Original Research Article

Synthesis, characterization and electrochemical studies on $Li_4Fe(CN)_6$ as cathode material for Li-ion batteries

ABSTRACT

An easy and cost effective method of synthesis of $Li_4Fe(CN)_6$ has been reported. The material, as obtained, has been characterized by UV-VIS, FTIR, powdered XRD and SEM. Cyclic-voltametry and charge-discharge studies were carried out for electrochemical characterization of the synthesized material. A laboratory model Li-ion cell was fabricated using $Li_4Fe(CN)_6$ as cathode, lithium metal as anode and 1 molar $LiClO_4$ solution in ethylene carbonate and dimethyl carbonate (1:1) mixture as electrolyte. The cell shows an open circuit potential of 3.03 volts vs. Li and a discharge capacity of 90 $mAhg^{-1}$ (theoretical capacity, 112 $mAhg^{-1}$) in the first few cycles at 0.15 C rates. The charge-discharge behaviour remains practically unaltered up to 20 cycles. Thus $Li_4Fe(CN)_6$ may be considered as a promising cathode material for Li-ion battery.

Keywords: $Li_4Fe(CN)_6$ cathode; cost effective method; low temperature calcinations; charge-discharge; Li-ion battery.

1. INTRODUCTION

Lithium-ion batteries are one of the most powerful [1], and popular storage systems due to highest energy-to-weight ratios, no memory effect, and slight energy loss when not in use [2]. Beyond consumer electronics, lithium-ion batteries are being used for military, electric vehicles and aerospace

applications because it has the greatest electrochemical potential and provides the largest energy density, 125-150 $Whkg^{-1}$ [1].

Commercial lithium-ion batteries contain $LiCoO_2$ as the cathode material, in which the component element cobalt is very expensive and toxic [3, 4]. As a result large scale applications using this material is limited. Therefore, scientists are looking for new cathode materials, which are less expensive and compatible with the environment [4]. During last decade, a number of new cathode materials were proposed. However, none of them are found suitable for commercial applications due to different critical issues, such as toxicity, higher resistivity, smaller specific capacity, low operating potential, lower cyclibility and large capacity fading upon cycling. Among them layered $LiMnO_2$ and spinel $LiMn_2O_4$ compounds have been drawn more attention as alternative cathode materials for lithium-ion batteries [5-10]. But it has low diffusion co-efficient of lithium-ion and large capacity fading upon cycling.

Recently, lithium iron phosphate ($LiFePO_4$) become an attractive alternating cathode material for rechargeable lithium-ion batteries [11-16], due to low cost starting materials, environment friendly, excellent cycling performances, high theoretical capacity (170 $mAhg^{-1}$), high safety, good operating voltage and high temperature performance [2, 11-14]. Again the main disadvantage associated with this material is its low electronic conductivity and low diffusion coefficient of lithium ions, which lead to its poor rate capability [13, 14]. Some efforts to increase its conductivity have been made after doping with higher valence metal cations, like Ti^{4+}, Ga^{3+}, Zr^{4+}, W^{6+}, V^{3+} etc. and a few fold enhancements in conductivity is reported in the cost of intrinsic capacity [17-20]. It will be interesting to increase the conductivity without losing its capacity and that can be done by synthesizing nano $LiFePO_4$ through different particle size controlled techniques like water-based [21-26], sol-gel [27-30], sonochemical [31], solvothermal [32],**Error! Reference source not found.** ionothermal [33], and in-situ carbon coating via solid-state synthetic method [34]. Most of the reported methods are lengthy and expensive. There are few reports available on the synthesis of nano $LiFePO_4$ [16, 24, 25, 31], over large surface area carbon powder with better performance and cyclibility.

However, it is very much difficult to synthesize pure $LiFePO_4$ in solid state or sol-gel methods because in these methods an inert atmosphere is required during calcinations to protect oxidation of Fe^{2+} to Fe^{3+} [11-20]. Therefore nitrogen or argon gas and an instrumental set up are required to make inert atmosphere which is costly and difficult also.

Here, we report a new cathode material $Li_4Fe(CN)_6$ [35], which is synthesized in a simple route without using inert atmosphere and high temperature calcinations [15-25]. Material retains its discharge capacity close to its theoretical value 112 $mAhg^{-1}$, which is slightly lower than the commercial material [36]. On the other hand, $Li_4Fe(CN)_6$ is soluble in water, and thus it can be used as liquid cathode [37], in aqueous lithium-ion battery.

