

Supporting information

A room temperature multivalent rechargeable Iron ion battery with ether based electrolyte: new type of post-lithium ion battery

*Ajay Piriya Vijaya Kumar Saroja, Sai Smruti Samantaray, Ramaprabhu Sundara**

Alternative Energy and Nanotechnology Laboratory (AENL), Nano Functional Materials Technology Centre (NFMTC), Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

Materials and Methods

Preparation of electrolyte

The Fe ion battery electrolyte was prepared inside the argon filled glove box. 1M $\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ (Alfa aesar) was added slowly into tetraethylene glycol dimethyl ether (TEGDME) (9.99 % Sigma Aldrich) and stirred till the salt is completely dissolved into the solvent. Once the electrolyte reached pale green colour the stirring is stopped and are used for the fabrication of cells.

Preparation of anode

Mild steel was used as the source of Fe. Before using the surface of mild steel is polished with sand paper till the surface shines like metallic lustrous.

Preparation of cathode

The cathode is prepared by mixing V_2O_5 , multiwalled carbon nanotubes and polytetrafluoroethylene with a weight ratio of 75:15:10 in N-methyl pyrrolidone and coated on stainless steel foam or carbon paper. The multiwalled nanotubes is added as the conductive additive for V_2O_5 which is prepared as reported in ²⁷. The coated electrode was dried in a vacuum oven at 80 °C overnight. The mass loading of the electrode is 4-5 mg/cm².

Electrochemical characterisation

Iron ion battery is assembled inside argon filled glove box as well as in ambient condition using 2032-coin cell type battery model. Glass fiber membrane (GF/C) (Whatman microfiber filter 47 mm) is used as the separator. The galvanostatic charge discharge measurements at room temperature were carried out using Biologic BCS 810 battery cycler in the potential range of 0 to 2.1 V. Cyclic voltammetry curves were carried out in Biologic SP 300 at the scan rate of 0.1 mV s⁻¹. For ex-situ XPS measurements, the electrodes were cycled at a current density of 30 mA g⁻¹ for 50 cycles and the cycled electrodes are washed with tetraethylene glycol dimethyl ether solvent and dried inside an argon filled glove box.

Before measurement, the sample is transferred to an airtight container and transferred for XPS measurement.

Reversible electro stripping and electroplating of Fe^{2+}/Fe in mild steel

The reversible electroplating and electro stripping of Fe/Fe^{2+} ions from the mild steel anode is confirmed using cyclic voltammetry studies. The cyclic voltammetry studies are carried out in a three electrode system using platinum wire as the counter electrode, copper foil as the working electrode and mild steel as the reference electrode in 1M $\text{Fe}(\text{ClO}_4)_2$ in tetraethylene glycol dimethyl ether (TEGDME) solvent. The voltage scan is done in the potential range of -1 V to 1 V at a scan rate of 20 mV s^{-1} .

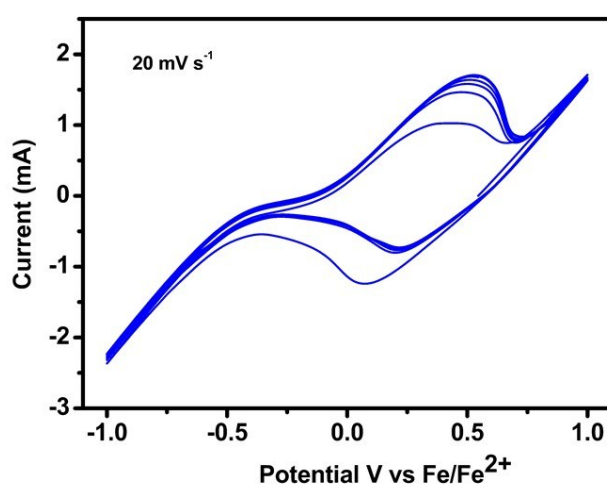


Fig.. S1. Cyclic voltammetry curve of copper electrode in 1M $\text{Fe}(\text{ClO}_4)_2$ in tetraethylene glycol dimethyl ether at a scan rate of 20 mV s^{-1}

There is a slight improvement in coulombic efficiency in the later cycles, but the coulombic efficiency is not close to 100 %. The reason for the low coulombic efficiency of the developed rechargeable iron ion battery can be described as follows.

