

Short communication

Fabrication of all-solid-state thin-film secondary cells using hexacyanometallate-based electrode materials

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Abstract

All-solid-state thin-film secondary cells were prepared using transition metal hexacyanometallates as anode and cathode materials. Two different approaches were employed to prepare highly stable films of the electroactive materials viz. using aluminum substrate as current collector and deposition under centrifugal forces. At the first stage, the cell design was examined for a well-known case, Prussian blue (PB) secondary cell. The experimental results were indicative of the fact that the cell properties such as its charge/discharge behavior, specific capacity, cyclability, and coulombic efficiency are significantly improved. At the second state, the cell design proposed was successfully used to fabricate a high-voltage secondary cell based on chromium hexacyanochromate (CrHCC) anode and Prussian blue (PB) cathode. Then, eight unit cells were connected in series to prepare a rechargeable battery with an operating voltage of ca. 20 V. Thus, the results are of interest for the preparation of microbatteries with specified properties.

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1. Introduction

Development of all-solid-state secondary cells is of great interest to prepare power sources for high-tech devices due to their decreasing size. Design of this type of rechargeable batteries is mainly related to the field of solid-state electrochemistry. Various reversible electrochemical redox systems involving insertion/extraction of counter ions have been introduced as half-cells to fabricate this type of secondary cells. An important redox system in solid-state electrochemistry is insertion/extraction of counter ions into/from Prussian blue (PB) and its analogues. PB and its analogues are excellent candidates for the preparation of all-solid-state secondary cells due to their desirable advantages.

There has been a considerable attention to fabrication of all-solid-state secondary cells using PB and its analogues as electrode materials [1–12]. Of course, the main investigations have been related to PB batteries. In this type of secondary cells, both anode and cathode are prepared from PB, and could be considered as the best example of hexacyanoferrate-based secondary cells. It is due to the fact that two redox systems of PB viz. Prussian white (PW)/Prussian blue occurring at 0.18 V versus SCE and

Prussian blue/Berlin green (BG) occurring at 0.86 V versus SCE are the least and the most positive potentials among different redox systems of transition metal hexacyanoferrates, respectively. The PW/PB and PB/BG redox systems have been well studied in the electrochemical literature, and it is not necessary to be described in detail here.

This type of redox batteries has excellent cyclability for battery performance due to electrochemical stability of PB and its analogues, but they suffer from low-voltage of the cell, which is an important problem for the practical applications. Indeed, an anode material with a sufficiently negative potential and a cathode material with sufficiently positive potential is needed to fabricate a high-voltage cell. Unfortunately, this was the main disadvantage and obstacle for practical application of hexacyanoferrate-based secondary cells, as the redox systems of all transition metal hexacyanoferrates are in the same potential range and the difference of two redox potentials in this family is always lower than 1 V. It is obvious that this cell voltage is not of interest for the practical applications. Fortunately, due to recent reports introducing transition metal hexacyanochromates as excellent anode materials with redox systems proving negative potentials about -1.5 V versus SCE [13,14], a new opportunity was made to this type of secondary cells. However, further developments are needed to gain practical applications of this type of secondary cells. For example, the cell

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design used in preliminary (fundamental) investigations of this type of secondary cells is not suitable for the practical applications.

2. Experimental

2.1. Electrode preparation

All of electrodes were fabricated by electrodeposition of the active materials onto aluminum substrate surfaces. In a series of papers, it has been shown that aluminum can act as an excellent substrate electrode for the deposition of a variety of electroactive materials [15–19]. The main advantage for this purpose is enhanced stability of the electroactive films deposited, which can be attributed to the formation of a passive aluminum oxide on the substrate surface during the formation of first layers of the depositing materials. Incorporating of the electroactive materials into such thin passive layer significantly increases the film stability. Interestingly, superior properties of aluminum as a substrate electrode for the deposition of thin-films of transition metal hexacyanoferrates have also been reported [18,19].

A small sheet of aluminum with a geometrical area of 0.2 cm^2 was used as the substrate electrode. The substrate surface was polished before the deposition process. Thin-film of PB was deposited galvanostatically onto the substrate surface from a solution of 10 mM FeCl_3 and $10\text{ mM K}_3\text{Fe}(\text{CN})_6$ in 0.1 M KCl supporting electrolyte by applying a current density of 20 mA/cm^2 . The electrolyte solution was buffered with a phosphate buffer to achieve pH of 4.0. The amount of the electroactive deposited is controlled by the charge passed through the cell. The thickness of the electroactive film was about $1.0\text{ }\mu\text{m}$ for the present study. The chromium hexacyanochromate (CrHCC) was deposited on the substrate with a similar procedure, but from a solution containing 10 mM CrCl_3 and $10\text{ mM K}_3\text{Cr}(\text{CN})_6$ in the same supporting electrolyte.

