

DESIGN AND FABRICATION OF LI-ION BATTERY USING TURMERIC POWDER

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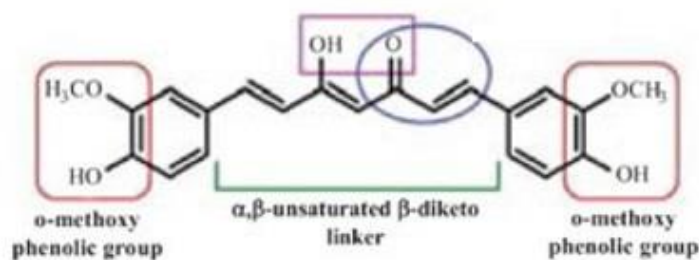
Keywords: Organic electrode, Li-ion batteries, Curcumin (Turmeric), Curcumin-Cu complex, Curcumin-Fe complex.

Introduction

Due to the rapid development of energy storage systems in power supply and electrical vehicles, the search for sustainable cathode materials to boost the energy density of lithium-ion batteries (LIBs) has assumed a central role in both academic and industrial investigations. Inorganic cathode materials, which are widely utilized, have historically been beset by issues like low capacity, high manufacturing energy consumption, major safety risks, and expensive raw materials. As a result, it is crucial to offer cathode materials that are sustainable and friendly to the environment and have more specialized functions, improved safety features, and a greater quantity of natural resources. The benefits of high capacity, environmental friendliness, changeable structure design, systemic safety, and natural abundance make organic cathode materials intriguing as alternatives.

An organic molecule with electro active groups like carbonyl, hydroxyl and natural product-based compounds provides prospective benefits like structural diversity, flexibility, molecular level controllability. The Conjugated carbonyl compounds have attracted a lot of attention as a special class of electrochemical redox energy storage materials. [1] Large conjugated systems with several carbonyl functional groups are a common feature of carbonyl conjugated compounds, and they largely dictate the benefits such structural diversity, high specific capacity, and quick reaction kinetics. [2,3] Another benefit of carbonyl conjugated organic compounds as cathode materials is that they may be produced in huge quantities at low cost as derivatives of natural biomass extracts. [4,5].

Curcumin, an active component of *Curcuma longa* (Turmeric), was chosen to explore its electrochemical behaviour in LIBs because it consists conjugated carbonyl group. Due to its quick enolisation capabilities under basic conditions, it also works as an excellent ligand and forms stable complexes with copper, manganese, iron, vanadium, gallium, indium, and other elements. These complexes have been demonstrated to be more antioxidant than curcumin. In biological systems, the curcumin-metal complex undergoes redox reactions that signal biological activity. As a result, curcumin metal complexes were chosen as electrode materials for Lithium ion microbatteries.



Structure of enolic form of curcumin acting as a ligand

Objectives:

- The Structure, Size and morphology and characterization of curcumin metal complex nanoparticles through UV-Visible, FTIR, NMR, Mass, XRD, SEM and EDX spectroscopic analyses.
- The study of electrochemical performance (mechanism, kinetics and thermodynamics of redox process, Charge discharge cycling, Study of cyclability, Rate capability, Temperature dependence, cycle life testing etc)of Cu(II)-(Curc)₂, Fe(III)-(Curc)₃ complex nanomaterial as cathode material in non-aqueous system
- The fabrication of lithium ion micro battery (Li coin cell) CR2032 using curcumin-metal complex nanomaterial having high electrochemical performance as cathode and lithium metal as anode and lithium fluorophosphates (LiPF₆) as electrolyte.
- The Extraction, Isolation and Synthesis of curcumin nanoparticle.
- The preparation of 1:2 Cu(II)- Curcumin complex [Cu-(Curc)₂] and 1:3 Fe(III)- curcumin complex [Fe-(Curc)₃].

Materials:

Curcuma Longa rhizome was purchased from local market in Bangalore, Ethyl acetate, Methanol(MeOH), Hexane, Chloroform(CHCl₃), Copper Acetate monohydrate [Cu (OAc)₂. H₂O], Ferric nitrate nonahydrate [Fe(NO₃)₃. 9H₂O], Et₃N were procured from Sd fine chemicals, Acetylene Black, poly tetra fluoroethylene (PTFE), N-methyl pyrrolidine were obtained from Sigma Aldrich chemicals.

