

Potassium secondary cell based on Prussian blue cathode

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Abstract

A potassium secondary cell was designed employing a potassium anode and a Prussian blue (PB)-based cathode. The electrolyte solution for the nonaqueous battery was 1 M KBF_4 in 3:7 EC/EMC. The potassium battery designed had some valuable advantages in comparison with similar lithium batteries. The cell design is simple, and both the material used and the procedure needed for the cell fabrication are cheaper. In addition, the cell has an excellent cyclability for more than 500 reversible cycles. There is only a negligible capacity fade for the battery performance at elevated temperatures. Moreover, the chemical diffusion coefficient of K^+ in the cell is higher than that of Li^+ in lithium batteries, which is due to a smaller Stoke's radius of K^+ in electrolyte solution (solvated ions). The results obtained from the experimental measurements and the prospective of this rechargeable cell suggest it as a promising alternative to lithium secondary cells. © 2003 Elsevier B.V. All rights reserved.

Keywords: Nonaqueous battery; Potassium secondary cell; Cyclability; Prussian blue; Cathode material; Potassium anode

1. Introduction

Lithium secondary batteries are one of the most interesting types of power sources for portable devices, due to their noticeable advantages. Unfortunately, there are serious problems for metallic lithium employed as anode material in lithium secondary batteries [1]. Due to the formation of lithium dendrites during deposition, the use of a separator and lowered coulombic efficiency (stripping/plating) is needed [2,3]. This separation of the electrodes is accompanied by high resistance and low current density. Whereas, similar alkali metals (sodium and potassium) can be used with a minimum free electrolyte between the electrodes, as they can be evenly deposited on the electrode surface. On the other hand, the latter alkali metals are cheaper than lithium. Kohl and co-workers [4], Su and Winnick [5] have investigated the possibility of using sodium anode-based batteries in molten media. Designing potassium secondary cell can be of interest due to excellent intercalating/deintercalating properties of potassium ion into/from different electroactive materials, however, less attention has been paid to this type of rechargeable batteries.

Potassium secondary cells can be used as well as lithium batteries, providing high-voltages with high energy density, which is strongly needed for new technologies. Interestingly,

the potential of potassium anode and lithium anode are approximately the same with only a 0.12 V difference. Indeed, among alkali metals, the potential of potassium anode is the closest one to that of lithium anode. Even for the sodium anode, this difference is 0.32 V. Therefore, potassium batteries has no disadvantage related to the cell voltage in comparison with available lithium batteries.

An interesting feature of potassium batteries is the opportunity for using new cathode materials due to excellent properties of a variety of compounds for K insertion/extraction. For example, Prussian blue (PB) and its analogues are one of the interesting classes of materials in modern electrochemistry providing reversible redox systems due to the insertion/extraction of alkali metal ions [6–10]. PB and its analogues are interesting materials for the preparation of rechargeable cells due to their excellent cyclability [11–13]. More recently, we have shown their possibility for the fabrication of high-voltage batteries (as high as 2.0 V) [14,15]. However, these inorganic materials cannot be used for Li intercalation/deintercalation in lithium batteries performance. Imanishi et al. have investigated this process [16,17]. As expected, their results were not satisfactory for the practical performance, as the PB-based cathode of lithium battery lost 30% of its capacity after only 10 cycles. It is obvious that such performance is not suitable for the practical applications. The problem can be attributed to the fact that PB is not a suitable electroactive material for Li insertion/extraction. While, stable PB films can participate in K insertion/extraction for 10^7 reversible

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cycles, Li insertion/extraction into such film destroys the lattice structure to fade its electrochemical activity during only several cycles [10]. Therefore, PB as an excellent cathode material (due to excellent cyclability of PB for K insertion/extraction) can be used for the fabrication of potassium secondary batteries, which is the aim of the present research. Possibility of using PB (and its analogues) for the preparation of a high-voltage rechargeable battery is of practical interest, as PB (and generally its analogues) can be simply synthesized and deposited during a simple electrochemical process and even by direct modification method [18–20] during a simple electroless formation and deposition of the electroactive film onto electrode surfaces.

