Electron Transfer Reactions in Thin Films of Prussian Blue and Related Compounds

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URL	http://hdl.handle.net/10097/37598

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学 位 授 與 年 月 日　平成 19 年 9 月 12 日
学 位 授 與 の 根 拠 法 規　学位規則第 4 条第 1 項
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学 位 論 文 題 目　Electron Transfer Reactions in Thin Films of Prussian
　　　　　　　　　　　　Blue and Related Compounds (プルシアンブルー及び関連
　　　　　　　　　　　　化合物の薄膜中の電子移動反応)
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論　文　内　容　要　旨

Chemically modified electrodes (CMEs), made of conducting or semiconducting materials are the electrodes coated with selected molecular, ionic, or polymeric films of chemical modifiers. CMEs exhibit excellent chemical, electrochemical, and/or optical properties by means of charge-transfer reactions or interfacial potential differences. In the dissertation, promising CMEs, Prussian Blue (PB) and its Osmium analogue, Osmium Purple (OP), have been studied by electrochemical and spectroelectrochemical methods. In addition, $LiMn_2O_4$, which is one of the promising materials for the rechargeable batteries, have been studied by microvoltammetry.

Cyclic voltammograms of the PB and OP films on disk shaped Pt electrodes in different electrolytes showed that both electron transfer reaction and ion transportation occur at the electrode/solid redox species/electrolyte interfaces. The transportation of the ions depends upon the size of the hydrated ion compared to the area of the open space of the PB or OP crystals into the films. In general, smaller the size of the hydrated ion, easier to be transported through the open space of the crystals of PB and OP stated below.

In the case of the PB thin films, the films immersed in the solutions containing K^+, NH_4^+, Rb^+ and Cs^+ ions show the stable voltammograms and therefore the ions can be transported through the PB thin film as the radii of these hydrated ions (K^+ =1.25Å, NH_4^+ =1.25Å, Rb^+ =1.18Å and Cs^+ =1.19Å) are smaller than the channel radius of the open space of the film (~1.6Å). Steady and almost symmetrical waves were obtained after repeated scans of the PB film on a Pt electrode in the solution containing K^+ ion; while, in the solutions containing NH_4^+, Rb^+ and Cs^+ ions, slightly less

symmetric waves were observed than that in the solution containing K^+ ion. On the other hand, much less stable and symmetric voltammograms were obtained in the solutions containing Li^+, Ba^{2+} and Na^+ than containing K^+, and about 40% loss in total charge were observed at the reduction wave from 1st cycle to 4th cycle in the solution containing Li^+ and Na^+ ions. Therefore these three ions can not be transported through the PB film because the radii of these hydrated ions (Li^+ =2.37Å, Ba^{2+} =2.88Å and Na^+ =1.83Å) are larger than the channel radius of the open space of the PB film (~1.6Å).

In the case of the OP films, the films immersed in the solutions containing K^+, NH_4^+ and Rb^+ ions show stable voltammograms and therefore the ions are concluded to be transported through the OP film because the radii of these hydrated ions (K^+=1.25Å, NH_4^+ =1.25Å, and Rb^+ =1.18Å) are lower than the channel radius of the open space of the OP film (~1.6Å). Similar to the electrochemical behaviors of PB film, steady and almost symmetrical waves are obtained for the OP film on Pt disk electrode after repeated scans in the solution containing K^+ ion, while, in the solutions containing NH_4^+ and Rb^+ ions, slightly less symmetric waves are observed than that in a solution containing K^+ ion. On the other hand, much less stable voltammograms were acquired in the solution containing Li^+ and Ba^{2+} ions. In fact, about 56% and 40% losses in total charge at the reduction wave are observed during 1st cycle to 3rd cycle of the cyclic voltammogram in the solutions containing Li^+ and Ba^{2+} ions, respectively. Therefore, these two ions can not be transported through the OP film, which can be reasonably explained by the fact that the radii of these hydrated ions (Li^+=2.37Å, and Ba^{2+}=2.88Å) are much larger than the channel radius of the open space of the film (~1.6Å). From the results obtained for the thin films of PB and OP, it can be concluded that on PB and OP films on the electrodes, one electron transfer reaction as well as ion transportation occur in both cases. The reduction wave for Fe^{3+} ion in PB or OP film shows the same peak position, indicating that high spin ferric (Fe^{3+}) ions in the nitrogen holes are not affected by the low spin metal ions in the carbon holes (Fe^{II} ion in PB and Os^{II} ion in OP). More symmetric and sharper waves obtained in the solutions containing K^+, NH_4^+ and Rb^+ ions for OP film than those for PB film indicate that electron transfer reaction in OP film is faster than that in PB film.