It should be taken into account that the electroactive material contains significant numbers of hydration water molecules. For example, it is known that PB has about 14 water molecules. The role and importance of the number of such water molecules in the compound on its electrochemical behavior has been extensively studied in the literature for PB and its analogues [20–23]. In the absence of any hydration water in a solid-state cell, electrochemical activity of such compounds is very weak. In fact, it is very difficult to investigate totally free-water PB film, as the electroactive material is significantly subject of hydration even upon air-drying and under solvent-free conditions [24].

As a covalently attachment of the electroactive material to the current collector is needed to achieve a good rechargeability of the secondary cell prepared, the deposition process was performed in the presence of an external mechanical force. It has been described that electrodeposition under centrifugal forces increases the stability of the electroactive

film deposited [25–28], and can be used as an efficient approach to improve physical properties of different electroactive films including transition metal hexacyanoferrates [26]. Interestingly, it has been reported that capacity of the electroactive film electrodeposited in the presence of an applied centrifugal force is higher [25]. To this aim, the deposition process is performed similar to the conventional case, but the electrochemical cell is incorporated into a centrifuge tube. The desirable apparatus for this purpose has been described in the literature [28]. It should also be noted that this approach (electrodeposition under centrifugal forces) is desirable for the present study, as the size of the electrodes are small. However, design of appropriate apparatus to provide a uniform deposition of the electroactive film on large electrodes is difficult. As an alternative method, for the preparation of electrodes (and consequently secondary cells) with large dimensions, the deposition in the presence of an external mechanical force can be performed in the presence of a magnetic field, as it has been reported that deposition of PB in the presence of even a weak magnetic field of ca. 0.5 T is significantly accompanied by higher capacity and enhanced stability of the electroactive film deposited [29].

2.2. Cell design

The thin-film cathode and anode with geometrical areas of 0.2 cm^2 were placed on each other with a separator of Nafion 117 obtained from Aldrich with thickness of $180\text{ }\mu\text{m}$ to fabricate a secondary cell. As each electrode had a thickness of $61\text{ }\mu\text{m}$ ($1\text{ }\mu\text{m}$ thick electroactive material and $60\text{ }\mu\text{m}$ thick Al current collector), the total thickness of the secondary cells was about $300\text{ }\mu\text{m}$. Thus, the secondary cell dimension was $0.2\text{ cm}^2 \times 300\text{ }\mu\text{m}$, which can be classified for design of microbatteries. To gain a complete contact of the electrode surface, careful attention should be paid to avoid any bending of the Al substrate, as it is very thin. In particular, it should be carefully fixed on a hard sheet for experiments under centrifugal forces.

Two different cells were constructed for the present research: (i) a PB secondary cell containing both PB anode and cathode materials and (ii) a hexacyanometallate secondary cell containing CrHCC as anode material and PB as cathode material.

2.3. Electrochemical measurements

The anode/Nafion/cathode structure sandwiched between two aluminum current collectors to set up a solid-state electrochemical cell was investigated as a secondary cell, and characterized using a potentiostat/galvanostat. The experiments were performed using solid-state cells at room temperature. 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 [30–32].

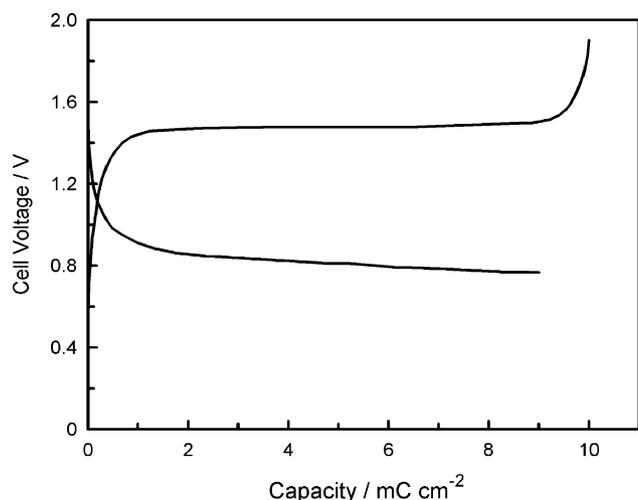


Fig. 1. Charge/discharge profiles of the PB secondary cell obtained at $C/10$. The capacity is reported for $1 \mu\text{m}$ thick electrode.

