

Short communication

A high-voltage solid-state secondary cell based on chromium hexacyanometallates

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Abstract

A solid-state secondary cell was fabricated using two different transition metal hexacyanometallates as anode and cathode materials. To reach a high-voltage cell, a hexacyanometallate with less negative redox potential, chromium hexacyanochromate (CrHCC), was employed as the active material of the anode and a hexacyanometallate with high positive redox potential, chromium hexacyanoferrate (CrHCF) was employed as the active material of the cathode. Consequently, a secondary cell with relatively high voltage of about 1.5 V was obtained, which is relatively high for this type of batteries. The preliminary studies of the battery performance were carried out based on a simply designed cell. The results indicate that the idea for the fabrication of this type of secondary cells is of interest and further investigations (improving the battery properties) can lead to reach an acceptable situation for the practical performances.

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1. Introduction

Electrochemistry of transition metal hexacyanometallates is well known in both aqueous and solid-state media. It is due to special and interesting properties of these inorganic compounds. Preparation and electrochemical studies of thin films of hexacyanometallates on electrode surfaces are one of the most active subjects of research in modern electrochemistry. They have been successfully used for various applications. A comprehensive list of different hexacyanometallates utilized in solid-state electrochemistry can be found in [1]. However, the most of these studies are related to Prussian blue (PB) (iron hexacyanoferrate) and its analogues and less attention has been made to other hexacyanometallates.

Neff have first reported that Prussian blue (PB) and its analogues could be used as electrode materials for battery performances [2]. Although, PB analogues are acceptable candidates to be used as electrode materials for battery performance, there are few reports on this subject in the literature [3–8]. Development of this type of secondary batteries has great interest due to many advantages of hexacyanoferrate-based batteries. Indeed, hexacyanoferrates

are very promising materials to be used as electrode materials for battery applications from commercial point of view. Even, they have been used as cathode materials for lithium batteries in an aprotic electrolyte solution [4]. PB and its analogues are inexpensive materials and have non-toxic nature. On the contrary of cyanide compounds, hexacyanoferrates are not hazardous compounds for human health and even they have medical (pharmaceutical) application. Moreover, PB and its analogues are well-known compounds, which it is very useful for their preparation and fabrication procedure of commercial cells. The main disadvantage of this type of secondary cells, which made them unsuitable for commercial performance, is low cell voltage, as the redox potential of PB analogues are at the same range. The practical voltage of hexacyanoferrate-based secondary cells is usually lower than 1.0 V.

On the other hand, all of these studies are related to hexacyanoferrates, whereas electrochemical behaviors of other hexacyanometallates are similar to hexacyanoferrates. Indeed, they can be used as well as hexacyanoferrates for various applications. It is accompanied with the fact that different properties of various materials are very useful and interesting for the practical performances, as they can be utilized for various purposes. In the present paper, we would like to introduce a secondary cell with two different hexacyanometallates as the electrode materials.

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Due to the existence of different hexacyanometallates (as a big group of inorganic materials), various secondary cells can be prepared by similar method with different specification, e.g. cell voltage, rechargeability, etc. In addition to the possibility of such materials for the construction of secondary cells, the present research shows that relatively high-voltage cells could be fabricated based on hexacyanometallates. It is described that a secondary cell can be achieved by applying chromium hexacyanometallates with cell voltage of about 1.5 V, which is relatively high voltage for such types of batteries. Reaching such high-voltage performances make this type of secondary cells suitable for technological application.

2. Experimental

The electrochemical measurements were carried out using a homemade potentiostat connected to a computer running CorrView software. All chemical reagents were of analytical grade. Electrode materials were synthesized according to the available methods in the inorganic literature [9,10]. The electrodes (anode and cathode) were prepared by mixing 0.25 g powder of the transition metal hexacyanometallate, chromium hexacyanochromate (CrHCC) or chromium hexacyanoferrate (CrHCF) with 2.0 g powder of graphite. Then, a paste form was obtained by adding a few drops of diluted HCl (0.1 M). In addition, as the proton transfer is strongly involved in the cell processes, the acidic medium is very useful to avoid any local pH changes.