2. MATERIALS AND METHOD

2.1 Material Synthesis Procedure

Concentrated solutions of $K_4Fe(CN)_6.3H_2O$ (BDH, USA, 99%) (6 g in 25 ml) and $LiClO_4$ (Alfa-Aesar, USA, 99%) (6.045 g in 15 ml) were prepared separately. They were then mixed together at room temperature under constant stirring condition. A white crystalline precipitate of $KClO_4$ was appeared (because the solubility of $KClO_4$ in water is 1.5 g/100 ml at 25 °C [38]. The precipitate was filtered and the filtrate was cooled down to 10 °C and kept overnight. Again a white precipitate of $KClO_4$ was appeared which was collected by filtration and the remaining solution was concentrated by evaporating the water at a temperature of 60-70 °C with the help of vacuum evaporator. Then concentrated solution was cooled down to 10 °C and left for 12 hours. Again a crystalline precipitate of $KClO_4$ was appeared. The precipitate was filtered out and the process was repeated to remove $KClO_4$ completely. The filtrate containing $Li_4Fe(CN)_6$ was then evaporated to dryness and sintered at a temperature of 180 °C. Now the synthesized anhydrous material was cooled down to room temperature and kept in a sealed moisture free bottle for further analysis.

2.2 Thermal Gravimetric Analysis (TGA)

Thermo-gravimetric analysis of the solid material, obtained after dehydration of filtrate containing $Li_4Fe(CN)_6$, was made using a Perkin-Elmer TGA/DTA thermal analyzer in nitrogen atmosphere at a heating rate of 20 °Cmin^{-1} and the graph is shown in Fig. 1.

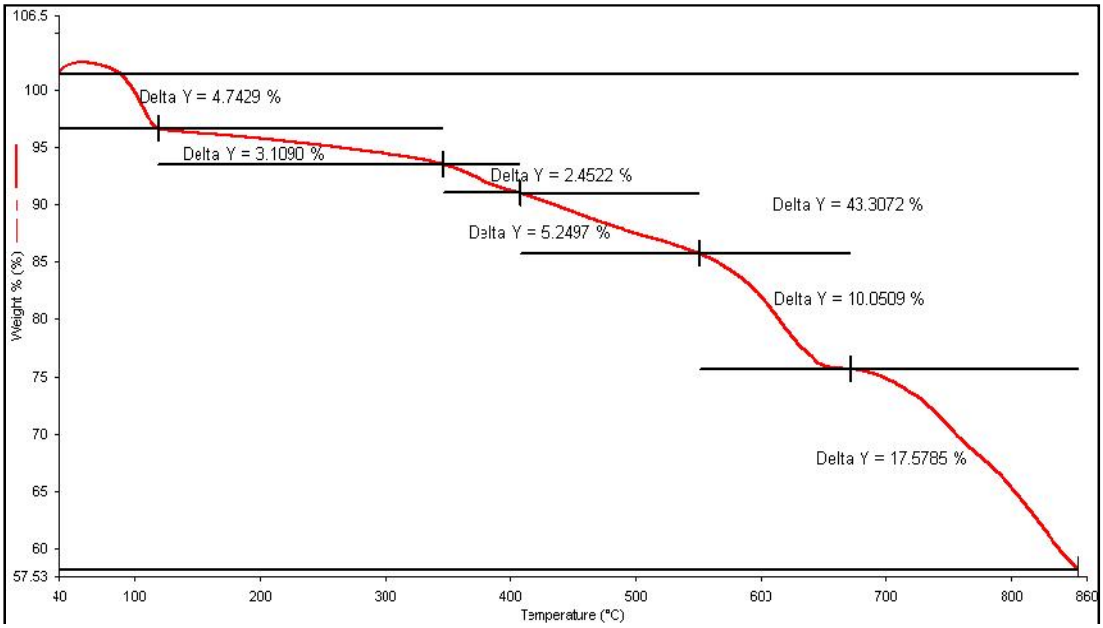

Fig. 1. TGA of solid material obtained after dehydration of filtrate containing $Li_4Fe(CN)_6$.