Method:

Extraction and Isolation of Curcumin from Curcuma Longa (Turmeric Rhizome):

The Curcuma Longa rhizomes were washed thoroughly with water, dried in the sun for one week and again dried at 60°C in a hot air oven for 24 hours to remove the moisture content. The dried rhizomes were pulverised using a chemical blender and subjected to soxhlet extraction in ethyl acetate solvent. The obtained crude extract was filtered by Whatmann no. 1 filter paper and concentrated using a roto evaporator. 20ml Hexane was added to crude extract and stirred at 800rpm for 60mins. The solution was centrifuged to get dry powder and column chromatographed on silica gel 60-120 mesh using CHCl₃: MeOH :: 9:1 mobile phase to get 95% pure curcumin.

Preparation of curcumin nanoparticles

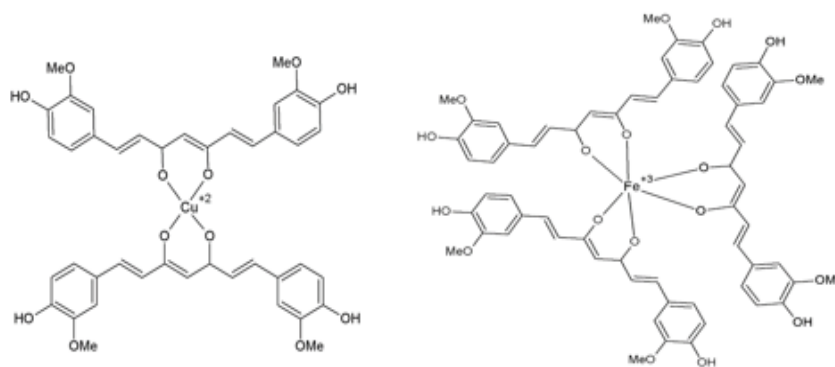
The solution of purified curcumin in DMSO(0.5mg/ml) was slowly added drop wise to 100ml Double distilled water cooled to 10⁰ C at the rate of 0.5ml/min under constant stirring. The resultant solution was ultrasonicated at 50W power for 2hours in pulsed mode with pulse ratio on/off 50/10 (s/s). The obtained solution was concentrated and dried to get Nanocurcumin.

The preparation of 1:2 Cu(II)-curcumin[Cu-(Curc)₂]complex nanoparticle.

The 1:2 Cu(II)-curcumin complex was synthesized by dropwise addition of 0.02 mole of curcumin in 10ml of methanol to 0.01 mole aqueous solution of Cu (OAc)₂ · H₂O under reflux condition with continuous stirring for 3 h. After that the excess solvent was removed under reduced pressure and the residual solid was dried out under vacuum.

The synthesis of 1:3 Fe(III)-Curcumin [Fe-(Curc)₃]complex nanoparticle

Iron–Curcumin complex was prepared by drop wise addition of aqueous solution of Fe (NO₃)₃(0.1mM) to 0.3mmol curcumin methanolic solution with gentle heating and stirring, followed by reflux for 2hr, and then cooling to room temperature (RT), afforded a solid product that was then isolated by vacuum filtration, washed with cold methanol and dried overnight in vacuum at room temperature.



The structure of Cu(II)-Curcumin Complex [Cu(II)-(Curc)₂] and Fe(III)-Curcumin Complex [Fe(III)-(Curc)₃]

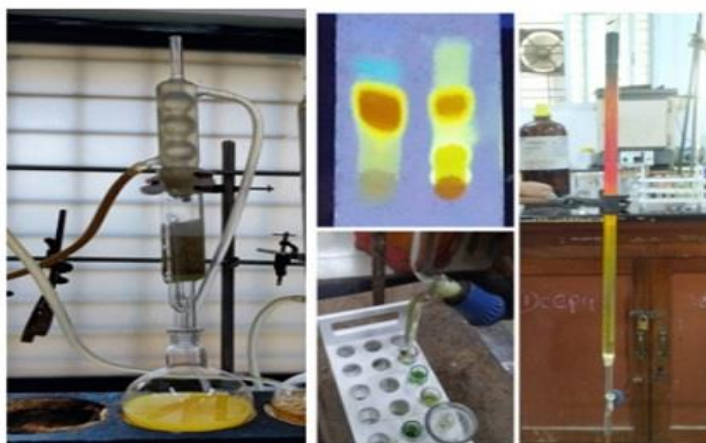


Fig 1 : (a) Soxhlet Extraction set up (b) Column Chromatography with TLC

Result and Discussion:

The characterization of curcumin and curcumin metal complexes was confirmed by recording the IR, UV-Vis, ¹H NMR, Mass, XRD, SEM, and EDX spectra of the synthesized sample.