2. Experimental

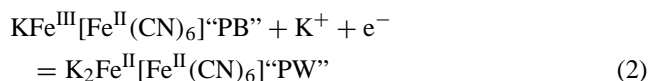
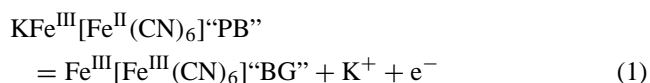
A platinum electrode was employed as the substrate surface for the deposition of cathode material. Prussian blue was synthesized electrochemically to form a thin film on the substrate electrode. This process was performed galvanostatically at a current density of 20 mA/cm² in a plating bath containing 20 mM K₃Fe(CN)₆ and 20 mM FeCl₃ in aqueous solution of 0.1 M HCl and 0.1 M KCl as supporting electrolyte. Then, the electrode was thoroughly washed with deionized water and stored in the supporting electrolyte. To ensure potassium ion insertion into the electroactive film, the electrode was cycled between –0.2 and 0.6 (versus SCE) for 10 times. Finally, the electrode was dried in a nitrogen atmosphere at 40 °C for 72 h, followed by complete drying at 150 °C for 24 h. By the latter action, some of the hydration molecules are removed from the electroactive material [16]. The total amount of the cathode material loaded was about 80 µg. The thickness of PB film estimated by SEM was approximately 1 µm.

Design of the potassium battery was similar to that of conventional lithium batteries (CR2032 coin cells assembled with the cathodes fabricated). A potassium electrode was used as anode and the PB electrode prepared as cathode. All chemicals including the solvents ethylene carbonate (EC, 99.95%) and ethylmethyl carbonate (EMC, 99.9%) were of analytical grade. The electrolyte solution was 1 M KBF₄ in 3:7 EC/EMC (wt.). Although, LiPF₆ is successfully used for the fabrication of commercial lithium batteries due to its advantages over other electrolyte salts, there is an attention to LiBF₄ as an alternative electrolyte salt due to thermal instability and moisture sensitivity of LiPF₆ [21]. Thus, using KBF₄ electrolyte salt in the potassium secondary cell designed is of practical interest. The electrochemical measurements were performed using a homemade potentiostat/galvanostat connected to a computer running CorrView software. The absorption spectra were recorded using a Viga 740 spectrophotometer. The design of optical/electrochemical cell employed was similar to those widely used in the literature [6–8].

3. Results and discussion

As most of investigations on the electrochemical properties of PB are related to aqueous media, it is appropriate to examine its electrochemical behavior in a nonaqueous medium, which is needed for nonaqueous battery performance (e.g. potassium secondary cell). Of course, there is no significant difference between the electrochemical behaviors of PB in aqueous and nonaqueous media, due to excellent ion-exchange properties of PB. It is known that PB can act as an excellent intercalating/deintercalating material even in solid-state condition in the absence of electrolyte solution [23,24].

Fig. 1 shows a typical cyclic voltammetric characteristic of the PB film electrode in the nonaqueous medium. Similar to aqueous media, the cyclic voltammetric behavior is accompanied by two redox couples in accordance with the following reactions:



The reaction (1), which occurs at 0.86 V versus SCE (the second pair of peaks), is referred to the oxidation of PB to so-called “Berlin green” (BG) via one-electron transfer oxidizing high-spin iron in PB lattice. And the reaction (2), which occurs at 0.18 V versus SCE (the first pair of peaks) is referred to the reduction of PB to so-called “Prussian white” via one-electron transfer oxidizing the low-spin iron system.

