# Immobilization of Methylene Blue between Electrodepsoited Manganese Oxide Multilayers

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Cationic methylene blue (MB) ions were intercalated into the galleries of a layered manganese oxide film that was deposited anodically on an indium–tin oxide electrode. The $MB^+$ ions once incorporated are not ion-exchanged with small cations and can communicate with the electrode surface through manganese oxide sheets.

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The widespread interest in developing chemically modified electrodes is driven by their potential applications as electrocatalysts and/or electron-transfer mediators. Methylene blue ($C_{16}H_{18}N_3S^+$, MB), a cationic dye with reversible redox processes in aqueous solution, has been considerably attractive because it can work as an electron mediator between enzymes and substrates as a result of its redox potential being close to those of many biomolecules.[1,2] For this reason, MB has been immobilized in different environments and utilized for the electrocatalysis of various species.[3,4] On the other hand, birnessite-type layered manganese oxides can accommodate a variety of guest cations in their interlayer space by ion-exchange. Small cations ($K^+$, $Na^+$, $H^+$, etc.) are normally located there to compensate negative charges on manganese oxide layers. A number of procedures have so far been developed for the synthesis of birnessite because of their unique adsorptive, ion-exchange, and electrochemical properties. Very recently, we found a one-step electrochemical route for fabricating thin films of layered manganese oxides intercalated with various alkylammonium ions.[5–7] The process involves potentiostatic oxidation of aqueous $Mn^{2+}$ precursors in the presence of tetraalkylammonium salts. The interlayer spacing of products can be regulated by the size of electrolyte cations used, while the film thickness is controllable by simply changing the delivered electrical charge. Although incorporation of MB molecules into chemically-prepared lamellar Mn oxide colloids has been achieved by the group of Suib using an ion-exchange method,[8] no experimental insight is available on the ion-exchanged and electrochemical properties of MB-loaded manganese oxides.

We present here that MB can be incorporated by ion-exchange into the gallery space of the layered manganese oxide film deposited anodically. The $MB^+$ ions once incorporated are not replaced with small cations in solution phase, and they can communicate electrochemically with the underlying electrode surface.

Tetrabutylammonium chloride (TBACl, Fluka) and MB (Chroma) were used as received. All solutions were deoxygenated by bubbling purified nitrogen gas just prior to use. Electrochemical experiments were conducted in a conventional three-electrode cell. A platinum sheet and an Ag/AgCl (in saturated KCl) electrode were used as the counter and reference electrodes, respectively. Manganese oxide films with TBA were deposited on an indium-doped tin oxide (ITO) electrode by applying a constant potential of +1.0 V for 30 min in an aqueous $MnSO_4$ (2 mM) solution with 50 mM TBACl.[5] The resulting ITO-supported film was rinsed with water and was subsequently immersed in a 50 mM aqueous MB solution for given periods of time. The film-coated electrode thus prepared was rinsed again with copious amounts of water and dried under vacuum. X-ray diffraction (XRD) patterns of the sample films were measured in a Shimadzu XD-D1 spectrometer using a Cu K$\alpha$ radiation source ($\lambda = 0.15405$ nm). X-ray photoelectron spectra (XPS) were collected using a Fisons Escalab 210 spectrometer, with an Al K$\alpha$ (1486.6 eV) unmonochromatic source.

Figure 1a shows the XRD pattern of the as-deposited film from TBA-containing solution. Peaks marked with an asterisk (∗) and a broad hump between 20 and 40° in $2\theta$ are due to the ITO substrate. Two peaks appearing at $2\theta = 7.2$ and 14.4° can be indexed to 001 and 002 reflections of manganese oxide layers, respectively, and the third order diffraction appeared at 21.6° together with the ITO peak. This pattern is consistent with that of the $TBA^+$-intercalated birnessite prepared by Suib et al. through an ion-exchange reaction with proton birnessite.[9] The $d_{001}$ value, 1.23 nm according to Bragg's equation, corresponds to an interlayer spacing and is essentially identical to that observed for the $TBA/MnO_x$ film prepared similarly on Pt.[5]