The UV-visible absorption spectra were recorded using a Shimadzu 2450–SHIMADZU spectrometer. Fourier transform-infrared (FTIR) spectra were recorded over the range of 400– 4000 cm⁻¹ using a Bruker spectrometer by using powder sample mixed KBr thin transparent pellet. X-ray diffraction (XRD) patterns were recorded by emergent matter. PANalyticalX'pert pro diffractometer at 0.02 degree/s scan rate using Cu- α 1 radiation (1.5406 Å, 45 kV, 40 mA). The morphologies of the samples were characterized using field emission scanning electron microscopy (FESEM, Zeiss Ultra-60). The chemical composition analysis of the samples was performed using EDXS(X-ray energy dispersive spectroscopy) connected to the SEM. The NMR spectrum (Proton NMR spectrum was recorded on Bruker -400 MHz spectrometer with TMS as internal standard)

UV visible Spectra

UV visible spectra of Curcumin and its complexes in DMSO solvent is shown in **Figure 2a**. The maximum absorption band of curcumin appeared at wavelength 435 nm. The main absorption band appeared at curcumin due to π - π^* was shifted to 8-15 nm in Copper and iron complex due to the contribution of carbonyl group after complexation with metals. Owing to a curcumin (L) - metal (M⁺) ion the shoulders appeared at 420-425 nm.

FT-IR analysis

The IR Spectrum of curcumin and its metal complex is shown in **Figure 2b**. Curcumin showed its signature absorption peaks at 3417 cm⁻¹ (phenolic O-H stretching vibration), 1628 cm⁻¹ (C=O and stretching), 1603cm⁻¹ (benzene ring stretching vibrations), 1509 cm⁻¹ (C=C vibrations), 1428 cm⁻¹ (olefinic C-H bending vibrations), 1282cm⁻¹ (aromatic C–O stretching vibrations), 1026 cm⁻¹ (C–O–C stretching vibrations).

The shift of C=O stretching frequency to 1609 cm⁻¹ in Cu-curcumin complex and 1618 cm⁻¹ in Fe-Curcumin complex from 1628 cm⁻¹ confirms its involvement in complexation. The appearance of bands at 460-480cm⁻¹ indicates the M-O bond[6].

NMR and Mass spectra analysis of curcumin and its complexes:

The proton NMR spectrum of curcumin (**Figure 2c**) has been recorded using DMSO as solvent.

¹H NMR (δ ppm, DMSO-d₆): δ 9.6 (s, 2H, OH), δ 3.8 (s, 6H, OCH₃), δ 7.1-7.5 (m, 6H, ArH), δ 6.0 (s, 1H, C-H olefinic), δ 6.0 (d, 4H, C-H olefinic).

The ¹H and ¹³C NMR of Cu-(Curc)₂ and Fe-(Curc)₃ in DMSO has shown broad peak confirming the formation of complex and ¹³C NMR of Cu-(Curc)₂ and Fe-(Curc)₃ has shown no peaks which confirmed the paramagnetic nature of material, thus confirming the formation of complex.

