxide (400 nm).¹⁸ Such observations are consistent with small particle sizes (~100 Å) since the film is prepared from a colloidal solution. The other absorption band at 584 nm with a shoulder around 700 nm is attributed to intercalated MB because it appears after the ion-exchange reaction, as shown in Figure 3. This band is due to π - π^* transitions of the MB aromatic system, which is blue-shifted with respect to the value (λ_{\max} 664 nm) of the aqueous dye solution (metachromasy).¹⁹ The XRD data for the MB-MnO_x film show three broad reflections consistent with a layered structure with an interlayer spacing d_{001} around 9.7 Å due to MB⁺ incorporation. These data indicate that the MB⁺ ion (1.70 nm × 0.76 nm × 0.32 nm)²⁰ should be oriented with the plane of the aromatic rings approximately parallel to the manganese oxide layers (slab thickness of 4.5 Å).¹² This type of interaction should be responsible for most of the metachromasy of the dye since the value of the interlayer spacing is not big enough to allow significant aggregation of the dye between the MnO_x layers.²¹

In conclusion, lamellar inorganic films of manganese oxide can undergo fast and quantitative ion-exchange reactions with retention of the layered structure. Film quality can be excellent if drying, agitation, thickness, and time of exchange are optimized. The low charge density of TEA⁺ and its large hydration sphere make it easy to be displaced by cations of higher charge density. This in addition to the small size of the particles forming the films may explain their excellent ion-exchange properties. The present results indicate that extensive modifications of these films can be made with different types of cations, which could be important for sensors.

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