

A novel aqueous $\text{Li}_4\text{Fe}(\text{CN})_6$ cathode and hydrophobic ionic liquid electrolyte combined lithium-ion battery

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Abstract

Present study reports an easy and cost-effective method of synthesis of $\text{Li}_4\text{Fe}(\text{CN})_6$ cathode from $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ and LiClO_4 in aqueous medium for its use in lithium-ion battery. The synthesized $\text{Li}_4\text{Fe}(\text{CN})_6$ is characterized by UV-Vis, FTIR and cyclic-voltammetry studies. A special laboratory model lithium-ion battery is designed, where aqueous $\text{Li}_4\text{Fe}(\text{CN})_6$ solution acts as a cathode, metallic lithium as anode and 1 molar solution of LiPF_6 dissolved in water immiscible ionic liquid, 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM- PF_6) as electrolyte. The cell exhibits an open circuit potential of 3.12 volt and a good charge-discharge cycling behaviour. The cell delivered a maximum discharge capacity of 86 mAhg^{-1} (theoretical capacity 112 mAhg^{-1}) at 0.2 C rates with an average discharge potential of 2.1 volts. Although the ionic liquid is a little bit cost intensive, but the easy synthesis methodology with the cheapest raw materials and overall cycling efficiency, makes this technology available as a green economical energy storage device in the current battery industry. Copyright © 2017 VBRI Press.

Keywords: $\text{Li}_4\text{Fe}(\text{CN})_6$ aqueous cathode, cost effective method, hydrophobic ionic liquid electrolyte, charge-discharge, lithium-ion battery.

Introduction

Lithium-ion batteries are an interesting topic today especially in the field of portable energy storage devices. The popularity is arisen due to their best energy-to-weight ratios, greatest electrochemical potential and the highest energy density [1-3].

However, the commercial lithium-ion batteries use LiCoO_2 as the cathode material and thus the existing technology finds limited applications due to less abundant of its one component element cobalt in the earth-crust, which is once again toxic in nature. Therefore, priority is given to search an alternate environmentally benign, cost effective cathode for next generation lithium-ion battery. In the recent years, few compounds such as layered LiMnO_2 [4-8], spinel LiMn_2O_4 [9-12] and environment friendly LiFePO_4 [13-17] have been gained more attention as an alternating cathode material for lithium-ion batteries. However, problems are still remained associated with them because LiMnO_2 and LiMn_2O_4 suffer from slow lithium ion diffusion and large capacity fading upon

cycling [18]. On the other hand, LiFePO_4 has limited applications due to its deprived electronic conductivity, which leads to its poor rate capability [18-22].

In addition to all these problems, the cost of synthesis of all these materials become very high. This high synthesis cost is arisen in account to the cost intensive high temperature calcinations and use of sophisticated inert gas reaction-chamber during material synthesis [7, 9, 10, 23-28].

Taking into account of all these disadvantages, a new type of solid cathode material, $\text{Li}_4\text{Fe}(\text{CN})_6$ has been synthesized for lithium ion battery [29, 30]. In continuation to our previous work [29], we intend to synthesize aqueous $\text{Li}_4\text{Fe}(\text{CN})_6$ possessing high ionic conductivity and use it as liquid cathode in lithium-ion battery. Thus the present study deals with the synthesis of aqueous $\text{Li}_4\text{Fe}(\text{CN})_6$ possessing high ionic conductivity and reversibility using an easy and cost effective route from the cheaper and environment friendly raw materials for its use as cathode in lithium-ion battery [29, 31-33].

Experimental

Materials

$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (BDH, USA, 99%), LiClO_4 (Alfa-Aesar, USA, 99%), LiPF_6 (Sigma-Aldrich, USA, 99.9%) 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) (Sigma-Aldrich, USA, 97%), Li (Sigma-Aldrich, USA, 99.9%) have been used as they are received.