The source of oxygen can be from the electrolyte since hydrated $\text{Fe}(\text{ClO}_4)_2$ is used as the electrolyte salt. During the process of repeated cycling, the surface oxides formed on the surface of anode may leads to pits/cracks as observed from the SEM image Fig.S10. which can still lead to the side reactions of the electrolyte with the anode. The presence of iron (II) oxide in the initial discharge cycle and iron (III) oxide on the surface of the anode in the later cycles implies that surface of the anode undergoes less side reactions in the later cycles. At the cathode, the formation of different iron vanadium oxide can lead to structural distortion at the cathode which can subsequently lead to further interaction of electrolyte with the fresh electrode surface.

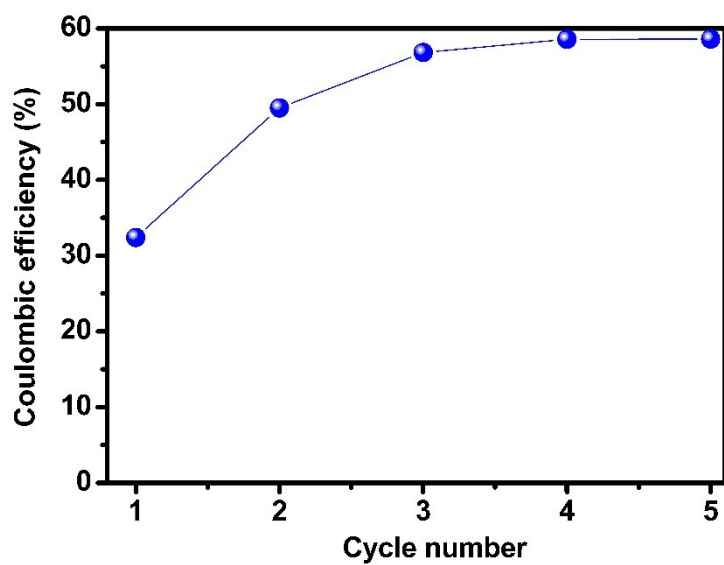


Fig. S2. Coulombic efficiency for the first five cycles

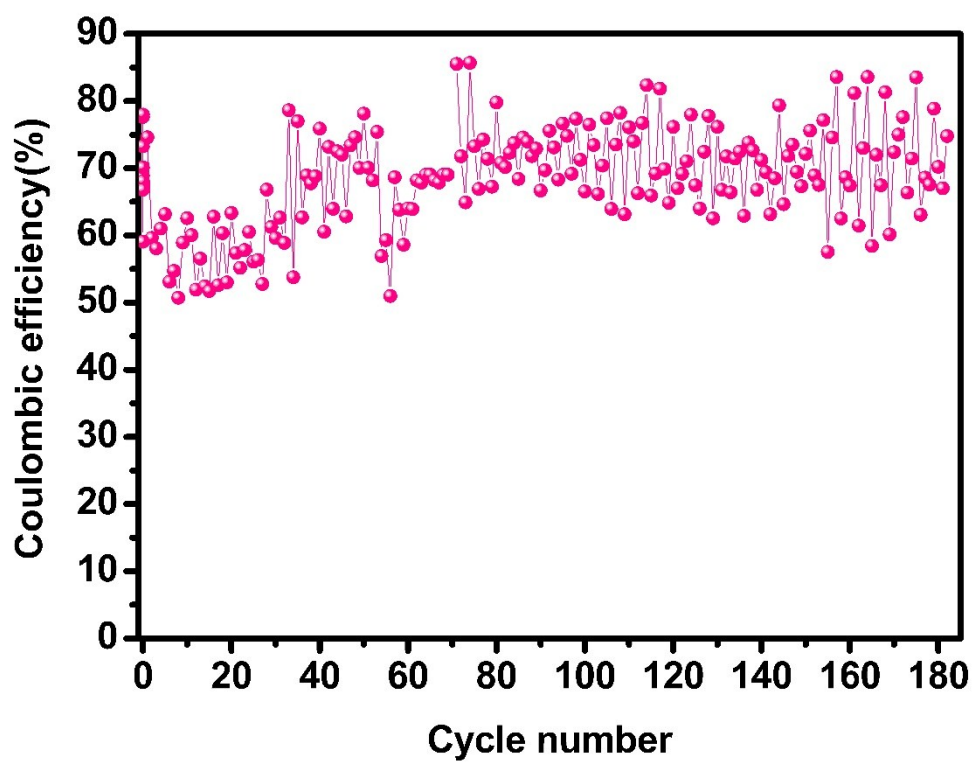


Fig. S3. Coulombic efficiency of the cell for long cycles

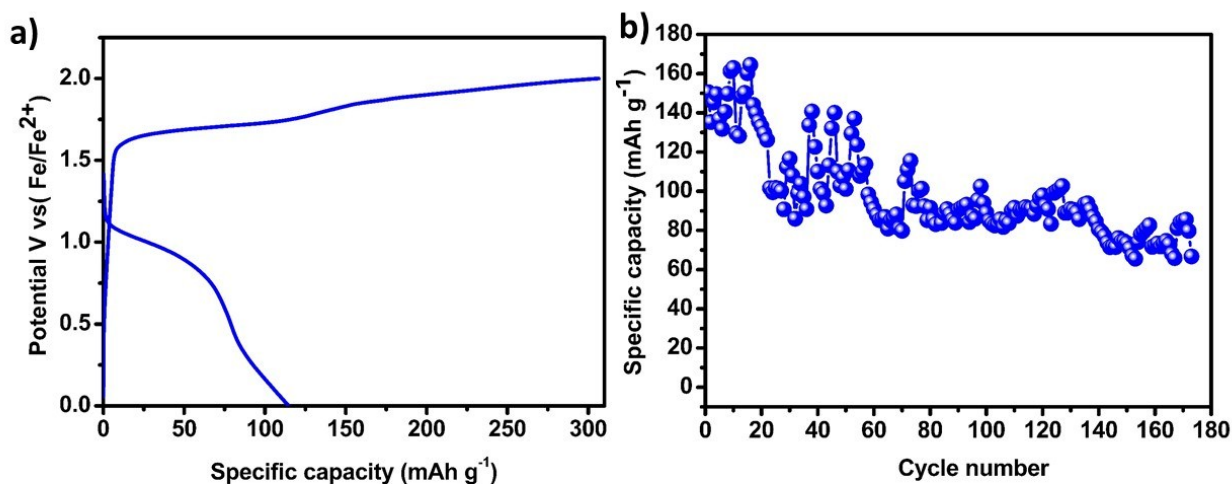


Fig. S4. (a) Galvanostatic charge discharge curve and (b) Cyclic stability curve of V_2O_5 cathode coated on carbon paper for iron ion battery at a current density of 100 mA g^{-1}

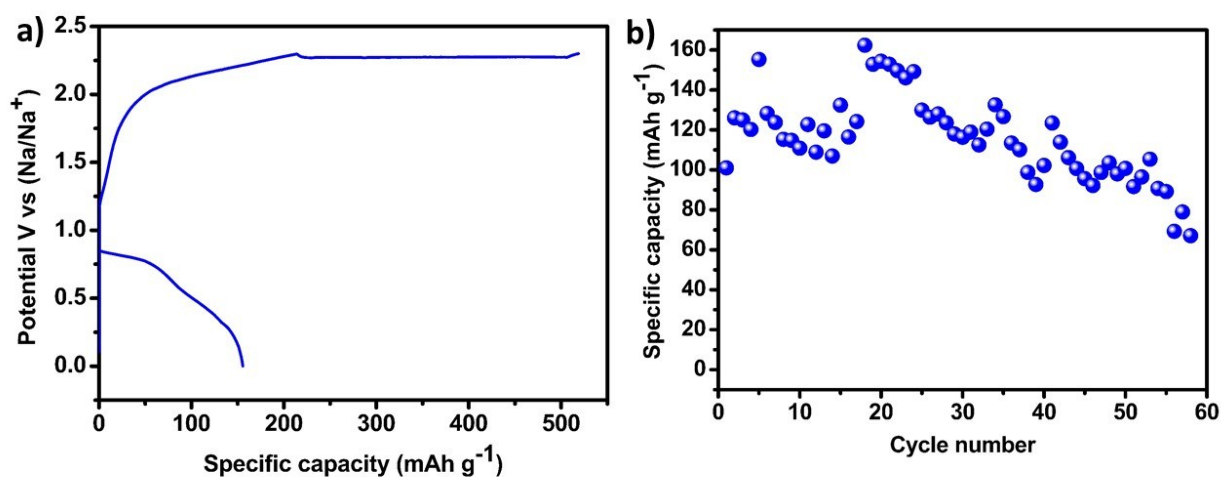


Fig. S5. (a) Galvanostatic charge discharge curve and (b) cyclic stability curve of V_2O_5 cathode for iron ion battery at a current density of 30 mA g^{-1} assembled in ambient condition