From the figure, it is seen that 4.7% mass loss occurred due to water loss within 120 °C. Above this temperature mass loss occurred stepwise due to dehydration and decomposition of $Li_4Fe(CN)_6$. Therefore, sintering the material within 180 °C can produce dehydrated material because within this temperature the material does not decompose, but undergoes dehydration only.

2.3 Characterization Part

$Li_4Fe(CN)_6$ was characterized by UV-Visible spectrophotometer (OPTIZEN POP), Fourier Transform Infrared (FTIR, FTIR-8400S, Shimadzu, Japan), Powdered X-ray diffraction (XRD, Ultima III Rigaku Cu Kα, λ=1.5406 Å) and Scanning Electron Microscope (SEM, JEOL, JSM-6360, UK).

Cyclic-voltametry and Charge-discharge studies were carried out by a Galvanostat/Potentiostat (VersaStat™II, Princeton Applied Research). The reversibility and the storage capacity of the synthesized material were studied by cyclic-voltametry and chrono-amperometry studies, respectively after preparing a laboratory model cell. The cathode mixture was prepared by mixing the synthesized material (80 wt %) with carbon conductive additive i.e., carbon black (Alfa Aesar, USA, 99.9%) (8 wt %), graphite powder (Alfa Aesar, USA, 99.99%) (8 wt %) and Polyvinylidene fluoride (Aldrich, USA) (4 wt %) in N-methyl pyrrolidone (Merck, USA, 99.5%) as solvent to make homogeneous slurry [26-34]. This slurry was then spread over a thin aluminum foil so that they are equally distributed. N-methyl pyrrolidone and moisture was removed by heating the foil at 80 °C with the help of a vacuum evaporator. The positive electrode was ready for cell fabrication upon cooling down to room temperature. Li (Aldrich, USA, 99.9%) ribbon pasted on a nickel plate was used as anode. One molar $LiClO_4$ (Alfa Aesar, 99%) solution in equal solvent mixture of Ethylene carbonate (Sigma-Aldrich, USA, 98%) and Dimethyl carbonate (Sigma-Aldrich, USA, 99%) and porous polypropylene (PP) film soaked with this electrolyte, was used as electrolyte and separator, respectively. The cell was assembled inside a glove bag after removing air and moisture by purging argon gas.

3. RESULTS AND DISCUSSION

3.1 UV-Visible spectroscopy

The UV-Visible spectrum of aqueous solution containing $Li_4Fe(CN)_6$ is shown in Fig. 2.

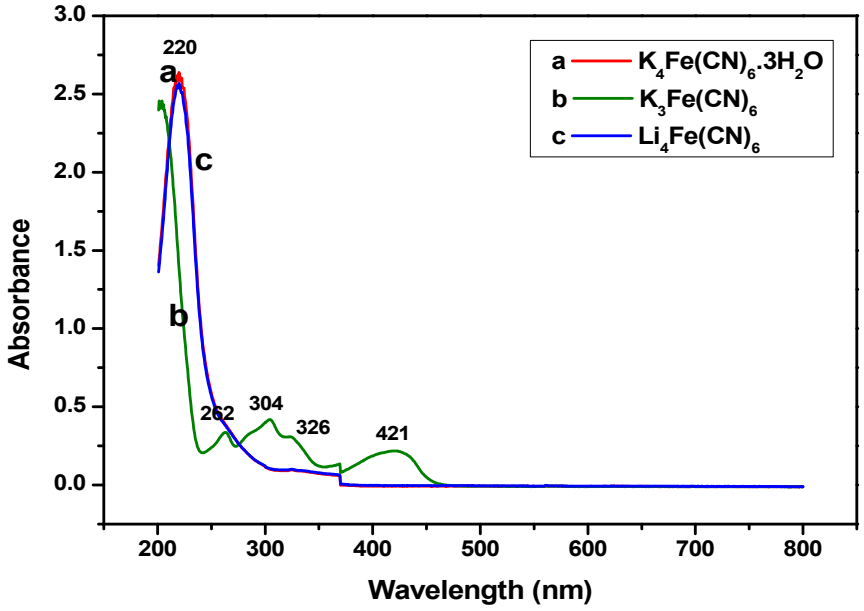

Fig. 2. UV-Visible spectroscopy of $K_4Fe(CN)_6.3H_2O$, $K_3Fe(CN)_6$ and $Li_4Fe(CN)_6$.