3. Results and discussion

3.1. PB secondary cell

Fig. 1 shows typical charge/discharge characteristics of the PB secondary cell. The results indicate a well-defined charge/discharge behavior for the secondary cell. It has been reported that charge/discharge behavior of PB secondary cells and generally hexacyanoferrate-based secondary cells [11,12] is accompanied by an increase in terminal voltage with continuous cycling (particularly for low charging rates), which can be attributed to the fact that the discharge products are resistive and tend to be cumulative with cycling. However, this failure is absent for the thin-film secondary cell under investigation. Indeed, generation of cumulative discharge products in the composite-based secondary cells is due to a tend to destroy the paste homogeneity during electrochemical cycling, whereas this is inappropriate for the film electrodes where the electrode is just prepared from the electroactive material.

Interestingly, the PB secondary cell provides a significantly high-voltage in comparison with those reported in the literature. Cyclic voltammetric measurements of PB secondary cells have shown that difference of two redox peaks of a solid-state PB cell is 1.36 V [6]. However, appearance of a weak peak between these two redox peaks depending on the contact of the electroactive film with the substrate electrode hinders reach of this potential. Of course, this peak would be almost negligible if the electrical contact was fairly good. As seen, such failure is absent for the all-solid-state secondary cell fabricated, as the cell has a significantly high-voltage.

The PB secondary cell fabricated has a higher capacity in comparison with those reported in the literature. This suggests that the insertion/extraction of potassium ions into/from the PB film is more successful in comparison

with composite-based PB electrode. According to the results reported in Fig. 1, the PB secondary cell prepared with the design proposed here achieves more than 60% of its theoretical capacity, whereas, the other types of PB secondary cells rarely achieve 50% of the theoretical capacity. The theoretical capacity of the cell fabricated is about $16.5 \text{ mC/cm}^2 \mu\text{m}$ corresponding to the electroactive material loading of about $1.7 \times 10^{-7} \text{ mol cm}^{-2}$. Upon more charging, an increase in the cell voltage appears, which is due to higher redox states of PB. At such high potentials, the oxidation/reduction process is irreversible [33], which is unfavorable for battery performance.

One of the main advantages of PB as a promising electrode material for the fabrication of rechargeable batteries is the excellent reversibility of its electrochemical redox. It has been reported that PB can participate in insertion/extraction of potassium ions for 10^7 reversible electrochemical cycles [30]. However, there is no report on such superior behavior of PB as an electrode material for the preparation of secondary cells, and the available works have just reported ordinary cyclability, up to 100 reversible cycles. Indeed, such excellent cyclability of PB has been obtained for a PB film deposited onto an ITO substrate surface [30], and cannot be expected for a composite-based PB electrode.

The results presented in Fig. 2 indicate that excellent cyclability of PB for a secondary cell can be achieved by using the design of the all-solid-state secondary cell proposed here. In addition to the film stability, the approaches employed for the preparation of thin-films electrodes were strongly efficient. In fact, the aluminum electrode can act as an excellent substrate, as well as ITO, to deposit highly stable films. Moreover, the mechanical force induced to the deposition process significantly enhanced the film stability. The influences of such approaches to deposit highly stable films have been previously described in detail [27].

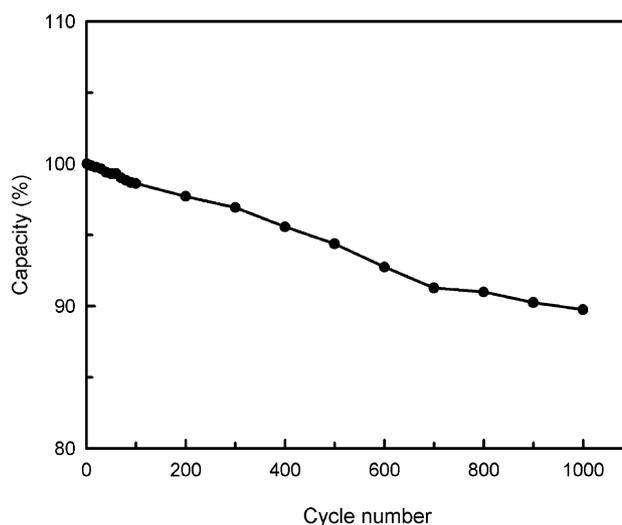


Fig. 2. Cyclability of the PB secondary cell investigated by charging/discharging at rate of $C/10$. This is comparative study of the cell in the course of cycling, as presented the percent of the cell capacity (in $\text{mC/cm}^2 \mu\text{m}$) as function of cycle number.