It is useful to compare cyclability of the PB electrode in the nonaqueous medium for Li insertion/extraction and K insertion/extraction. In aqueous media, Li insertion/extraction into/from PB film is not very reversible and the electroactive film loses its electrochemical activity after only several cycles [10]. It is due to large radius of hydrated Li⁺ ion in aqueous media. Such behavior is also observable for Li insertion/extraction in Li-included nonaqueous media. This comes from the fact that the radius of solvated Li⁺ in nonaqueous media is still significantly larger than other alkali metal ions [25]. The weak cyclability of Li insertion/extraction into/from PB film in nonaqueous medium (Fig. 2) suggests that PB cannot be used as a cathode in lithium secondary batteries. On the contrary of Li, insertion/extraction of potassium into/from a stable PB film deposited onto ITO substrate can be performed reversibly for 10⁷ cycles [10]. This excellent cyclability is also achievable in nonaqueous medium (Fig. 2).

Comparison of the lithium and potassium insertion/extraction processes into/from PB film in aqueous media, as reported in the literature [10], and the data presented in Fig. 2 obviously lead to the conclusion that although PB is not a suitable material for Li intercalation/deintercalation

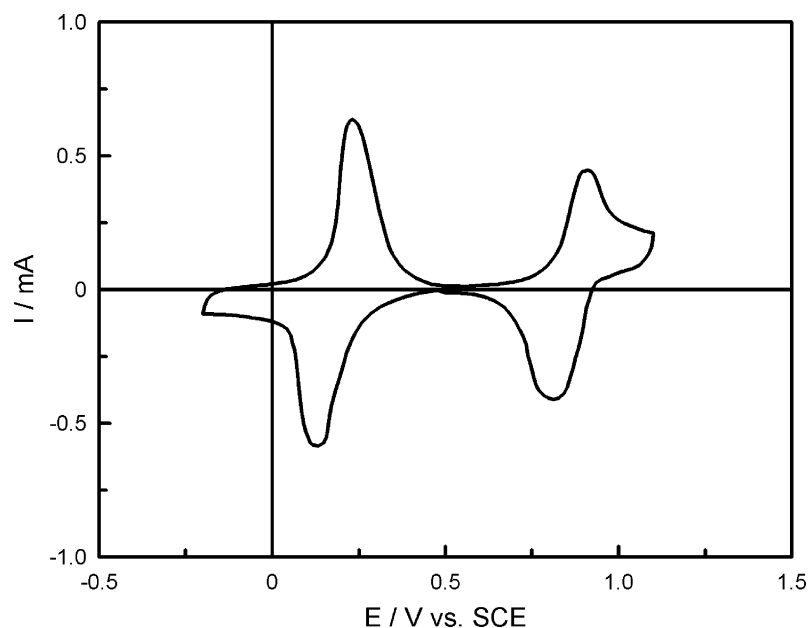


Fig. 1. Cyclic voltammetric behavior of the PB film electrode in a nonaqueous electrolyte solution of KBF_4 . Scan rate 10 mV s^{-1} .

(for lithium battery purpose), such process can be successfully employed to design potassium secondary cell with excellent cyclability.

It should be taken into account that the cyclability investigated in this research was related to slow scans (with low scan rate 10 mV s^{-1}), whereas, that reported in the literature was related to fast scans (with high scan rate 100 mV s^{-1}). Thus, a lesser film stability (and consequently lesser cyclability) is expected for the system under investigation.

Another important problem is the substrate electrode employed for the deposition of the electroactive material. As this is the first (preliminary) research in this context, we used platinum electrode as a conventional substrate to show the intercalating properties of PB, and the influence of substrate surface is expected to be reported in future works. However, it is known that stability of PB film on ITO substrate is higher than Pt substrate [10]. Interestingly, there is an additional advantage for PB cathode-based secondary cells due to the importance of substrate electrode.