The formation of compound was further confirmed by recording the mass spectrum of complexes(**Figure 3**), which exhibited a molecular ion peak at m/z 799.16 corresponding to the molecular weight of the Cu-(Curc)₂ complex

XRD Analysis

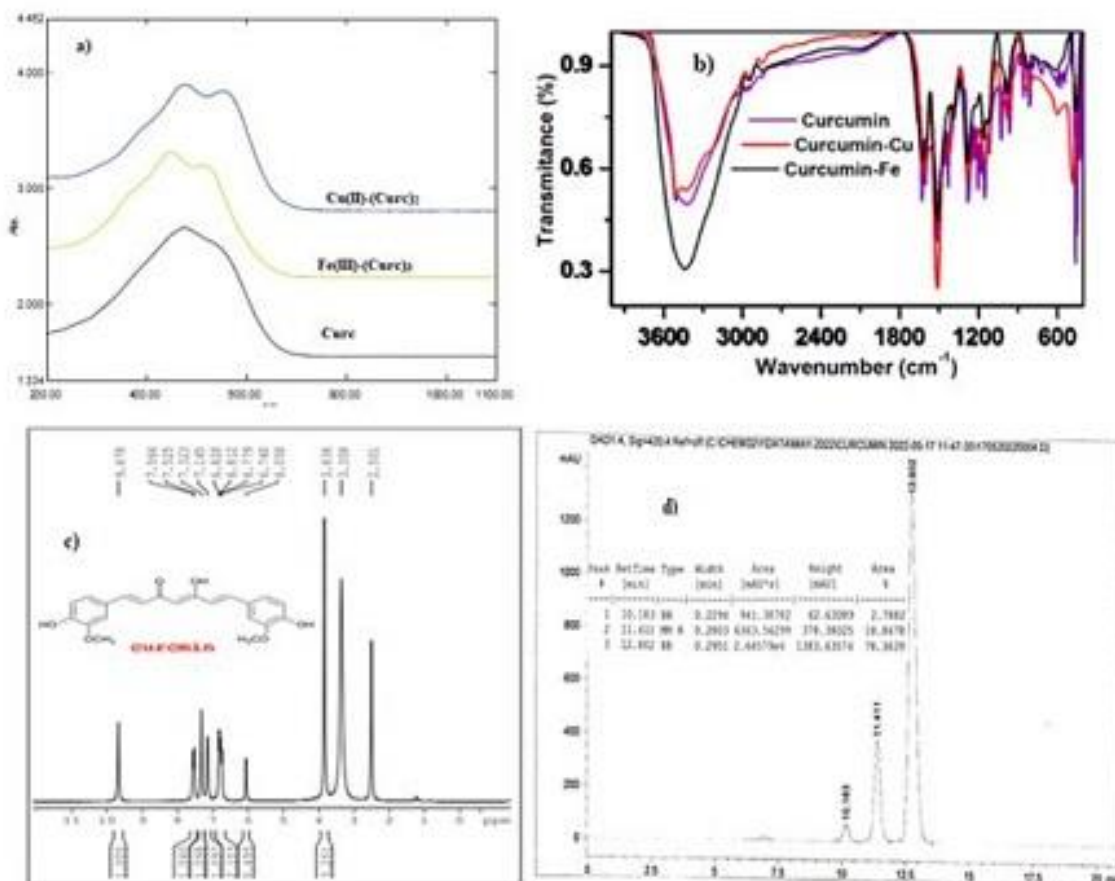


Fig 2 : (a) UV-Visible Spectrum (b) IR Spectrum (c) ¹H NMR spectrum of Curcumin d) HPLC chromatogram of column purified curcumin