A schematic of the designed cell is illustrated in Fig. 1. A Nafion layer was conditioned between two electrodes to separate two half-cell reactions to avoid any material

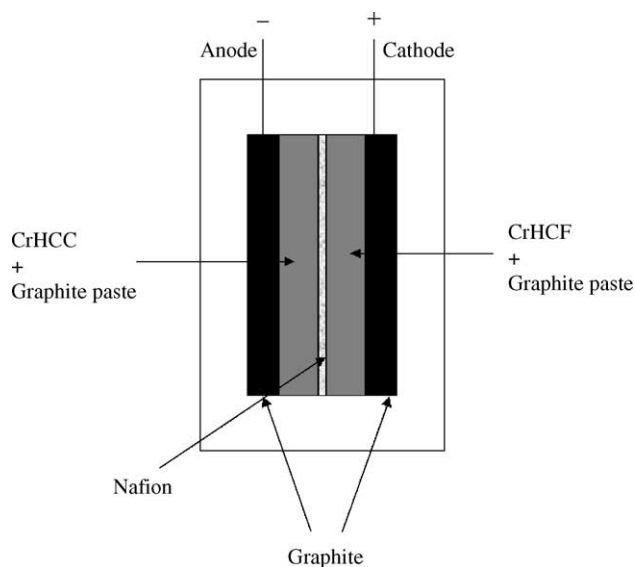


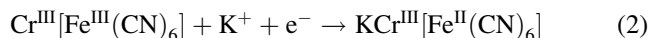
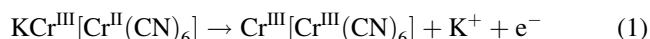
Fig. 1. Schematic of the designed cell for the chromium hexacyanometallates-based secondary battery.

exchange. Thus, this ion-exchange membrane just allows proton-exchange between two electrodes to maintain the charge balance. It means that potassium ions are the only species involved in the intercalating and deintercalating processes.

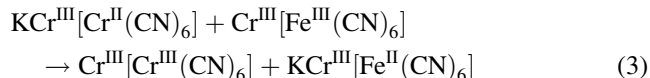
3. Results and discussion

To investigate redox systems of chromium hexacyanometallates employed for the battery fabrication, voltammetric studies of the materials were performed in a conventional electrochemical cell. To this aim, electrochemical behaviors of thin films of the hexacyanometallates were studied in an aqueous medium. Fig. 2 shows cyclic voltammetric behaviors of solid CrHCC and CrHCF films immobilized on a platinum electrode surfaces. As seen, a reversible redox peak is observed for each hexacyanometallate. According to the literature [11], the formal potentials of the CrHCC and CrHCF solid films are equal to -0.860 and 1.005 V versus SHE, respectively. The results presented in Fig. 2 for typical cyclic voltammetric characteristics of the hexacyanometallates are in agreement of such values and the literature reporting electrochemical behavior of the corresponding hexacyanometallates deposited on electrode surfaces [12–14]. According to the difference in the redox potentials of two materials, they can be used in two half-cells to prepare a high-voltage cell.

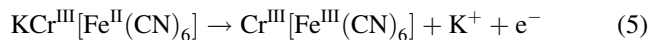
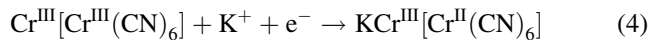
Thus, the designed cell works as the result of combination of these two redox systems. By writing the redox reactions of both systems during charge and discharge processes, the reversible overall reaction of the cell can be obtained. During the charging process, the reactions of the anodic and cathodic half-cells are as follows:



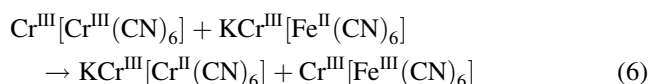
Thus, the overall reaction of the charging process is



Similar reactions can be written for the discharge process:



And the overall reaction of the discharge process is:



As can be seen, Eqs. (3) and (6) are the same reaction, but on reverse direction. As the overall reaction of the cell (including both half-cells) during the charging and discharging are Eqs. (3) and (6), it can be concluded that it is a