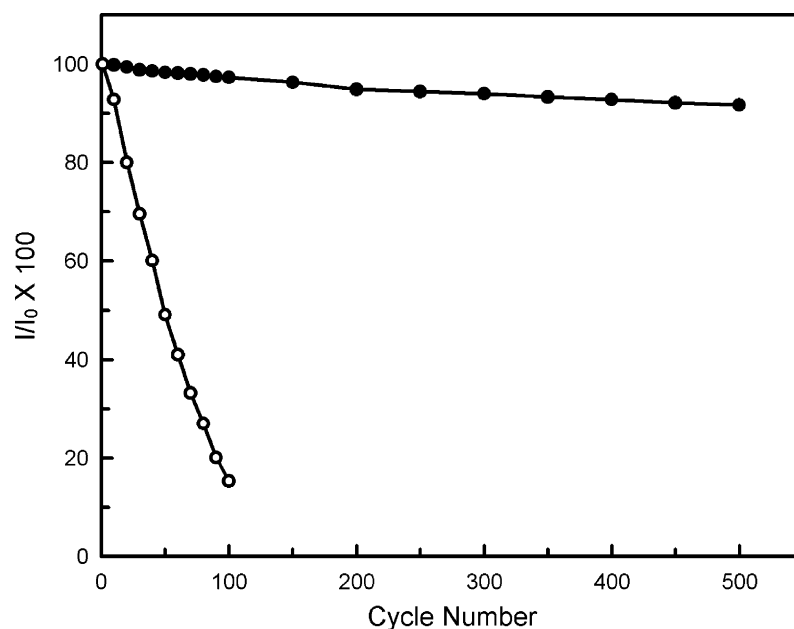


Fig. 2. Cyclability of the PB film electrode for K insertion/extraction (●) in a nonaqueous electrolyte solution of KBF_4 and for Li insertion/extraction (○) in a nonaqueous electrolyte solution of LiBF_4 . Normalized peak current are presented as a function of cycle number for the second redox couple. I_0 denotes the peak current of the first cycle. The cycling was performed by scan rate of 10 mV s^{-1} .

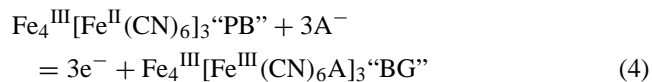
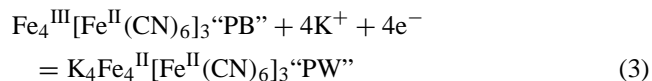
Generally, stability of an electroactive film deposited onto a substrate surface is mainly related to two factors: (i) the own stability of the compound and (ii) stability of the film/substrate connection. For relatively stable compound in solid state (those which are not subject of chemical decomposition), the own stability is referred to the insolubility of reduced and oxidized forms of the compound. Indeed, among different transition metal hexacyanoferrates, PB is the most stable compound and has the best cyclability for ion insertion/extraction. Thus, the second factor is important to enhance the film stability.

Al foil is the most common cathode current collector employed by manufactures to fabricate commercial lithium batteries, because it can naturally form an oxide-based surface layer and withstand high potentials at which the cathode operates. Thus, it is of importance to deposit cathode materials onto Al substrate. Interestingly, we have shown that various hexacyanoferrates can be simply deposited onto Al substrate with high stability [26–28]. This approach was even successful to enhance stability of PB analogues with less stability. Therefore, PB film deposited on Al foil with enhanced stability for the commercial application can be prepared, which is another advantage of PB cathodes.

Fig. 3 shows charge/discharge characteristics of the potassium secondary cell for different cycles. As a cathode material, PB is subject of oxidation to form Berlin green (BG) according to the reaction (1). The occurrence of this reaction for PB cathodes has been reported in the literature [12,13]. In the case of PB rechargeable battery using both PB-based anode and cathode, the reaction (1) occurs at cathode and the reaction (2) at anode [12,13].