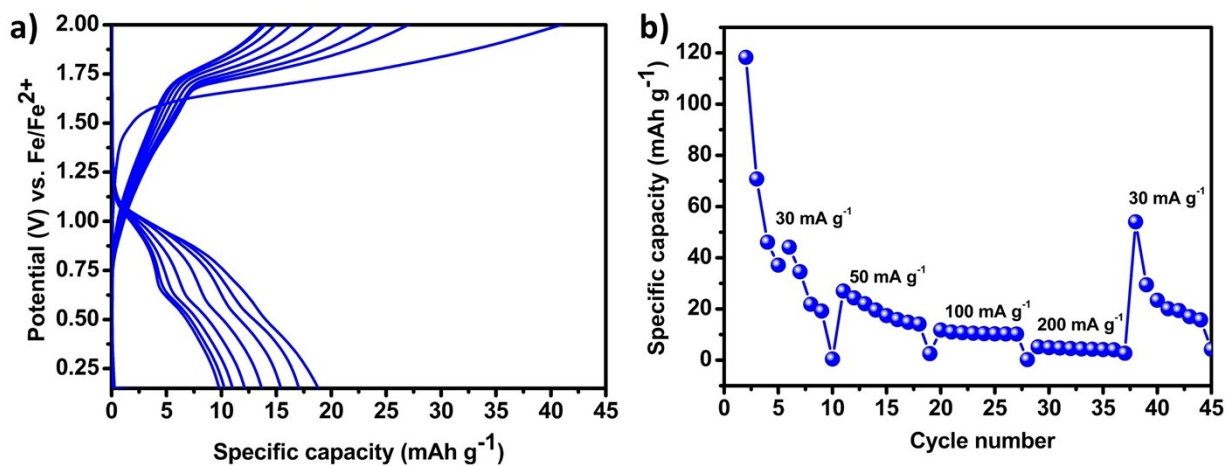


Fig.S6. (a) Galvanostatic charge discharge curves, (b) rate capability of V_2O_5 cathode and pure Fe anode

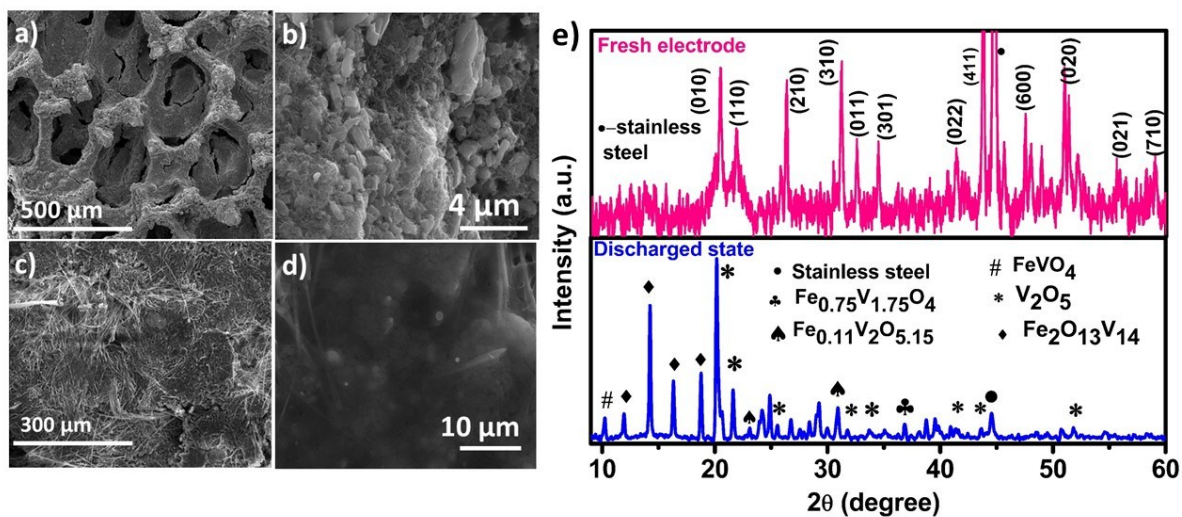


Fig. S7. (a, b) SEM images of pristine electrode, and (c, d) discharged electrode and (e) XRD pattern of pristine electrode and discharged electrode