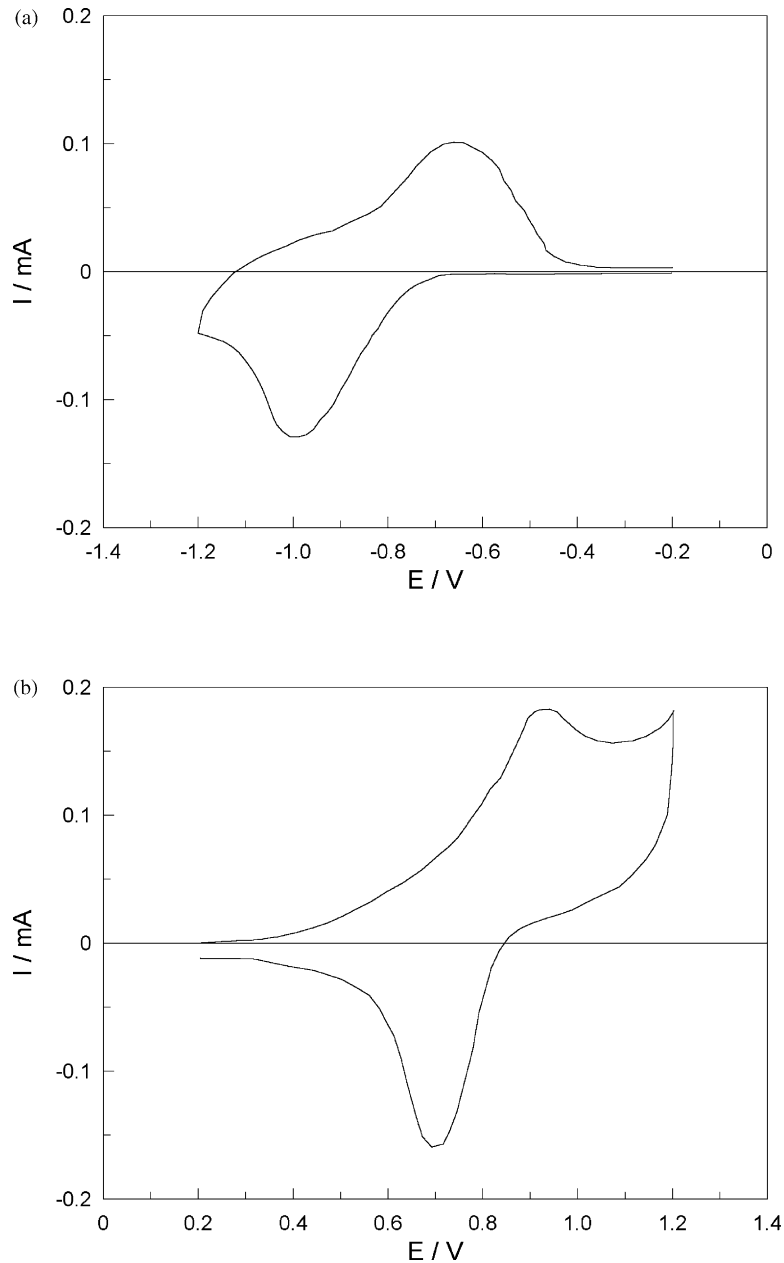


Fig. 2. Cyclic voltammetric behavior of chromium hexacyanochromate (CrHCC) (a) and chromium hexacyanoferrate (CrHCF) (b), immobilized on the surface of a platinum electrode recorded at supporting electrolyte of 0.1 M KCl with scan rate 100 mV s⁻¹.

reversible reaction which occurs all over again during the charge and discharge processes.

According to [11], the formal potentials of chromium hexacyanochromate (CrHCC) and chromium hexacyanoferrate (CrHCF) are -0.562 and 1.005 V versus SHE, respectively. Consequently, the theoretical cell voltage can be estimated to be 1.567 V. However, it is significantly different from the real cell voltage, as the formal potentials are related to counter ion of potassium in interaction with the hexacyanometallate lattice. Whereas, the protons are allowed to transfer between two half-cells to maintain the charge balance, as Nafion was applied as the cell separator.