It should be emphasized that electrochemical performance (potassium ion insertion/extraction process) of PB is highly dependent on its synthesis method. Itaya et al. [8] have found

that PB can be synthesized without potassium in the compound. In this case, the insertion/extraction for the oxidation and reduction of PB is expressed as:



where A^- denotes the anion supplied by the electrolyte. Indeed, these reactions are similar to those noted above (reactions 1 and 2), as these are the same compounds in accordance with the state of oxidation of iron atoms (PW: $\text{Fe}^{2+}/\text{Fe}^{2+}$; PB: $\text{Fe}^{3+}/\text{Fe}^{2+}$; BG: $\text{Fe}^{3+}/\text{Fe}^{3+}$). However, this is not appropriate for the system under investigation, as the PB synthesized has potassium in its structure. It has been described [29] that even in the case of potassium-free PB, potassium-included PB would be formed by cycling in potassium-rich environment (the action described in Section 2). It should be taken into account that both potassium-free and potassium-included PB compounds have the same structure of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and are referred to as PB, while the soluble PB compound quoted is PW (not potassium-included PB). Indeed, solubility of PB is due to the appearance of $\text{Fe}^{2+}/\text{Fe}^{2+}$ structure, not existence of potassium ion.

The formal potential of this redox system (0.86 V versus SCE) is even a little higher than that of usual cathode materials (LiMn_2O_4 and LiCoO_2) of lithium batteries [22]. Thus, there is no advantage for the positive potential of cathodes of lithium batteries upon that of potassium secondary batteries. This suggests that the potassium secondary batteries have high cell voltages as well as lithium batteries, as their anodes have the same potential (only a tiny difference of

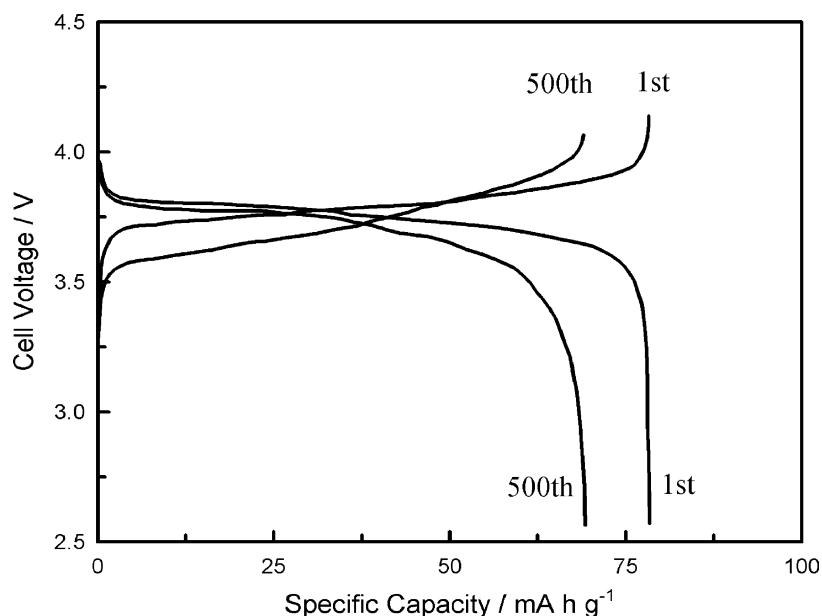


Fig. 3. Charge/discharge characteristics of the potassium secondary cell designed based on potassium anode and PB cathode at a rate of C/10.

0.12 V between Li/Li⁺ (−3.045 V versus SHE) and K/K⁺ (−2.925 V versus SHE couples) [30]. Such behavior is observable in the charge/discharge profiles of the potassium secondary battery reported in Fig. 3.

The theoretical capacity of the cathode in accordance with its molecular mass (306.8 g/mol) can be estimated to be 87.36 mA h/g. According to the data reported in Fig. 3, the cell designed has been achieved about 90% of the specific capacity of the cathode material, which is an excellent value in this type of rechargeable batteries. It should also be emphasized that such excellent performance was achieved at the first (preliminary) research and further investigation of such cathode material certainly lead to better results, as the satisfactory performances of cathode materials of lithium batteries have been achieved as the result of a numerous researches in this context during the last two decades.

As seen, the charge/discharge characteristics of the potassium secondary cell at different cycles display a negligible capacity fade. The value of discharge capacity of the secondary cell as a function of cycle number is presented in Fig. 4. Interestingly, the potassium secondary cell designed shows only a 12% capacity fade after 500 charge/discharge cycles. It is a superiority behavior in comparison with lithium batteries, e.g. LiMn₂O₄ loses more than 20% of its capacity after only 100 cycles.