The investigations were performed with a typical rate of $C/10$, which is an acceptable rate for such secondary cells. The PB secondary cell had a good rate capability, and could be investigated even with faster rates. In fact, weak rate capability of electrode materials is due to slow diffusion of counter ion for participating in the insertion/extraction processes. However, diffusion coefficient of K^+ for insertion/extraction into from PB is sufficiently high. For example, diffusion coefficient estimated for a similar PB film synthesized in our laboratory [34], the diffusion coefficient was comparable (and even better) with an excellent case of Li^+ diffusion for lithium secondary batteries [35]. The results obtained from experimental measurements showed that coulombic efficiency of the PB secondary cell approaches 100% for a fast charging/discharge rate of ca. $C/2$ during 10 cycles. The coulombic efficiency of the PB secondary cell investigated with $C/10$ achieved 100% after only five cycles, which is an excellent behavior for this type of secondary cells.

It is known that absorption spectroscopy is an excellent method for the investigation of oxidized and reduced states of transition metal hexacyanoferrates appearing as 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 [30–32]. Fig. 3 displays typical absorption spectra of the cathode material at the charged and discharged states obtained from the second charge/discharge cycle. The results suggest that the electroactive film (PB) transforms to BG after charging

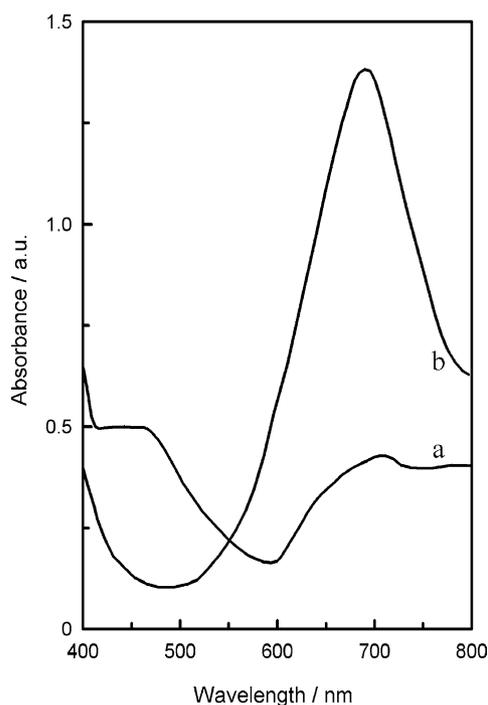


Fig. 3. Spectral change of the PB cathode accompanying charging (a) and discharging (b) of the PB secondary cell.

and turns back to PB after discharging. Similar behavior was also observed for the formation of PW and PB during charge/discharge processes (not shown). Indeed, this provides strong evidence for the fact that the mechanism of the secondary cell fabricated is similar to those reported in the literature, due to two redox systems of PW/PB and PB/BG occurring at anode and cathode, respectively.

3.2. Hexacyanometallate secondary cell

After showing the suitability of the proposed design of all-solid-state thin-film secondary cell for a well-known rechargeable battery viz. PB secondary cell, we attempt to investigate its usefulness for the fabrication of high-voltage secondary cells. As we have recently introduced transition metal hexacyanochromates as excellent anode materials for this type of rechargeable batteries [13,14], a high-voltage cell can be prepared by replacing the anode of the PB secondary cell with CrHCC film electrode. This new secondary cell is called hexacyanometallate secondary cell, as two transition metal hexacyanometallates viz. chromium hexacyanochromate and iron hexacyanoferrate (PB) were used as anode and cathode materials, respectively.

The charge/discharge behavior of the high-voltage secondary cell is presented in Fig. 4. Similar to the PB secondary cell described in the previous section, charge/discharge behavior of the hexacyanometallate cell is improved in comparison with the previous report for the same system but with the composite-based electrode [13,14]. The other improvements reported for the PB secondary cell as the result of this new cell design are also expected for this high-voltage hexacyanometallate-based secondary cell. Our preliminary investigation of the hexacyanometallate secondary cell showed similar improvements.