After immersion in MB solution (Figures 1b and 1c), the peaks due to the TBA-intercalated phase decreased in intensity, disappearing at 3 h, and being replaced by two peaks at 12.3 and 25.0° which are similarly assignable to the 001 and 002 reflections, respectively. This pattern with $d_{001} = 0.72$ nm demonstrates deintercalation of bulky $TBA^+$ ions with accompanying shrinkage of the interlayer. Instead, the gallery space was found to be occupied with positively charged MB ions, as described later. The interlayer spacing of ≈0.7 nm has been frequently observed for bulk birnessites with hydrated small cations

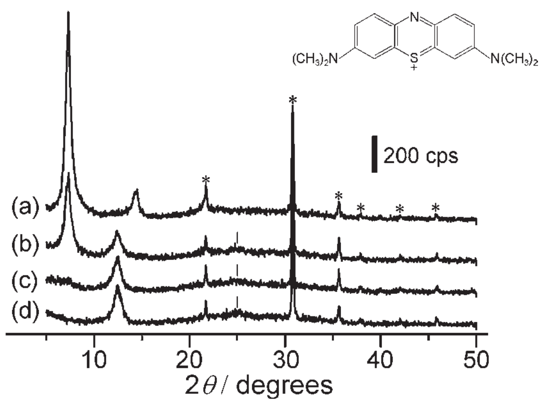

**Figure 1.** XRD patterns obtained from a $TBA/MnO_x$ film on an ITO substrate before (a) and after immersion in a 50 mM MB solution for 1 (b) and 3 h (c). Curve d was taken after immersing the film c into a 0.1 M KCl solution for 12 h. The film deposition was carried out in a 2 mM $MnSO_4$ and 50 mM TBACl solution by applying a constant potential of +1.0 V for 30 min.

($Na^+$, $K^+$, $H^+$, etc.), in which the interlayer spacing is maintained by water moleculeas.[10] Considering the size of the planer molecule MB on the basis of van der Waals radii (1.60 × 0.7 nm),[11] we should remove the possibility that the polyheterocycles orient perpendicular to the manganese oxide layers since the $MnO_2$ nanosheet is ≈0.45 nm in thickness.[12] Although it is not yet clear whether the $MB^+$ ions or water molecules are responsible for the diffraction pattern, the observed multilayer spacing (0.72 nm) means that the planer MB fits tightly into the gallery. When the MB-intercalated film was immersed in KCl solution for 12 h, the diffraction pattern remained unchanged (Figure 1d). As demonstrated below, the MB ions were not replaced with potassium ions in solution.

Figure 2 shows XPS survey and core level spectra of the $MnO_x$ films obtained in Figure 1. In the survey spectra, the Mn 2p (645 eV), Mn 3s (85 eV), and O 1s (530 eV) peaks coming from the manganese oxide were commonly observed. The TBA/$MnO_x$ film (a) exhibited the N 1s peak at 401.7 eV which can be attributed to positively charged nitrogen atoms of TBA.[6] After immersion in a MB solution (b), the higher BE component disappeared and was replaced by the new peak at 399.6 eV, characteristic of neutral nitrogen atoms (amine structure).[13] At this time, the S 2p spectrum showed an asymmetric signal that can be curve-fitted with two peaks at 163.3 and 164.3 eV with an area ratio of 2:1, corresponding to the $2p_{3/2}$ and $2p_{1/2}$ states.[14] These observations clearly indicate that the $TBA^+$ ions between the manganese oxide multilayers are replaced with $MB^+$ ions in solution.

Subsequent immersion of the obtained MB/$MnO_x$ film in KCl solution resulted in no significant changes both in the N 1s and S 2p regions (Figure 2c). This behavior is distinct from that of the TBA/$MnO_x$ film, where $TBA^+$ is rapidly ion-exchanged with potassium ion in solution.[5] This difference may reflect a strong affinity of manganese to sulfur.

Figures 3a and 3b display cyclic voltammograms of the MB/$MnO_x$ film-coated ITO electrode taken in KCl solution during the first ten cycles in each potential region. Figure 3a provides a stable CV response with a rectangular shape which is typical of the pseudocapacitive nature of manganese oxide.[15] This indicates that the multilayer film is electrochemically active. Potential cycling between 0 and +0.8 V yielded no change in the crystalline structure (not shown). As shown in Figure 3b, cathodic and anodic currents occur with onset potentials of 0 and −0.05 V, respectively. These currents could not be seen for the TBA/$MnO_x$ film (Figure 3c), and therefore they are attributable to the reduction and oxidation of MB ions within the $MnO_x$ multilayers. This observation strongly suggests that the incorporated $MB^+$ ions can communicate electrochemically with the underlying electrode. A less conductive property of manganese oxide layers may be responsible for the larger peak separation compared to that of bulk MB. The MB redox response decreases with the number of cycles, which can be accounted for by the exclusion of non-charged MB species generated during the reduction step.