An important problem in design of lithium batteries and the main obstacle in commercialization of some good cathode materials (e.g. LiMn₂O₄) is the appearance of significant capacity fades during usage and storage at elevated temperatures. Thus, it is of importance to examine this problem for the cathode material proposed for the preparation of potassium secondary cell. Fig. 5 displays the cyclability of the PB cathode in the potassium secondary cell at different

temperatures. As expected, electrochemical performance of the cell is accompanied by higher initial capacities at elevated temperatures. It is obvious that even at very high temperature (which may be applicable for this type of battery performance), the cyclability of the cell is completely satisfactory. Similar results were also obtained for the storage at elevated temperatures (not shown).

Rate capability is very important for the preparation of lithium secondary cells due to slow diffusion of Li⁺. Thus, there is an additional advantage for potassium secondary cell due to faster diffusion of K⁺. The chemical diffusion coefficient was estimated in accordance with the approach employed in our previous works [22,32] for the determination of Li diffusion coefficient using chronoamperometry technique (and also the results were checked by potentiostatic intermittent titration technique (PITT) [33]). For the time domain of $t \gg h^2/\pi^2 D$, the current is dependent on the time as the following equation:

$$\ln(i) = \ln\left(\frac{2nFAD \Delta C}{h}\right) - \left(\frac{\pi^2 D_{\text{app}}}{4h^2}\right)t \quad (5)$$

where h and A are the thickness and the surface area of the electroactive film, and ΔC is the variation of lithium concentration in the film during potential step. According to Eq. (5), there are two ways to calculation of the diffusion coefficient: from intercept of the $\log i$ versus t curve using the first part of the equation, and slope of the $\log i$ versus t curve using the last part of the equation. As the precise measurement of ΔC is very difficult, the later approach is more suitable for this purpose. Therefore, the second approach was used for the determination of the apparent diffusion coefficient (D_{app}).

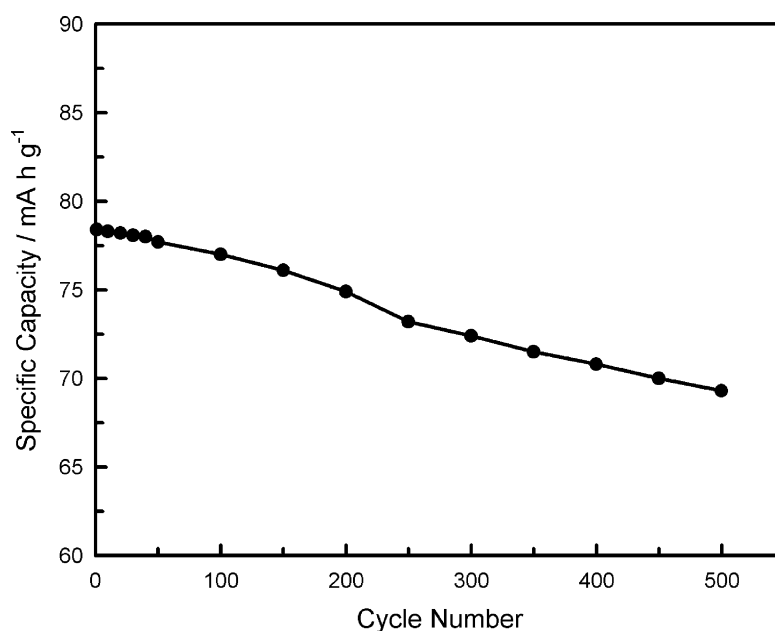


Fig. 4. Cyclability of the potassium secondary cell at a rate of C/10.