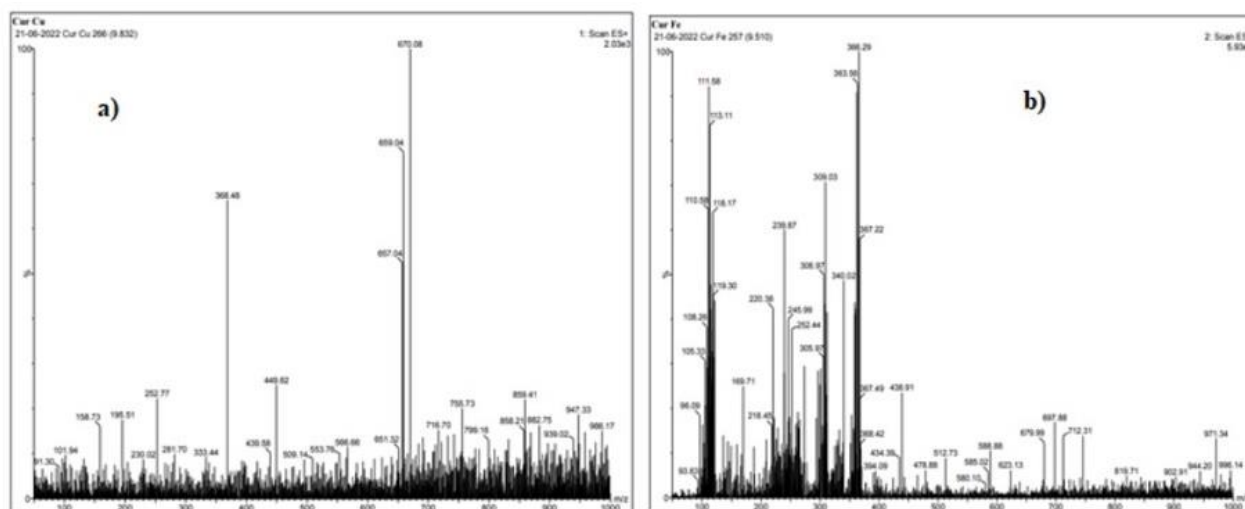


Fig 3: Mass Spectrum of (a) Cu-(Curc)₂ (b) Fe-(Curc)₃

The powdered XRD pattern of curcumin (**Figure 4a**) showed several intense peaks, which indicated the crystal forms of curcumin. The characteristic peaks of curcumin appeared at a diffraction angle of 2θ (14.20° , 17.53° , 18.44° , 22.55° , 24.54° , 25.86° and 27.01° , etc.) implying the presence of curcumin in crystalline form [7]. However, broadening of peaks occurred in the curcumin Nanoparticles, Cu-(Curc)₂ and Fe-(Curc)₃ patterns, indicating that curcumin was converted from a highly crystalline to an amorphous form.

SEM and EDX Analysis

Field emission scanning electron micrographs (FE-SEM) and the EDX spectrum of the Curcumin and Curcumin-Cu complex powder samples were shown in **Figure 4b**. SEM images reveal that the samples consist of regular shaped spherical nanoparticles with phase segregation and agglomeration. The EDX spectrum Curcumin-Cu complex shows the presence of Cu and The atomic wt% further confirms the formation of Cu(Curc)₂ complex .

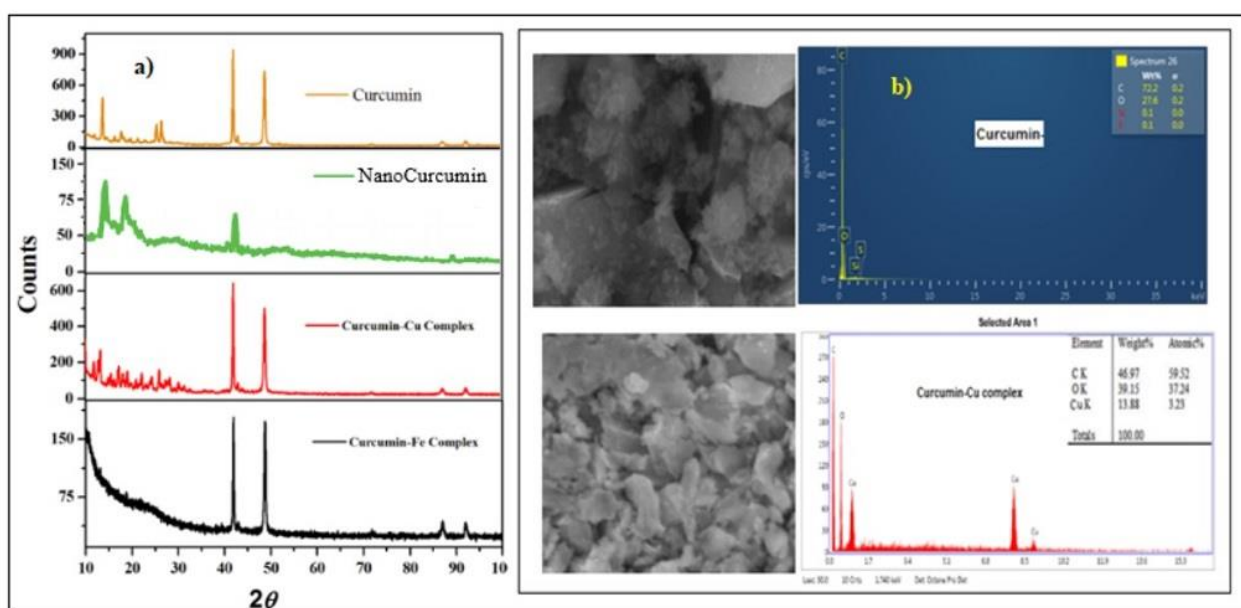


Fig 4: XRD Spectrum of (a) Curcumin, Nanocurcumin, Cu-(Curc)₂ and Fe-(Curc)₃ (b) EDX spectrum of Curcumin , Cu-(Curc)₂