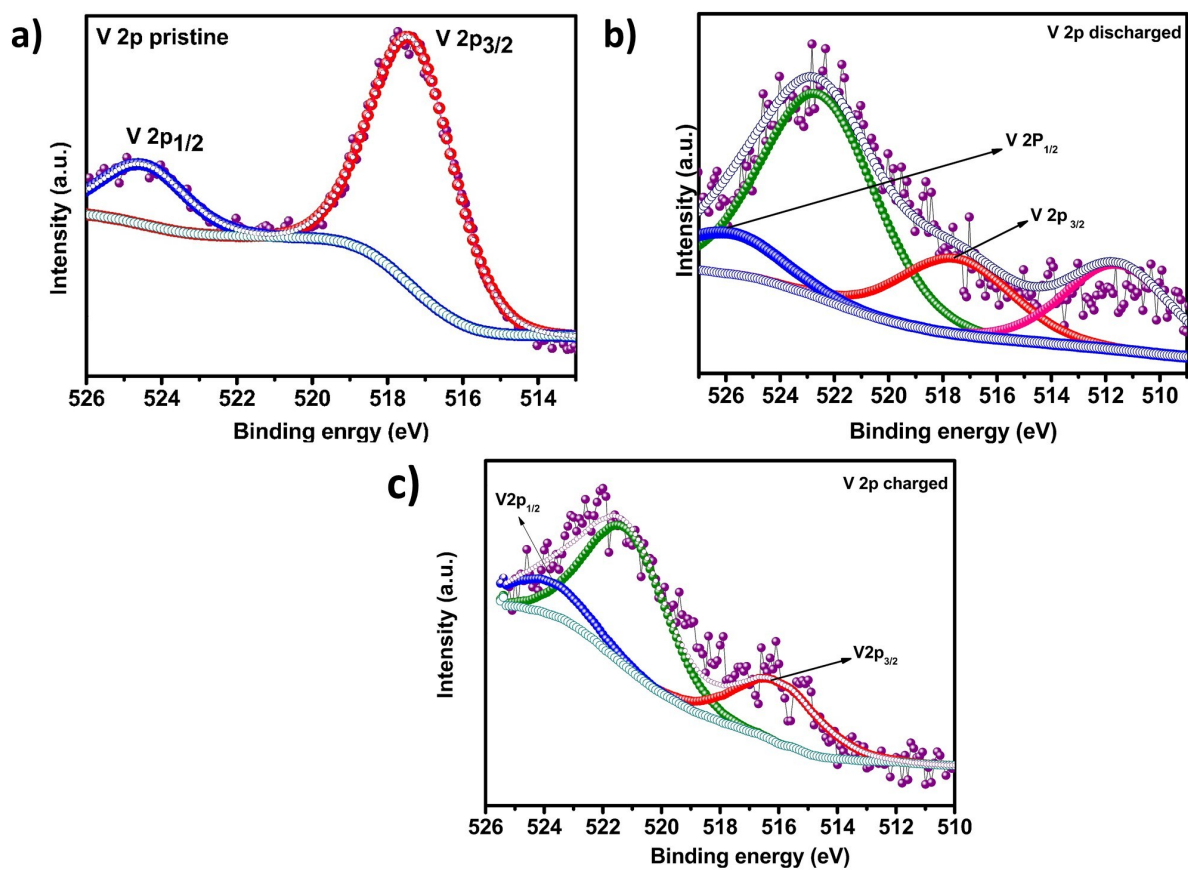


Fig. S8. X-ray photoelectron spectroscopy studies of the electrode V2p region of the XPS spectra of (a) pristine electrode, (b) discharged electrode and (c) charged electrode.

