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The Determination of the Selectivity Coefficient of Na^+ versus Li^+ on Prussian Blue Thin Film in Propylene Carbonate by Means of a Quartz Crystal Microbalance

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Synopsis. The cation selectivity on a Prussian Blue (PB) modified electrode in propylene carbonate was examined by means of a quartz crystal microbalance. It was found that the selectivity coefficient of Na^+ versus Li^+ on the PB film was about 15.

Since Neff established the redox and electrochromic (EC) behavior of a Prussian Blue (PB) electrode[1] and Itaya et al. reported an electroplating method of PB,[2] many works on Prussian Blue (PB) modified electrodes have appeared.[3] Much attention has been paid to the Prussian Blue thin films not only because of their potential use as electrochromic devices,[4,5] batteries,[6] and catalysts,[7] but also because of their use as model compounds for such basic research as electron-hopping kinetics study.[8] It has been shown that Prussian Blue electrodes could be electrochemically reduced to Prussian White reversibly by means of a mechanism which involves the injection of both cations and electrons. The cations with Stokes radii of smaller sizes could penetrate the PB lattice more easily. In fact, it has been reported that, in aqueous media, K^+, Rb^+, and Cs^+ can smoothly penetrate the lattice, while repeated redox cycles are blocked in the presence of Li^+ or Na^+.[2] In an organic solvent of propylene carbonate, however, the redox reaction of PB in the presence of Li^+ or Na^+ is very stable.[4,9] Although the mechanism of ion transport has not yet been completely elucidated in detail, one of the applications of the PB modified electrode would be ion-separation making use of the different selectivities of the cations. It has been reported, that is, that the electrochemical redox cycles of the PB electrode could make it possible to separate alkali metal ions.[10]

The quartz crystal microbalance (QCM) in solution[11–13] offers a direct way of measuring the mass change of the PB film during electrochemical reduction and oxidation,[14] which would lead to quantitative estimations of the cation selectivities.

This paper will describe a new method for the determination of the selectivity coefficient of a cation versus another one on the PB film by using QCM.

Experimental

Indium tin oxide (ITO) was sputtered (ca. 20 Ω/□) on one side of a 6-MHz AT-cut quartz crystal (Inficon) with gold film electrodes on both sides. ITO was sputtered in order to prevent a chemical deposition of PB on the gold substrates.[2] The oscillating surface area was about 0.33 cm². Films of PB on ITO-coated crystals were electrochemically deposited under galvanostatic conditions of 5 μA cm⁻² in a freshly prepared solution of an equivolume mixture of 10 mM† $FeCl_3$ and 10 mM $K_3[Fe(CN)_6]$ aqueous solutions. The charge passed through for electroplating was 9 mC cm⁻². After the deposition of the PB, the film was thoroughly rinsed with distilled water and then mounted in a Teflon-made electochemical cell using O-rings. The frequency of the oscillating circuit, made up by following the method in the literature,[15] was monitored with a frequency counter. Cyclic voltammetry was conducted under a nitrogen atmosphere. Unless otherwise noted, a scan rate of 10 mV s⁻¹ was used. Simultaneously the charge passed through was recorded with a coulometer. A Pt wire and an Ag/AgCl electrode were used as the counter and the reference electrodes respectively. A propylene carbonate (PC) solution of 1 M $LiClO_4$, $NaClO_4$, or a mixture of them with 1.5 wt% H_2O[4] was used as the electrolyte solution. The mass change of the PB film upon reduction was calculated from the frequency change according to Sauerbrey's equation. The equation held within a 5% error, which was confirmed by the galvanostatic electrodeposition of Ag on Au quartz crystal electrodes.

Results and Discussion

Figure 1 shows typical cyclic voltammetric (A) and frequency-potential(B) curves of the PB thin film in the $NaClO_4$/PC system, the latter illustrating that the observed mass change is reversible. It is clear that, when PB is reduced to Prussian White (PW), the weight of the film increases, while the succeeding oxidation of PW to PB is accompanied by a mass loss. The ratio of the mass change to the charge passed through (molar mass) was 21.9 g mol⁻¹, indicating that the sodium ion penetrates into the PB film upon reduction and exits from it upon oxidation.