From Fig. 2, it is found that an intense absorption peak at 220 nm, attributed to the presence of ferrocyanide group which overlaps with absorption maxima of the commercial $K_4Fe(CN)_6.3H_2O$ crystals. On the other hand, the synthesized materials is free from ferricyanide impurity, as it is confirmed from the UV-Vis data (Fig. 2) of commercial $K_3Fe(CN)_6$ (BDH, USA, 99%) [39, 40].

3.2 Fourier Transform Infrared (FTIR) spectroscopy

The FTIR spectrum of $Li_4Fe(CN)_6$ crystal shown in Fig. 3 shows its characteristic peaks at 2044-2071 cm^{-1}, 552 cm^{-1} and 419 cm^{-1} due to the ν(CN) of $Fe(CN)_6^{4-}$, δ(FeCN) and ν(FeC), respectively, which matches well with the literature data [41-44].

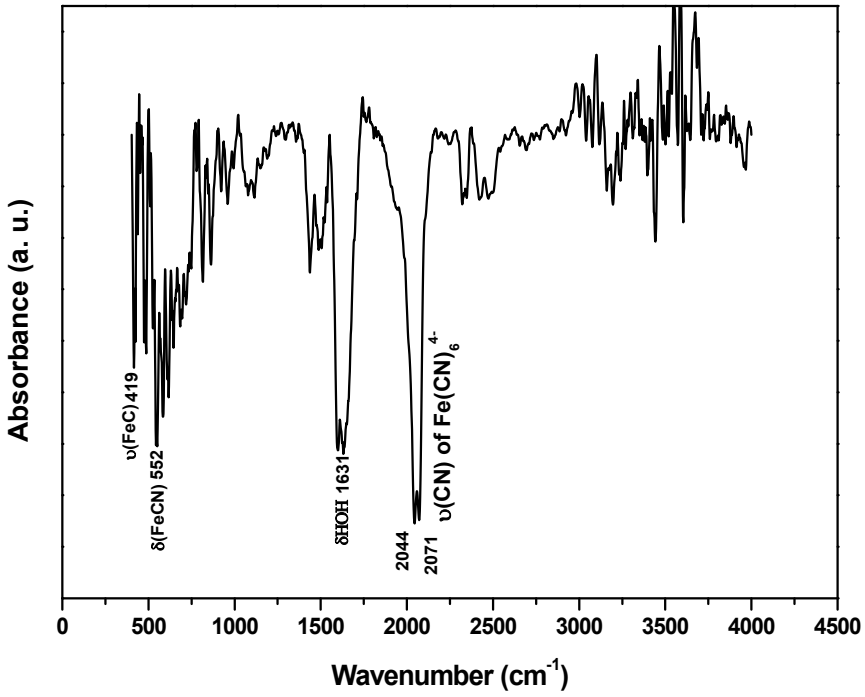

Fig. 3. Fourier Transform Infrared (FTIR) spectroscopy of $Li_4Fe(CN)_6$.

3.3 Powdered X-ray diffraction

The powdered XRD of the synthesized material was recorded in the range of 2θ = 10°-50° with scan rate of 5°min^{-1}. The XRD pattern of the synthesized $Li_4Fe(CN)_6$ is shown on Fig. 4.