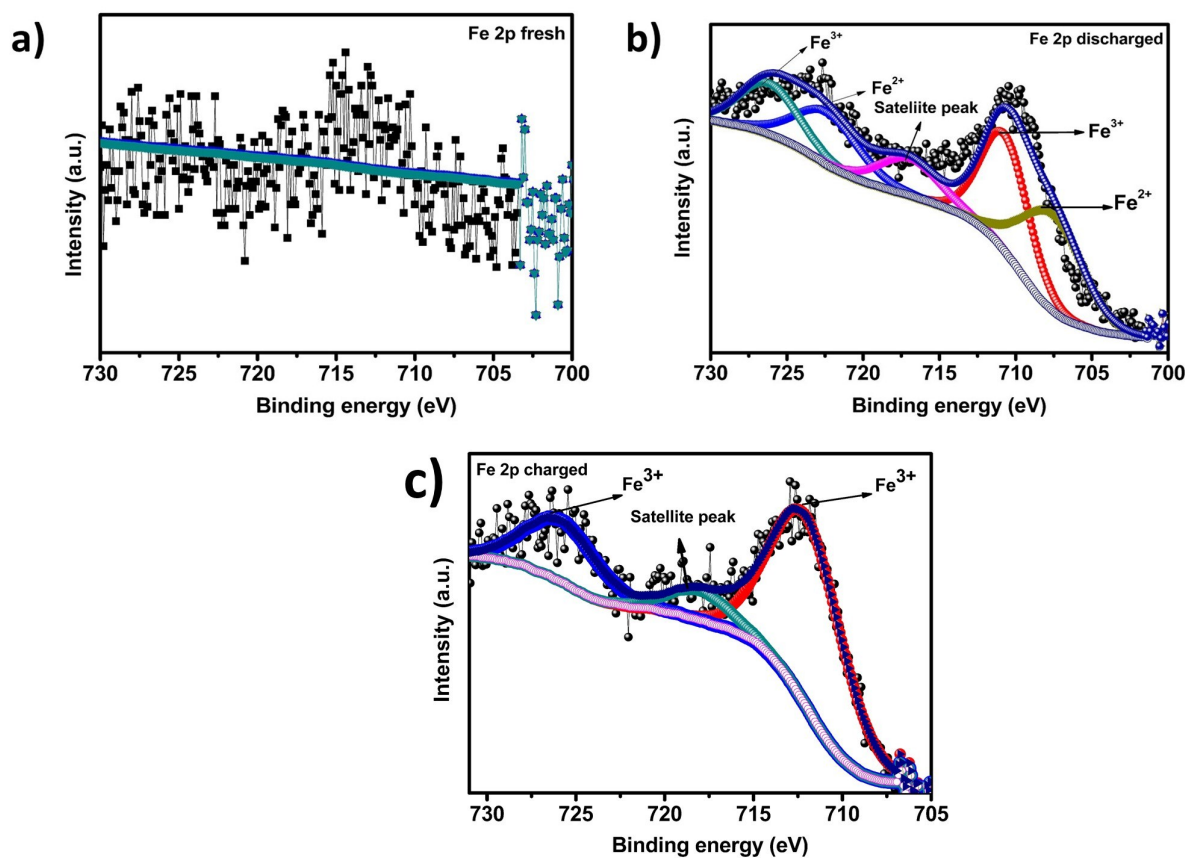


Fig. S9. X-ray photoelectron spectroscopy studies of the electrode Fe2p region of the XPS spectra of (a) pristine electrode, (b) discharged electrode and (c) charged electrode

The surface of the mild steel before the process of cycling is a smooth surface and the EDAX mapping indicates the presence of Fe, C and O (Fig. S10a). The presence of oxygen in mild steel before charging is due to the presence of surface oxides. After the process of cycling, the surface of the mild steel is covered with a layer of particles as shown in Fig. S10b. Since there are no traces of vanadium observed, these particles might be iron oxides formed on the surface during the electrochemical process. The EDAX mapping indicates the presence of Fe, C, Cl and O.