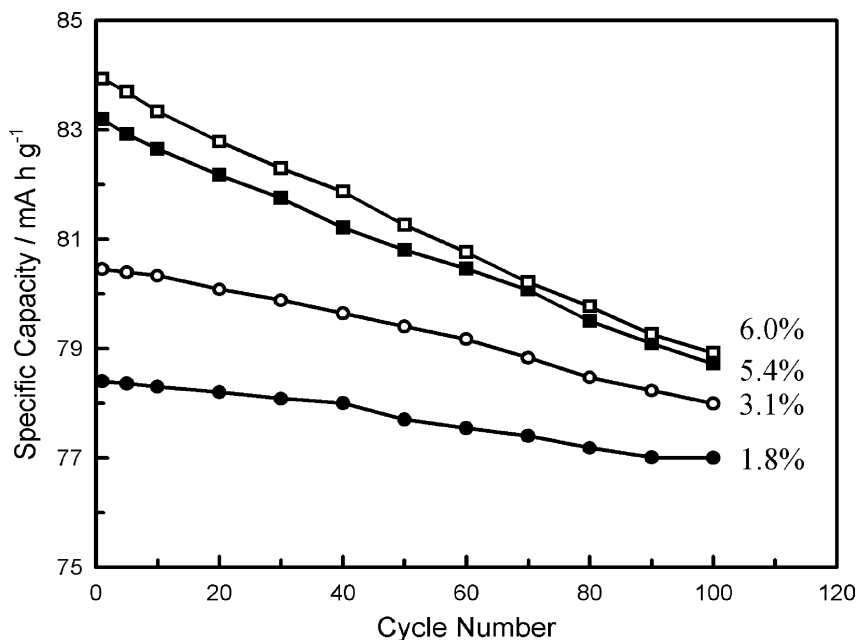


Fig. 5. Cyclability data of the potassium secondary cell containing PB cathode at different temperatures: 25 (●), 40 (○), 60 (■) and 70 °C (□). The specific capacity at each cycle was determined in the same condition of Fig. 3. The numbers on the plots denote the percent of capacity fade after 100 cycles.

Fig. 6 presents the chemical diffusion coefficient of K^+ as a function of the electrode potential during both insertion and extraction processes. The results suggest that the chemical diffusion coefficient of K^+ in the potassium secondary cell is significantly higher than that of Li^+ in lithium batteries [31] (and very higher than that of Na^+ in sodium anode-based batteries [5]). Another interesting feature is that the values of the chemical diffusion coefficient for the insertion and

extraction processes are approximately the same, suggesting a symmetric intercalation/deintercalation. Whereas, for the Li insertion/extraction, there is a one-order of magnitude difference between the chemical diffusion coefficients of the insertion and extraction processes [31].

It is known that absorption spectroscopy is an excellent method for the investigation of oxidized and reduced states of transition metal hexacyanoferrates appearing as