Electrochemical Characterization: Battery Studies

The Study of Electrochemical Performance of curcumin and its metal complex as cathode electrode material with Lithium is studied by fabricating a Li-Ion CR2032 coin cell using biologic SP CV Instrument.

Preparation of Electrodes:

Lithium anode is prepared by cutting lithium in argon environment. The cathode electrode is prepared by mixing 80% active material (Curcumin/curcumin-metal complex), 10% acetylene black, and 10% PVDF binder in N-methyl pyrrolidone solvent. After 3 hours of mixing, the casting of suspension onto steel mesh discs with a diameter of 1.0cm is done. To eliminate residual solvent and volatile contaminants, the electrodes are dried in a vacuum oven at 110°C for 24 hours.

Fabrication of Li-ion Coin Cell:

Fabrication of Li ion coin cell CR2032 was done in glove box. The prepared electrodes were kept between Positive case and negative case separated by separator dipped in 2M

LiPF₆ electrolyte as shown in **Figure 5**. At the end the cell was sealed by using a crimper machine.

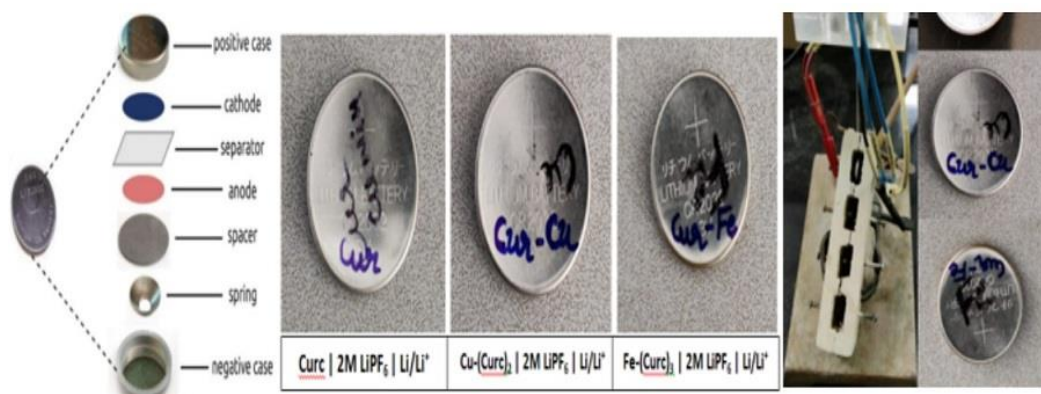


Fig 5: (a) Schematic representation of fabrication of coin cell (b) Photo of Fabricated coin cells (c) Photo of coin cell connection to Biologic CV Instrument

The Cyclic voltametric and Galvanostatic charge discharge studies of the curcumin and its metal Complex.

Curcumin, Copper-curcumin, and Iron-Curcumin complex were investigated as constituents in rechargeable Li ion batteries using electrochemical experiments in general battery electrolytic solution in coin cell form. Curc, Cu-(Curc)₂, and Fe(Curc)₃ as electrode materials in Coin Cell produced open circuit potentials (E_{OC}) of 2.970V, 3.223V, and 3.262 V, respectively. The Fe-(Curc)₂ | 2M LiPF₆ | Li/Li⁺ coin cell was not stable because the Fe-(Curc)₃ material was very hygroscopic, resulting in an incorrect cyclic voltammogram (**Figure 10c**) due to electrode material side reaction with electrolyte.