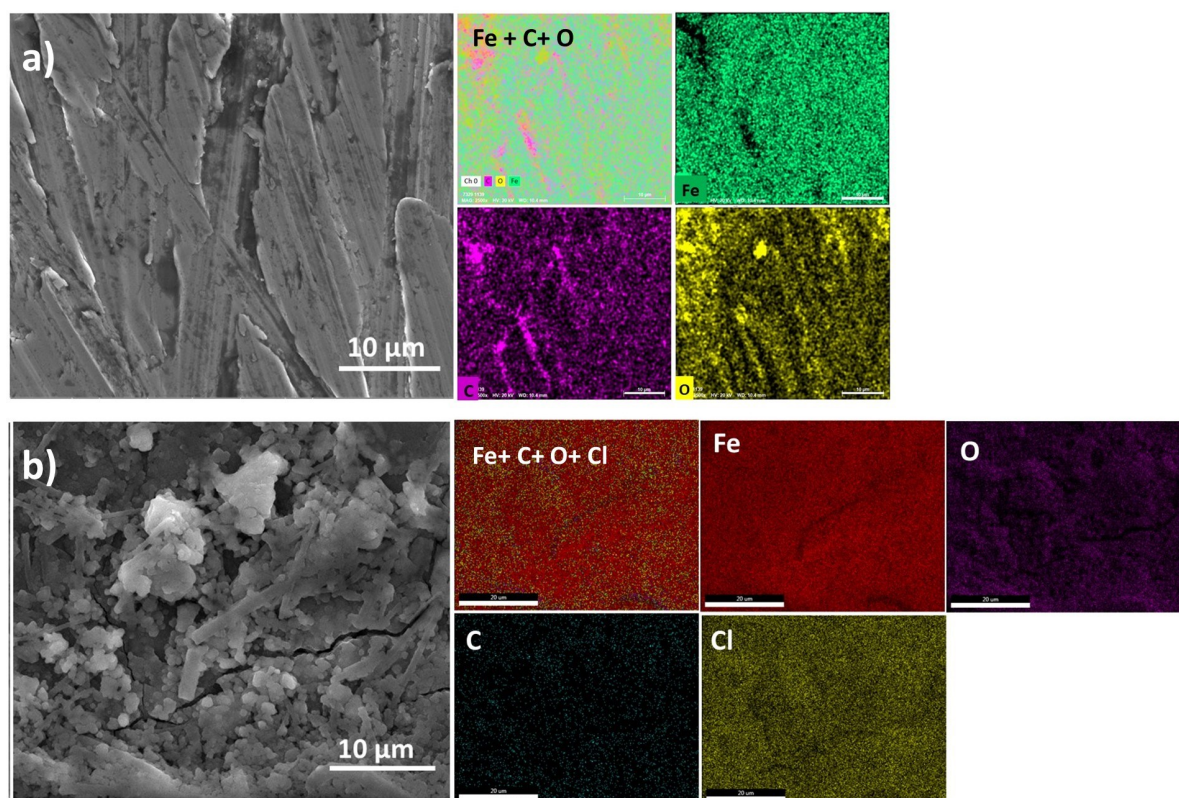


Fig. S10. SEM image and EDAX mapping of mild steel (a) before cycling and (b) after cycling