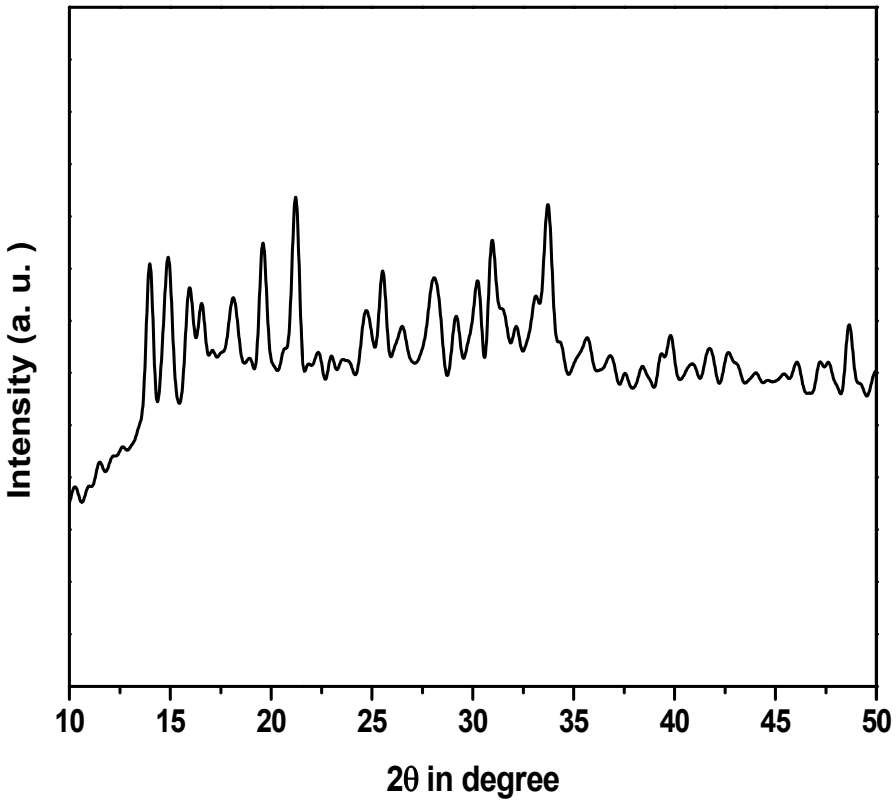

Fig. 4. Powdered X-ray diffraction of $Li_4Fe(CN)_6$.

There is no regular sharp peak in the XRD pattern indicating the formation of both crystalline and amorphous phase. Since there is no literature report available on the XRD pattern of $Li_4Fe(CN)_6$, we are not able to compare with the literature data. Crystal structure shall be determined from the single crystal data, which is under investigation and may be reported later.

3.4 Scanning Electron Microscopy (SEM)

The surface morphology and particle size of the synthesized material were studied from the SEM images, shown in Fig. 5.

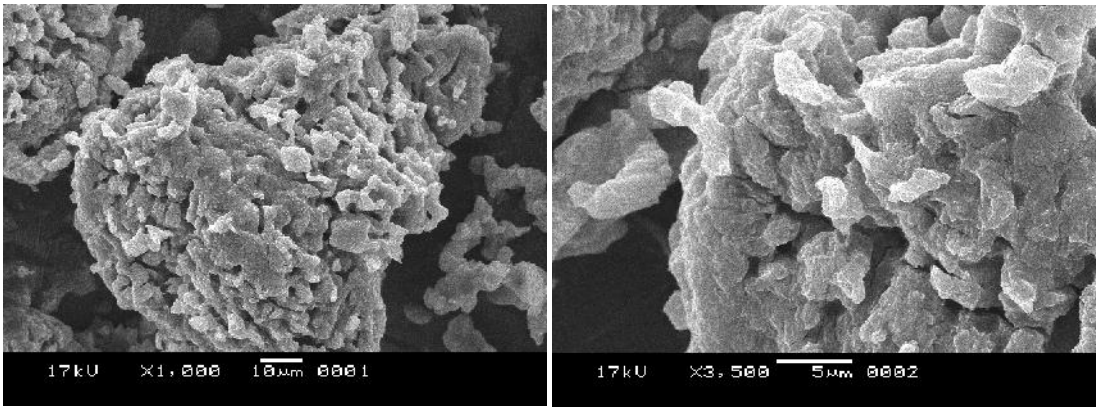

Fig. 5. SEM images of $Li_4Fe(CN)_6$.

From the images it is revealed that the particles are agglomerated in nature with average particle size in the range of 3-5 μm.

3.5 Electrochemical study

The cyclic voltammogram of the synthesized $Li_4Fe(CN)_6$ cathode were recorded, as shown in Fig. 6, in the potential window of 1.5 V to 4.8 V vs. Li at a scan rate of 0.5 mVs^{-1}.