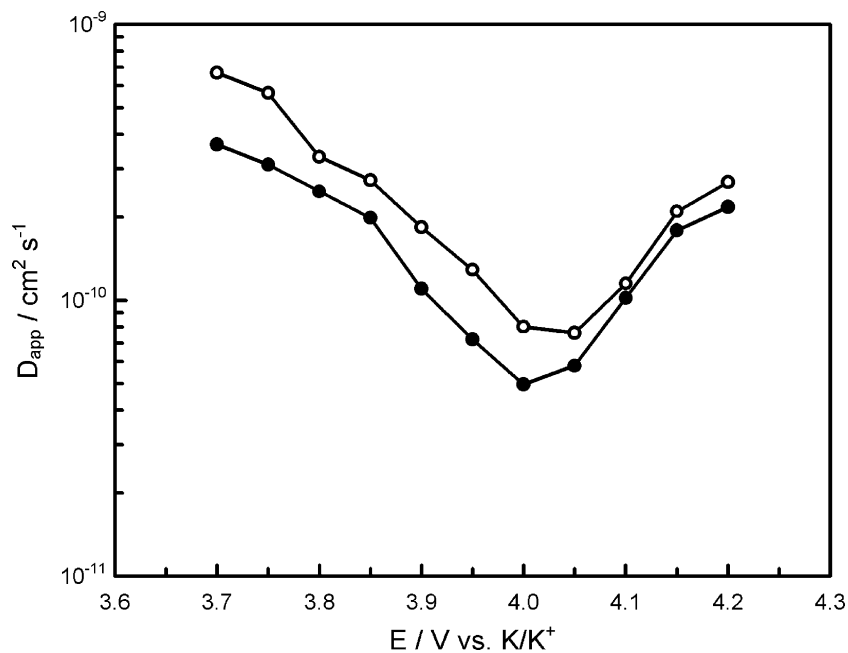


Fig. 6. Dependence of the chemical diffusion coefficient of K^+ on the applied potential for the insertion (●) and extraction (○).

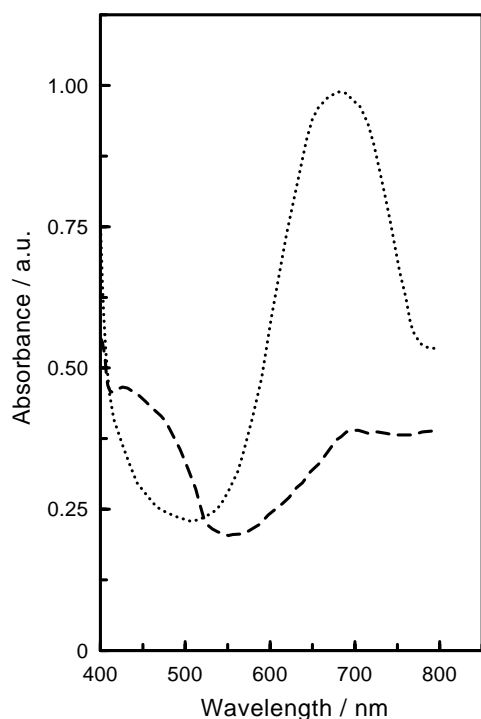


Fig. 7. Spectral change of PB cathode accompanying charging (dashed line) and discharging (interrupted line) of the potassium secondary cell.

the result of an electrochemical redox system. The distinction in the system under investigation can be recognized from the absorption maximum appearing at about 690 nm for PB and that appears for BG at 420 nm [6–8]. Fig. 7 displays typical absorption spectra of the cathode materials at the charged and discharged states obtained from the second charge/discharge cycle. These results provide another evidence for the battery performance of the potassium secondary cell in accordance with the PB redox system. This also suggests that the battery performance is accompanied by only the second redox couple of PB occurring at 0.86 V (not the first couple occurring at 0.18 V), as absorption spectrum of PW displays no active peak in the visible region [6–8].

The present preliminary report demonstrated possibility of the preparation of potassium secondary batteries with valuable advantages. Although, specific capacity of PB for K intercalation/deintercalation is low, however, its theoretical capacity can be achieved approximately. On the other hand, if we design a cell using potassium-free PB, it is possible to gain a $4K^+$ insertion/extraction according to reaction (4), which is accompanied by a significantly higher specific capacity. However, further investigations may lead to better cathode materials with higher specific capacity. In spite of this disadvantage, PB and its analogues are excellent materials for the preparation of cathodes. For example, a common structure of lithium battery cathodes is Si/Ti/Pt/CM (Si is the substrate, Ti is deposited for better adhesion of Si and Pt, Pt is the current collector, and CM is the cathode

material deposited by physical procedures). According to the approach recently proposed [34], highly stable films of PB and its analogues can be easily deposited onto Si substrate.

4. Conclusion

PB is an excellent material for intercalation/deintercalation purpose, due to its excellent ion-exchange properties and cyclability. Unfortunately, it cannot be used as cathode of lithium secondary batteries, as Li intercalation/deintercalation into/from PB film leads to the film destruction. Alternatively, it was demonstrated that such excellent intercalating material could be used to design potassium secondary battery. The potassium secondary battery proposed has some valuable advantages, such as higher cyclability, lower cost, simplicity of fabrication.

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