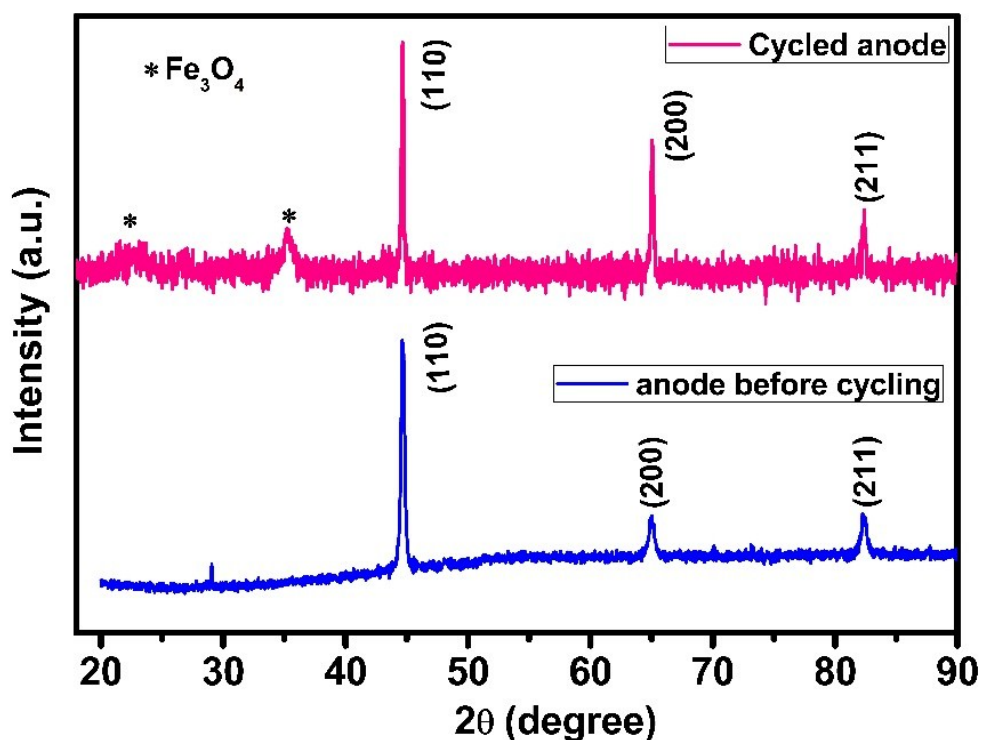


Fig. S11. XRD pattern of mild steel anode before and after cycling

The XRD pattern of the mild steel anode in the charged and discharged state during the initial cycle is carried out and it is observed the presence iron (II) oxide formed on the surface of the anode. During the initial charge/discharge cycles, the surface of the mild steel gets oxidised due to the presence of moisture content in the electrolyte and its interaction with the anode results in the formation of iron (II) oxide. This leads to the formation of irreversible compound resulting in low coulombic efficiency. As the number of cycles increases further oxidation of anode occurs, which leads to the formation of Iron (III) oxide as observed from Fig. S11. The formation of mixed iron oxides in the subsequent cycles on the surface of mild steel anode leads to decay in capacity over cycling as observed in Fig.2c. This can be prevented by adding additives to the electrolyte.

During charging, the occurrence of side reactions of the cathode with the electrolyte within the operating potential causes higher charge capacity than the discharge capacity. The presence of large plateau during charging in the initial cycle is due to the formation of irreversible compounds as evident from the XPS study which reveals the presence of Fe^{3+} ions in the charged state.

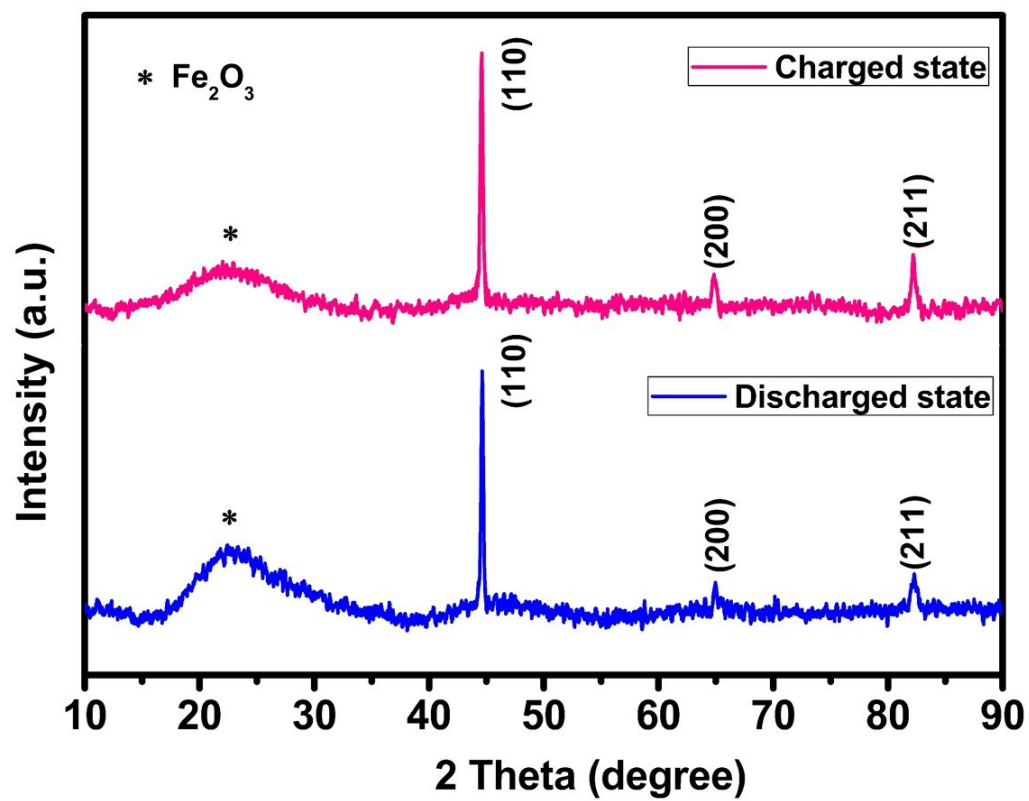


Fig.S12.XRD pattern of mild steel anode in the charged and discharged state in the initial cycle