Spectroelectrochemical analysis in the ultraviolet-visible region of the OP film on SnO_2 electrode demonstrated that absorption maxima shifts toward longer wavelengths and absorbance decreases by increasing the degree of the reduction of the OP film, while the maximum position of the spectra shifts toward shorter wavelength and absorbance increases in the reverse direction. The spectrum of the completely reduced form of OP shows no characteristic absorption feature. These results suggest that electronic and optical properties of the OP film depend upon the degree of the reduction of the OP film as in the case of the PB film.

Comparing the results of PB and OP thin films on electrodes in the solutions containing NH_4^+ and Rb^+ ions, the waves in OP film are much more symmetric than PB film, indicating that the electrochromic properties of the OP film is expected to be superior to that of the PB film.

Using the microvoltammetic technique on a $LiMn_2O_4$ polycrystalline particle, cyclic voltammetric results show that the peak current increases as the scan rate increases and the waves become distorted when the scan rate becomes more than 1mV/s. The slopes of $logI_{pA}$-log v plot (I_{pA} = peak current and v = scan rate) are estimated 0.79 and 0.80, which are intermediate values between 0.5 at infinite diffusion to 1 at finite diffusion. Since both the size of the $LiMn_2O_4$ particle and diffusion distance of Li-ions into the particle are finite, the Li-ion intercalation/deintercalation reaction can be completed up to the center of the particle only at the lower scan rate (<1 mV/s). Charge/discharge amount by the integration of current vs. scan rate plot shows that charge/discharge amount decreases as the scan rate increases more than 1mV/s.

These results demonstrate that the extraction/insertion of Li-ion can not follow the scan rate higher than 1 mV/s, and the Li-ion extraction/insertion reactions cannot be completed up to the center of the particle at the scan rate larger than 1 mV/s.

The diffusion process of Li-ion in $LiMn_2O_4$ polycrystalline particle using the potential step method was also examined. The result shows that the apparent diffusion coefficient of Li-ion varied in the region of 2~5 x 10^{-9} cm^2/s, depending on the electrode potential. In the point of view of the deformation of the crystal structure lattice constant decreases with increase of positive potential up to ~0.7V. This deformation is consistent with decrease of D_{app}, but at the larger potential, more than 0.7V, the variation of D_{app} can not be explained in terms of only variation of lattice constant.

In conclusion, the electrochemical as well as spectroelectrochemical studies of the PB and OP films have made it possible to acquire the basic insight into the role of high- and low-spin metal ions of PB and OP films and in addition find out the usefulness of the OP film as electrochromic devices. In addition, the Li-ion intercalation/deintercalation reactions through the supplied $LiMn_2O_4$ polycrystalline particles indicate that these particles can be used as the rechargeable battery materials.

論文審査結果の要旨

　第一章では、プルシアンブルー(PB)及びその類似化合物オスミウムパープル(OP)の、幾何学的構造・電子構造・電気化学特性・エレクトロクロミック特性について概説し、過去の研究及びその問題点について述べている。また、カチオンの層間反応を伴う $LiMn_2O_4$ の電気化学特性及び研究現状についても概説した。

　第二章では、PB 及び OP の化学的合成法、白金電極および SnO_2 電極への電気化学堆積法について述べている。また、電気化学的紫外可視吸収分光の測定法の詳細について述べている。また、$LiMn_2O_4$ の単一粒子の電気化学特性を調べるために用いた、マイクロ電極作製法、及びマイクロサイクリックボルタンメトリーについても述べている。

　第三章では、PB 及び OP の電気化学特性および電気化学的紫外可視吸収分光の測定結果について述べている。種々の電解質溶液中での PB および OP のサイクリックボルタンメトリ測定結果から、電極/固体レドックス種/電解質界面を横切って、電子移動反応及びそれに伴うイオン輸送が起こることを明らかにした。イオン輸送は、イオンの水和イオン半径に依存する。小さなイオン種(K^+, NH_4^+, Rb^+ and Cs^+)のイオン輸送は可能であるのに対して、大きなイオン種(Li^+, Ba^{2+} and Na^+)のイオン輸送は起こり難いことを明らかにした。また、高スピン Fe^{3+} は、低スピンイオン種(PB 中の Fe^{II} イオン及び OP 中の Os^{II} イオン)からの影響を受けないことも初めて明らかにした。特に、OP 薄膜の電子状態及び分光学的性質は、OP 薄膜の酸化還元状態により大きく変化することを世界で初めて明らかにした。

　第四章では、マイクロサイクリックボルタンメトリによる $LiMn_2O_4$ の単一粒子の電気化学特性を調べた。その結果、掃印速度 が 1mV/s 以下において、Li イオンの層間反応が、単一粒子全体にわたって起こることから、層間反応が律速過程である事を明らかにした。

　よって，本論文は博士(工学)の学位論文として合格と認める。