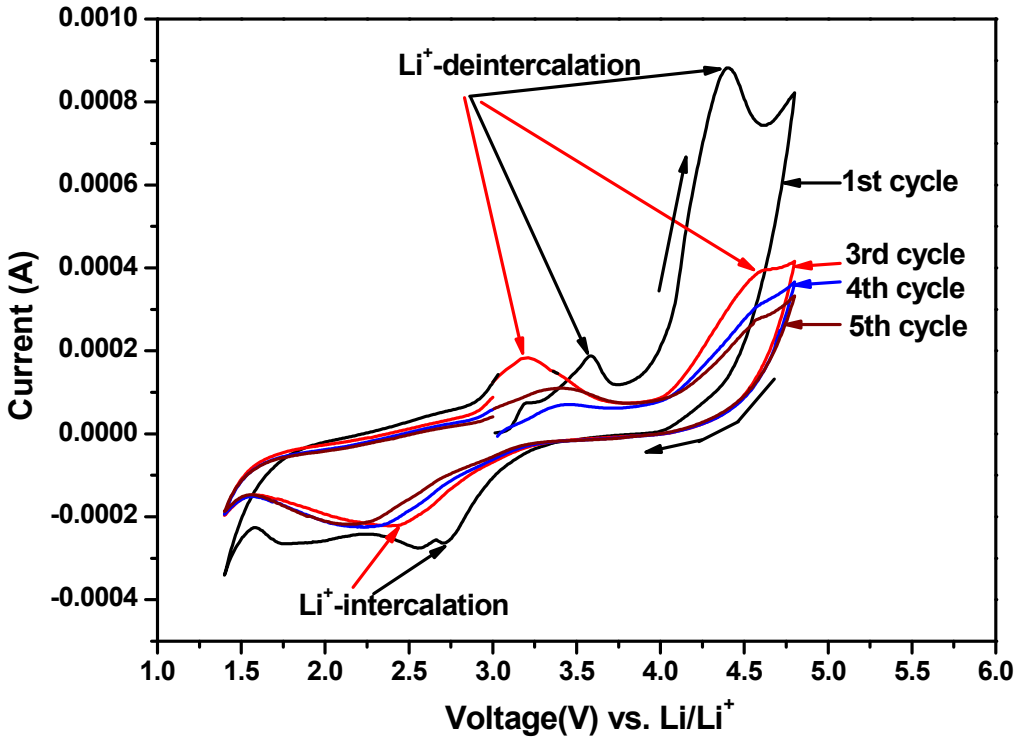

Fig. 6. Cyclic voltametry of $Li_4Fe(CN)_6$ in 1 Molar $LiClO_4$ solution in EC+DMC(1:1) mixture vs. Li/Li^+ at the scan rate of 0.5 mVs^{-1}.

In the first cycle during forward scan two oxidation peaks appeared at 3.58 volt and 4.4 volt and the corresponding two reduction peaks are observed around 2.71 volt. But in the next cycle, slight changes in the peak positions were observed. It should be noted that the multi peaks converges in to a single peaks in subsequent cycles. The extra peak might be due to structural changes within the molecule, because only a single oxidation and reduction peak is expected for $Li_4Fe(CN)_6$. More importantly, cyclic voltametry study reveals that the system is reversible in nature and reversibility retained in the subsequent cycles.

Galvanostatic charge-discharge behaviour of the assembled cell using $Li_4Fe(CN)_6$ as cathode shown in Fig. 7, were recorded at a rate of 0.15 C and 0.30 C.