At this stage, it is of interest to investigate the possibility of this high-voltage cell for the fabrication of high-voltage

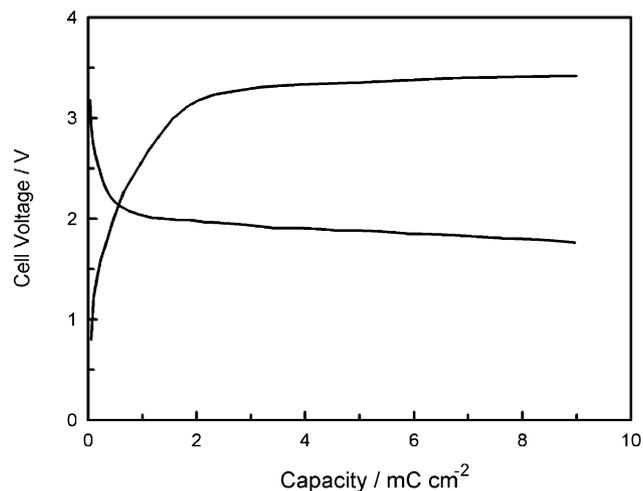


Fig. 4. Charge/discharge characteristics of the hexacyanometallate secondary cell recorded at $C/10$. The capacity is reported for $1 \mu\text{m}$ thick electrode.

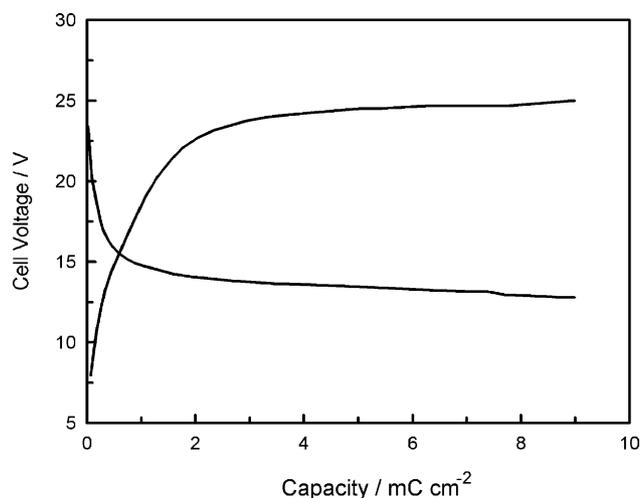


Fig. 5. Charge/discharge characteristics of the rechargeable battery prepared from serial connection of eight unit cells of the hexacyanometallate secondary cell. Charge/discharge rate $C/10$. The capacity was normalized for $1 \mu\text{m}$ thick electrode.

batteries to gain practical performances. To this aim, eight hexacyanometallate secondary cells were connected in series. By this action, the operating voltage can be increased to reach the values required for various technological applications. As illustrated in Fig. 5, the charge/discharge behavior of the rechargeable battery prepared by serial connection of eight unit cells is as well as that of the single cell presented in Fig. 4. In other words, the secondary cell designed exhibits an acceptable battery performance for the variety of eight unit cells.

3.3. The cell dimension and microbattery technology

Due to preliminary aim of the present report, the cell design was similar to classic structures (e.g., using Nafion membrane). Consequently, the cell had a dimension of $0.2 \text{ cm}^2 \times 300 \mu\text{m}$. However, it should be taken into account that the aluminum foil employed had a thickness of $60 \mu\text{m}$, whereas aluminum foils as thin as $6 \mu\text{m}$ are available in the market. On the other hand, a thinner electroactive film can be deposited onto the substrate surface, as modified electrodes with thickness of less than 100 nm of the electroactive films deposited have been widely studied in the electrochemical literature. Nafion is a well-known membrane, particularly, for such systems. However significantly thinner films (e.g., $1 \mu\text{m}$) have been successfully used for the preparation of all-solid-state rechargeable batteries. Due to similarity of such electrochemical systems, it is possible to find new membranes with lesser thickness. Therefore, in a next research, the size of the all-solid-state secondary cell can be reduced about one order of magnitude. In fact, the present report is of interest to develop new type of microbatteries.

4. Conclusion

Fabrication of all-solid-state secondary cell using thin-films of transition metal hexacyanometallates was described. Two different approaches were also employed to improve battery performance of the secondary cells fabricated. Comparison of the results obtained from the secondary cells fabricated in this research and those reported in the literature shows that better battery performance can be achieved by fabricating the cell in accordance with the procedure described here. Due to the improvements reported, hexacyanometallate-based secondary cells can be investigated as promising power sources. They have many advantages for the preparation of microbatteries.

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