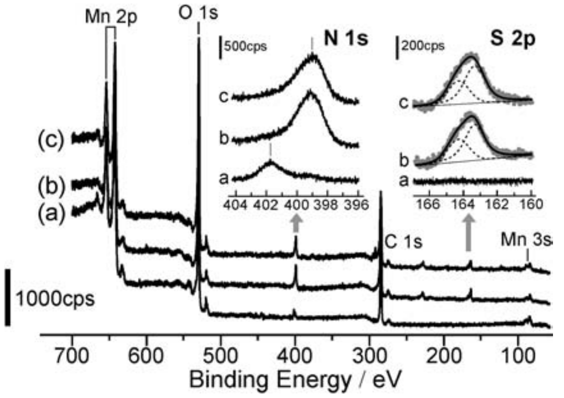

**Figure 2.** XPS spectra of the TBA/$MnO_x$ film on an ITO electrode before (a) and after being immersed in a 50 mM MB solution for 3 h (b), and then in a 0.1 M KCl solution for 12 h. The film deposition was carried out the same way as that in Figure 1.

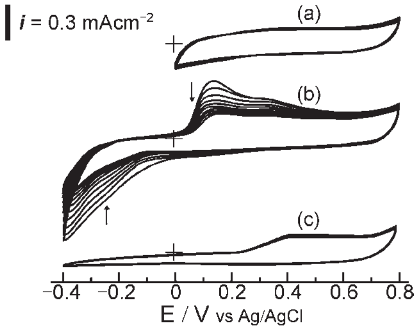

**Figure 3.** CVs of ITO electrodes coated with MB/$MnO_x$ (a and b) and TBA/$MnO_x$ (c) films in a 0.1 M KCl solution during the first ten cycles in the potential regions from +0.8 to 0 (a) and −0.4 (b and c). Scan rate, 20 mV/s.

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## References

1 V. Svetlicic, V. Zutic, J. Clavilier, and J. Chevalet, *J. Electroanal. Chem.*, **312**, 205 (1991).
2 A. Erdem, K. Kerman, B. Meric, U. S. Akarca, and M. Ozsoz, *Anal. Chim. Acta*, **422**, 139 (2000).
3 Z. Lu and S. Dong, *J. Chem. Soc., Faraday Trans. 1*, **84**, 2979 (1988).
4 W. H. Zhou and E. L. Clennan, *J. Am. Chem. Soc.*, **121**, 2915 (1999).
5 M. Nakayama, S. Konishi, A. Tanaka, and K. Ogura, *Chem. Lett.*, **33**, 670 (2004).
6 M. Nakayama, S. Konishi, H. Tagashira, and K. Ogura, *Langmuir*, **21**, 354 (2005).
7 M. Nakayama, H. Tagashira, S. Konishi, and K. Ogura, *Inorg. Chem.*, **43**, 8215 (2004).
8 O. Giraldo, S. L. Brock, W. S. Willis, M. Marquez, and S. L. Suib, *J. Am. Chem. Soc.*, **122**, 9330 (2000).
9 J. Luo and S. L. Suib, *Chem. Commun.*, **1997**, 1031.
10 D. C. Golden, C. C. Chen, and J. B. Dixon, *Clays Clay Miner.*, **35**, 271 (1987).
11 R. Hoppe, G. Sculz-Ekloff, F. Wöhrle, E. S. Shpiro, and O. P. Tkachenko, *Zeolites*, **13**, 222 (1993).
12 S. L. Brock, M. Sanabria, S. L. Suib, V. Urban, P. Thiyagarajan, and D. I. Potter, *J. Phys. Chem. B*, **103**, 7416 (1999).
13 Z. F. Li and E. Ruckenstein, *Macromolecules*, **35**, 9506 (2002).
14 H.-F. Lu, H. S. O. Chan, and S.-C. Ng, *Macromolecules*, **36**, 1543 (2003).
15 M. Nakayama, A. Tanaka, Y. Sato, T. Tonosaki, and K. Ogura, *Langmuir*, **21**, 5907 (2005).