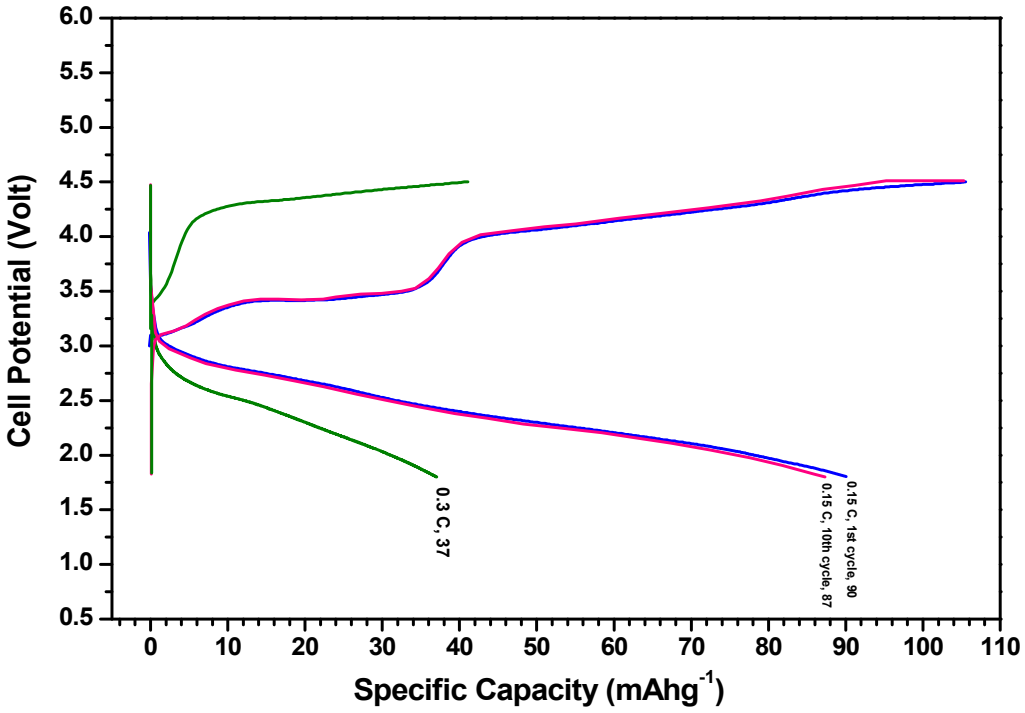

Fig. 7. Charge-discharge behaviour of $Li_4Fe(CN)_6$ vs. Li/Li^+ at 0.15 C and 0.30 C current densities.

At low rate (0.15 C), the cell shows the maximum faradic capacity of 90 $mAhg^{-1}$, which is about 80% of the theoretical value i.e., 112 $mAhg^{-1}$ and the value practically remain unaltered up to 15-20 cycles as shown in Fig. 8. At high drain condition the cell delivered a capacity of 37 $mAhg^{-1}$, due to migratory limitation of the Li^+ ions.

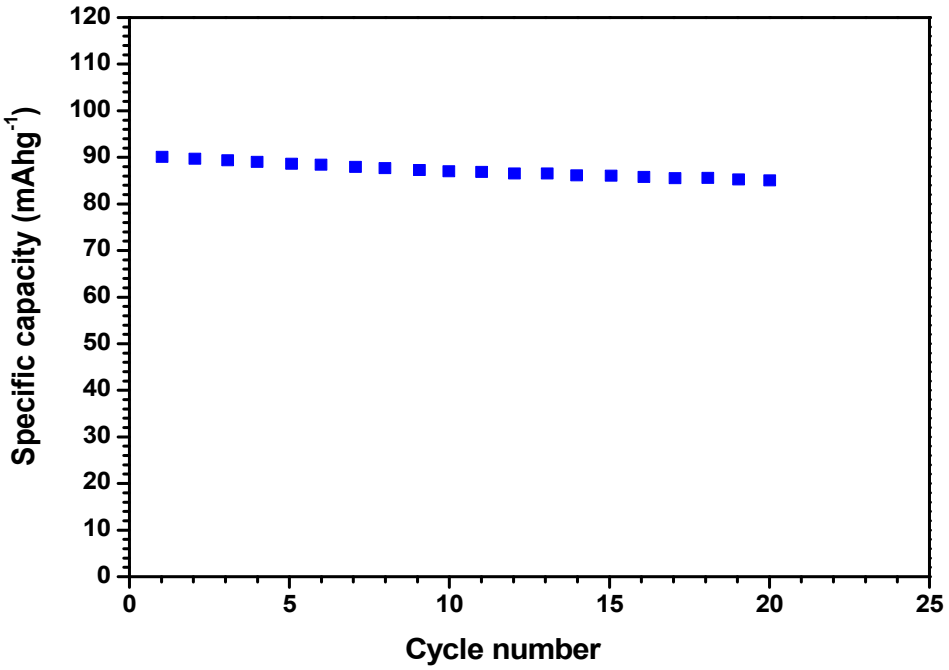

Fig. 8. Discharge capacities of $Li_4Fe(CN)_6$ cathode vs. cycle number at 0.15 C current density.

4. CONCLUSION

$Li_4Fe(CN)_6$ was successfully synthesized by a simple and cost effective route. Advantages of this method are that no inert atmosphere and no high temperature are required during synthesis [45-48]. Secondly, the material is non-toxic [35], and shows good cyclic ability, when used in rechargeable lithium-ion battery as cathode material. Low capacity fading upon cycling is observed at low drain discharge condition. Finally, it can be used as liquid cathode [37], in aqueous lithium ion battery, since it is soluble in water.

COMPETING INTEREST

Authors have declared that no competing interests exist.

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