The equivalent weight of the materials used for the anode and cathode were applied to calculate the theoretical coulombic capacity of the cell [15]. According to molecular weight of the hexacyanometallates and the applied weight of 0.5 g for the fabrication of anode and cathode (0.25 g CrHCF and 0.25 g FeHCC), the rate C (Q_{the}/t) for the cell can be obtained 0.089 (or 0.089 A) for the charging period of 30 min, as the estimated charge was 160.77 A s.

Fig. 3 shows charge/discharge behavior of the secondary cell. It is a typical curve obtained by applying charge and discharge rates of $C/6$ and $C/9$ (curves indicated by open-circles), respectively. As seen, a flat profile is observed at 0.8 V for the discharge, and at 3.5 V for the charge. Indeed,

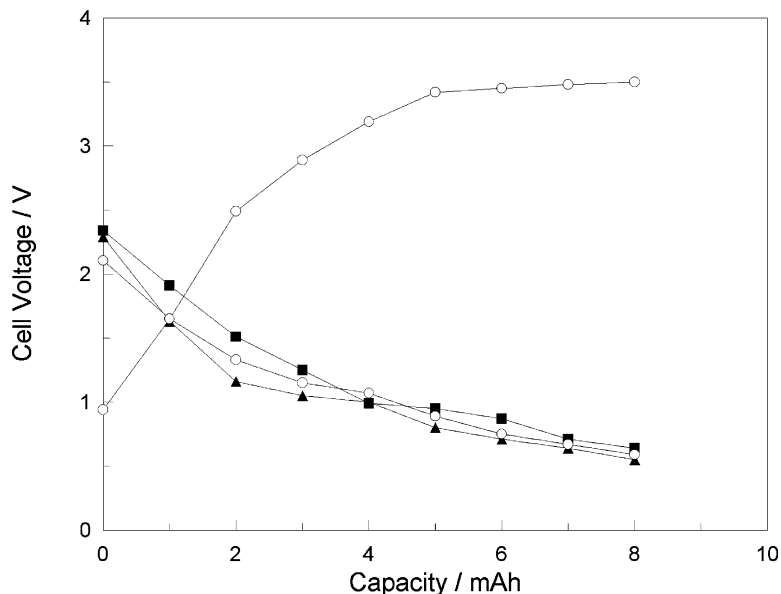


Fig. 3. Typical charge/discharge curve of the secondary cell (the curve presented by symbol ○) by applying typical charge rate of $C/6$ and discharge rate of $C/9$. And the discharge curves obtained at different discharge rate: $C/7$ (▲), $C/9$ (○) and $C/11$ (■).

the cell provides a relatively high voltage, which is very desirable. The output voltage is significantly higher than voltage of similar hexacyanoferrate-based batteries. This phenomenon is related to high difference between the electrochemical redox systems of the electrodes (materials used for the anode and cathode). It can be ascribed to the fact that the redox reaction of the cathodic half-cell occurs at relatively low potentials and the redox reaction of the anodic half-cell occurs at relatively high potentials.

There is a significant difference in the cell voltage at the end of charging in comparison with the beginning of discharging. It is an extraordinary behavior, which is not similar to usual behavior of secondary batteries. As described by

Jayalakshmi and Scholz [7], it might be ascribed to the lack of diffusion polarization at the beginning of the discharging, which allows irreversible interfering redox reactions. Whereas, this effect is not observed at charging, where the cell voltage slowly decreases. It is due to the reversible properties of hexacyanometallates, which is accompanied by diffusion polarization as the result of slow potassium ion diffusion into the hexacyanoferrate lattice.