Synthesis of aqueous solution of $\text{Li}_4\text{Fe}(\text{CN})_6$

Aqueous $\text{Li}_4\text{Fe}(\text{CN})_6$ solution was prepared following the same methodology as reported in our previous work [29]. Two concentrated solutions of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (6 g in 25 ml) and LiClO_4 (6.045 g in 15 ml) were mixed and stirred well. A crystalline precipitate of KClO_4 was formed, which was filtered out and the remaining filtrate was cooled down to 10 °C for ten hours for further precipitation. Again solid precipitate of KClO_4 was appeared and filtered. The remaining solution (filtrate) was heated at 60-70 °C in a closed vessel having an outlet tube connected to a vacuum pump to remove more water. When the solution became super saturated, it was again cooled down to 10 °C and kept at this temperature for overnight. A small amount of KClO_4 crystal was reappeared, which was filtered off and the process was repeated to remove KClO_4 completely from the solution. In this way, 96% K^+ ion was replaced by Li^+ ion. The resulted filtrate containing $\text{Li}_4\text{Fe}(\text{CN})_6$ was diluted to 0.1 M and kept ready for further use.

Characterizations

$\text{Li}_4\text{Fe}(\text{CN})_6$ was characterized by using various spectroscopic techniques such as, UV-Visible spectroscopy (OPTIZEN POP) and Fourier Transform Infrared (FTIR, FTIR-8400S, Shimadzu, Japan) spectroscopy. UV-Visible spectrum was recorded with the pre-prepared aqueous $\text{Li}_4\text{Fe}(\text{CN})_6$ solution and the spectrum was compared with the UV-visible spectrum of aqueous $\text{K}_4\text{Fe}(\text{CN})_6$ solution. On the other hand, FTIR spectrum was recorded with the solid $\text{Li}_4\text{Fe}(\text{CN})_6$, which was obtained after dehydration of $\text{Li}_4\text{Fe}(\text{CN})_6$ solution at 90-100 °C under vacuum. The result was compared with FTIR data of solid $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ for further confirmation.

Electrochemical characterization viz. cyclic-voltammogram (CV) and charge-discharge cycling studies were performed to investigate the redox behavior; and its performance as a cathode material in lithium-ion battery. CV was carried out with the aqueous solutions of $\text{Li}_4\text{Fe}(\text{CN})_6$ along with $\text{K}_4\text{Fe}(\text{CN})_6$ solution for comparison. Two platinum electrodes were used as working and counter electrode; and CV was recorded with reference to saturated calomel electrode (SCE) at the scan rate of 10 mVs^{-1} within the potential windows of -0.4 to 0.8 volts. Moreover, a special laboratory model cell was prepared to study the performance of the $\text{Li}_4\text{Fe}(\text{CN})_6$ solution as cathode vs. Li metal anode.

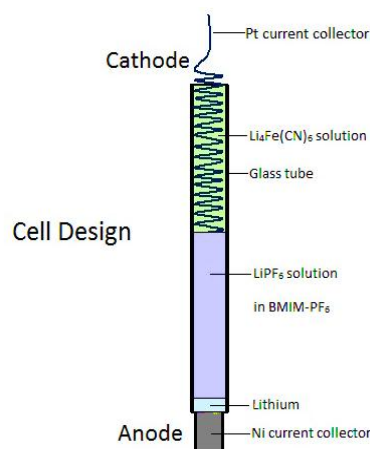


Fig. 1. Schematic diagram of laboratory model cell.

Design of a special laboratory model cell

Laboratory model cell was assembled with a glass tube of 4 mm diameter and 2.5 cm length. Lithium metal pressed on a nickel metal current collector (Fig. 1) was used as anode. Lithium metal remained dipped under the electrolytic solution prepared by dissolving LiPF_6 salt in water immiscible ionic liquid, 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) [34]. Above this solution 1 ml 0.1 M aqueous $\text{Li}_4\text{Fe}(\text{CN})_6$ solution was kept; thus two solutions form a bi-layer. A coiled platinum wire was dipped into the aqueous solution containing $\text{Li}_4\text{Fe}(\text{CN})_6$ as cathode current collector. The lithium metal which was kept inside the ionic liquid does not get any chance to react with water.