In contrast with the $NaClO_4$/PC system, the molar

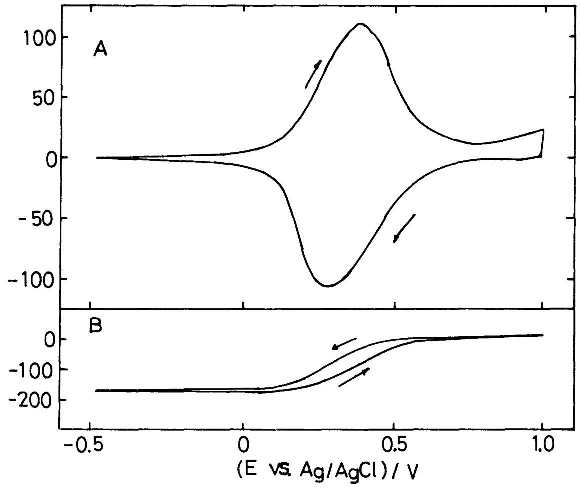

Fig. 1. Cyclic voltammetric (A) and potential-frequency curves (B) for a Prussian Blue modified quartz crystal electrode in 1M $NaClO_4$ of propylene carbonate. v=10 mV s⁻¹.

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† 1 M=1 mol dm⁻³.

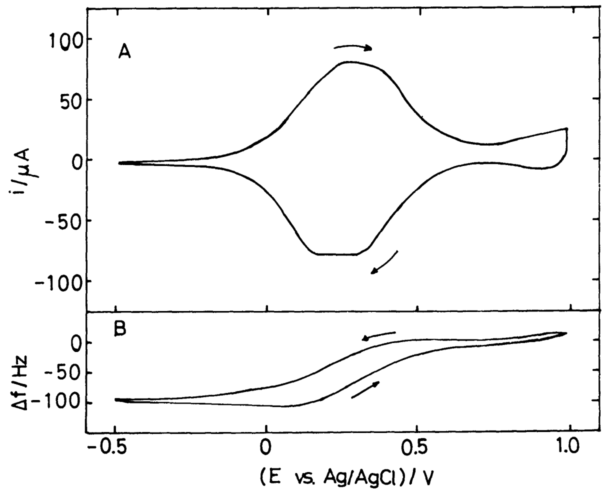

Fig. 2. Cyclic voltammetric (A) and potential-frequency curves (B) for a Prussian Blue modified quartz crystal electrode in 1M $LiClO_4$ of propylene carbonate. v=10 mV s^{-1}.

mass for PB in $LiClO_4$/PC of 10.9 g mol^{-1}, somewhat larger than that expected for Li^+ (6.9 g mol^{-1}), suggests that some water molecules are also incorporated into the PB film with Li^+ upon reduction. Typical cyclic voltammetric (A) and frequency-potential(B) curves in this system are shown in Fig. 2.

Figure 3 shows the relationship between the molar fraction of Na^+ and the molar mass in Na^+/Li^+ mixed electrolyte solutions. The molar mass was calculated for the reduction process of PB. The experimental curve indicates that Na^+ is more favorably intercalated into the PB lattice than is Li^+; this is consistent with the qualitative result in Ref. 9.

Since the molar mass was not much influenced by the scan rate, which ranged from 2 to 100 mV s^{-1}, it may be safe to conclude that distribution equilibrium of ions between the PB thin film and the electrolyte solution is established. The selectivity coefficient of Na^+ against Li^+ on the PB film (α) can be defined as:

$$\alpha = \frac{Y(1-X)}{X(1-Y)} \tag{1}$$

where X is the molar fraction of Na^+ in the solution and Y, the molar fraction of Na^+ in the PB film. The molar mass (Mm) in a Na^+/Li^+ mixed solution is the average of the Mm's for Na^+(ca. 22) and Li^+(ca. 11) obtained as above:

$$Mm = 22Y + 11(1-Y) \tag{2}$$

From Eqs. 1 and 2, we obtain:

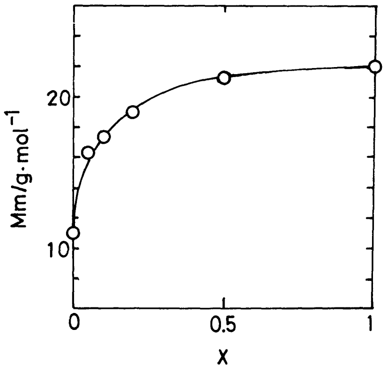

Fig. 3. Relationship between molar fraction of Na^+ in solution (X) and the molar mass (Mm) in Na^+/Li^+ mixed propylene carbonate solutions.

$$Mm = \frac{22X\alpha + 11(1-X)}{X\alpha + (1-X)} \tag{3}$$

which gives a good fit with the experimental curve provided that α is about 15. Consequently, when both ions are incorporated into the PB film, the concentration of Na^+ in the film is almost equal to that of Li^+, even in a solution with a Na^+ molar fraction lower than 0.1.

In conclusion, the quartz crystal microbalance can offer a direct and in situ measurement of ion selectivity on the PB thin film; this method may also be useful for other ion exchangers.

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