The effect of the discharge rate on the discharge characteristics is also illustrated in Fig. 3 (three lower curves). This shows the evolution of the cell voltage as a function of the discharge capacity at different discharge rates ($C/7$, $C/9$ and $C/11$). As expected, the discharge voltage is lesser for

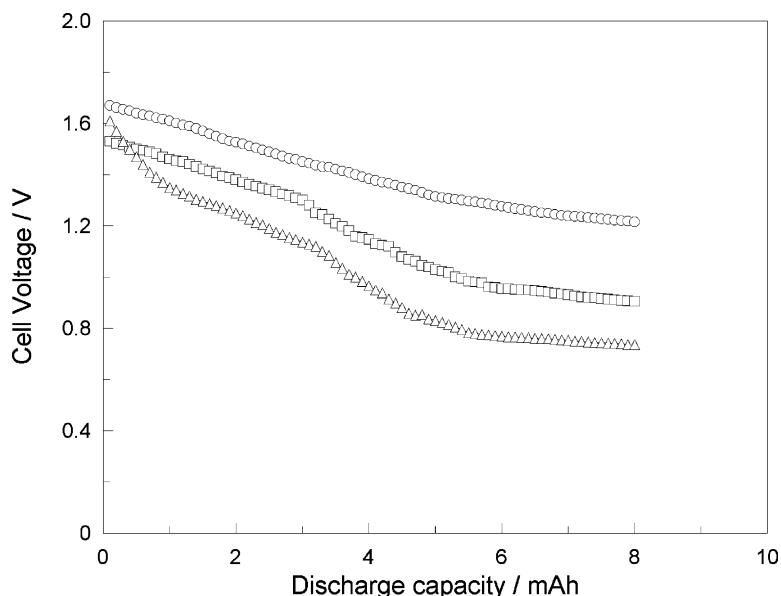


Fig. 4. Discharge characteristics of the secondary cell at different cycles: 1st cycle (○), 5th cycle (□) and 20th cycle (▲).

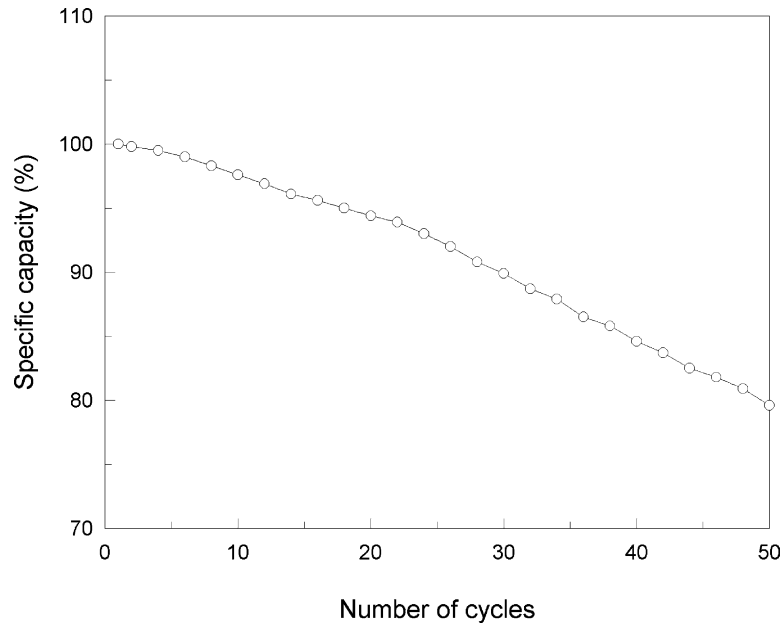


Fig. 5. Cycling lifetime characteristics of the secondary cell.

faster discharging rates and higher voltages can be obtained at the discharge curve by applying lower discharge rate. It comes from the fact that discharge products are resistive materials, and they should be reproduced homogeneously in a slow process. Otherwise, local reproduce of this materials as the result of sudden processes is possible during fast charging [2]. It is noticeable that this effect is complex and the mentioned dependence will not be simply fulfilled for all discharging rates.

To investigate the secondary cell at a condition close to equilibrium, discharge curves were obtained by applying a constant low current of 5 mA during a slow discharging

process. Discharge curves of the secondary cell are presented in Fig. 4. Difference of the curves at various cycles is observable. Moreover, discharging occurs at just a single plateau. It is on the contrary of PB-based batteries [8], which are accompanied by the appearance two plateau regions resulting from two-step redox system of PB. Of course, a similar behavior is observable for the appearance of the second plateau. Although, this behavior is weak, but it is related to the electrochemical oxidation of chromium hexacyanoferrate. It has been reported that oxidation of chromium hexacyanoferrate occurs at two steps, however, this behavior is not strong like PB [12,13].