Charge-discharge studies were carried out with this laboratory model cell galvanostatically at 0.2 C rates by a galvanostat/potentiostat (model VersaStat TM II, Princeton Applied Research, USA).

Results and discussion

UV-visible spectroscopy

The UV-Visible spectra of aqueous $\text{Li}_4\text{Fe}(\text{CN})_6$ solution (Fig. 2a) exhibits an intense absorption peak at 220 nm, which is attributed to the ferrocyanide group. The similar result was also obtained with the commercial aqueous $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ solution (Fig. 2b), which confirm the presence of ferrocyanide group.

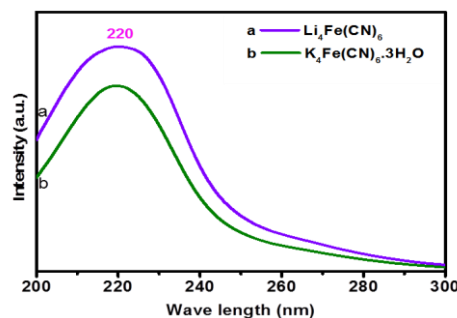


Fig. 2. UV-visible spectra of aqueous (a) $\text{Li}_4\text{Fe}(\text{CN})_6$ and (b) $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ solutions.

Fourier transform infrared (FTIR) spectroscopy

Fig. 3 has illustrated the FTIR spectra of solid $\text{Li}_4\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.

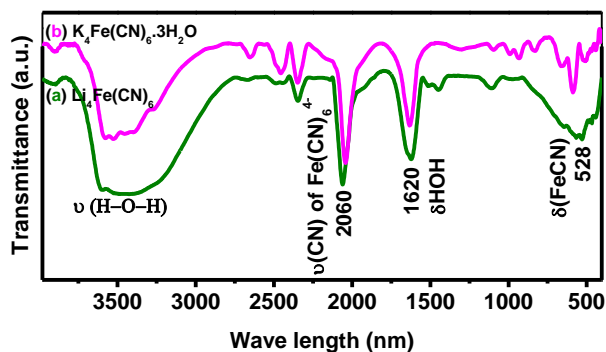


Fig. 3. FTIR spectra of (a) solid $\text{Li}_4\text{Fe}(\text{CN})_6$, and (b) $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.

The presence of ferrocyanide group is confirmed from the stretching frequency of $(\text{C} \equiv \text{N})$ bond in $\text{Fe}(\text{CN})_6^{4-}$ group, which is observed at 2060 cm^{-1} . In addition to that, a broad peak, appeared at 528 cm^{-1} , is due to the bending vibration mode of $(\text{Fe} - \text{C} \equiv \text{N})$ [35-38]. These observations support the presence of ferrocyanide group in $\text{Li}_4\text{Fe}(\text{CN})_6$.

Electrochemical characterization

Fig. 4 demonstrates the cyclic voltammograms of aqueous (a) $\text{Li}_4\text{Fe}(\text{CN})_6$ and (b) $\text{K}_4\text{Fe}(\text{CN})_6$. In the anodic scan, one oxidation peak at 0.295 V vs. SCE and in the reverse scan another reduction peak at 0.121 V vs. SCE are observed for $\text{Li}_4\text{Fe}(\text{CN})_6$ system. In case of $\text{K}_4\text{Fe}(\text{CN})_6$ system, the oxidation and reduction peaks are observed at 0.363 V and 0.071 V vs. SCE, respectively. From the ratio of the peak currents it is clear that both the system are completely reversible, which is the characteristics properties of ferrocyanide group [39]. The reversible behavior in CV is the indication of $\text{Li}_4\text{Fe}(\text{CN})_6$ can act as an electrode material.

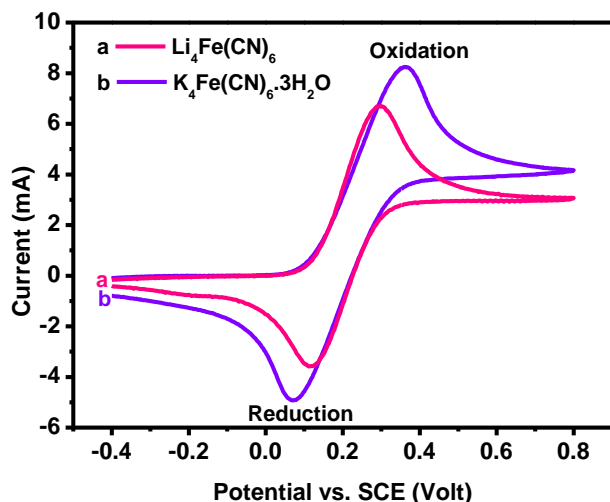


Fig. 4. Cyclic voltammogram of aqueous (a) $\text{Li}_4\text{Fe}(\text{CN})_6$ and (b) $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ vs. saturated calomel electrode (SCE).

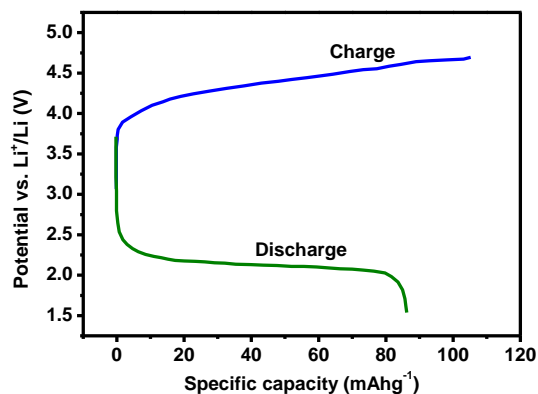


Fig. 5. Charge-discharge behaviour of $\text{Li}_4\text{Fe}(\text{CN})_6$ vs. Li^+/Li at 0.2 C rate.

An open circuit potential of 3.12 V was observed when the cell attained its equilibrium condition. The cell was charge-discharged at 0.2 C rates within the potential windows of 1.5 V to 4.5 V and a discharge capacity of 86 mAhg^{-1} was obtained with an average discharge potential of 2.1 V (Fig. 5). The observed capacity is 77% of its theoretical capacity (112 mAhg^{-1}) and the value remains practically unaltered within 10-15 cycles. $85\text{-}90 \%$ capacity with respect to its theoretical capacity is obtainable at slow charge-discharge rate ($\text{C}/20$). From the charge-discharge profile, it is clear that there is a huge gap between the charging and discharging plateau. This can be explained as follows; since the cathode is an aqueous system, its ionic conductivity is very high, overall charge-discharge process depends on the hydrophobic part, where diffusion process is slow and hence it is the rate determining step. Therefore, the large polarization loss is due to high resistive interface. However, this problem can be overcome by designing a cell, where the path length of the non-aqueous medium could be as shorter as possible.

Conclusion

An aqueous solution of pure $\text{Li}_4\text{Fe}(\text{CN})_6$ was prepared by a very simple and cost-effective method. UV-visible and FTIR spectra have confirmed the formation of pure material without any impurities. Cyclic voltammogram (CV) revealed that the material is highly reversible and suitable for an electrode material in rechargeable battery. The cell, comprised of liquid $\text{Li}_4\text{Fe}(\text{CN})_6$ cathode, a hydrophobic ionic liquid electrolyte prepared by dissolving LiPF_6 in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) and Li metal as anode, exhibited an open circuit potential of 3.12 V . A discharge capacity of 86 mAhg^{-1} (112 mAhg^{-1} theoretical capacity) with an average discharge potential of 2.1 V was obtained, when the cell was cycled within the potential windows of 1.5 to 4.5 V at 0.2 C rates. At last, the synthetic methodology is easy, precursor materials are of low cost and non-toxic, and thus an interesting economical, environment compatible and efficient electrochemical energy storage device has been designed.

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Author's contributions

Conceived the plan: BM, IBM, SG. Performed the experiments: BM. Data analysis: BM, IBM, SG. Wrote the paper: BMD, IBM, SG. Authors have no competing financial interests.

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