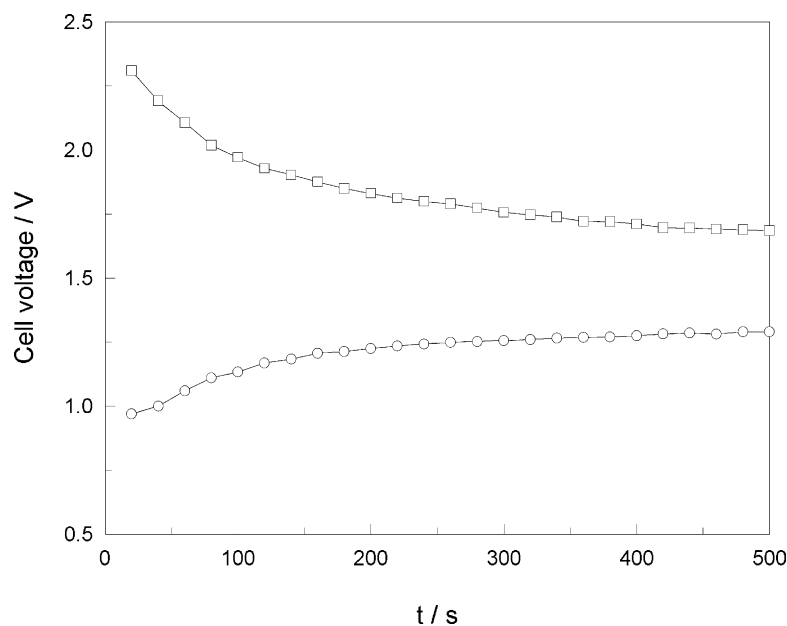


Fig. 6. Open-circuit voltage recovery (□) and voltage decay (○) of the secondary cell.

To investigate the battery performance, capacity loss of the secondary cell was investigated during cycling. To characterize the effect on cycle life in the discharged state, the secondary cell was cycled continuously more than 50 times at the $C/2$ rate. Fig. 5 indicates the variation of capacity as a function of cycle number. This shows that the cell is stable and has an acceptable cycleability. As seen, only a 20% loss in capacity of the secondary cell is observed. In addition, open-circuit studies were done for both recovery and decay behaviors of the secondary cell (Fig. 6). The results are similar to typical open-circuit behavior of batteries. It is thought that the cell reaction during recovery and decay transients are similar to those described in [8] for different hexacyanoferrate-based secondary cells.

It is worth nothing that the obtained results may not be very interesting from battery technological point of view at this stage, but it is of interest from a scientific point of view. It is due to the fact that real capacity of the secondary cell proposed is significantly lower than theoretical. However, scientific aspects of the study in a fundamental research are noticeable results. Indeed, the secondary cell fabricated is not suitable for battery applications due to insufficient technological knowledge for design of hexacyanometalate-based batteries. As a few numbers of papers have been published on this type of secondary batteries, it is expected that an optimized design for the cells will be very soon available.

4. Conclusion

A secondary cell was designed based on two novel anode and cathode materials namely chromium hexacyanochromate and chromium hexacyanoferrate, respectively. It is of interest in terms of new materials for the battery

applications. Both the applied materials are novel for this purpose. Indeed, this is the first study dealing with chromium hexacyanoferrate from PB analogues and the application of a transition metal hexacyanomethylate, not grouped in common PB analogues (hexacyanoferrates). In fact, two different chromium hexacyanomethylates were successfully employed for the fabrication of a secondary cell. This work provides strong evidence for usefulness and suitability of various hexacyanomethylates as candidate materials for the electrode materials in battery applications, which may be accompanied by vast range of applications of hexacyanomethylates in both classic and modern electrochemistry, and generally in the science and technology of inorganic materials.

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