Cyclic voltammetry studies:

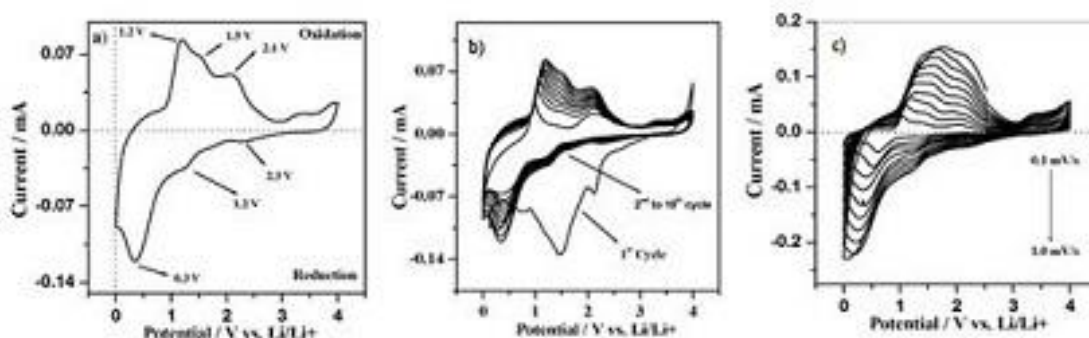


Figure 6: Cyclic Voltammogram profile of Curcumin (a) at 0.5 mV per sec (10th cycle). (b) At 0.5 mV per sec in 2M LiPF₆ electrolyte-10 Cycles. (c) At varying scan rates from 0.1 to 1.0 mV per sec

The electrochemical activities of Curcumin (Curc) and Curcumin-copper (Cu-(Curc)₂) complex under non-aqueous electrolytic condition showcase a promising result in comparison with the existing organic based rechargeable lithium ion battery. The cyclic voltammograms of Curc and Cu-(Curc)₂ complex are shown in **Figure 6** and **7** respectively.

Cyclic voltammetric studies were done by scanning the potential first in an anodic direction from the open circuit potential to render the oxidation potentials of the cell and reverse scan in a cathodic direction to ensure its reduction potential versus Li/Li⁺.

The cyclic voltammetry of Curc, shows three pairs of redox peaks 1.2 V / 0.3 V, 1.5 V / 1.2 V and 2.1 V / 2.3 V; this may be due to the three step redox process of electrode material under applied electrode potential(**Figure 6a**)[8]. The variation in the redox peak potentials and large difference in peak current at first cycle comparatively to the remaining cycles render the inference of polarization effect[9] on electrode material during electrochemical performance under applied potential. This kind of behaviour is also due to the formation of solid electrolyte interface (SEI) passive layer. The CV profile of Cu-(Curc)₂ complex shows two step redox process at 1.3 V / 1.1 V and 2.1 V / 2.2 V due to the reduction process of Cu(II) to Cu and cu-(Curc)₂ complex(**Figure 7a**). The decrease in the redox current indicated in CV may be due to the structural modification like electrochemical milling.

The effect of scan rate on cyclic voltammetry performance was recorded (**Figure 6c and 7c**) under increasing scan rates from 0.1 to 1.0 mVs⁻¹ for both the systems. This kind of studies typically used for determination of the redox behaviour of cell during electrochemical reactions and to locate the apparent chemical diffusion coefficient of Li-ions.

From the **Figure 6c and 7c**, it is clear that, the slight variations in anodic and cathodic peak potentials and increased peak currents under increased scan rates show the polarization effect.

Galvanostatic Charge Potential Limit (GCPL) studies

The coin cells Curc | 2M LiPF₆ | Li/Li⁺ and Cu-(Curc)₂ | 2M LiPF₆ | Li/Li⁺ were subjected for galvanostatic studies at C/10 rates applied current. The cell potentials were recorded as the cathode (Curc / Cu-(Curc)₂ Complex) verses anode (lithium metal). The initial reversible capacity of Curc and Cu-(Curc)₂ Complex systems were observed around 445mA h g⁻¹ with 40% efficiency and 625mA h g⁻¹ with 60% efficiency respectively as shown in Figure 9. The result shows that, the discharge capacity of Curc | 2M LiPF₆ | Li/Li⁺ is less in comparison with Cu-(Curc)₂ | 2M LiPF₆ | Li/Li⁺ cell. Also. From the figure it is clear that, the discharge capacity of Cu-(Curc)₂ | 2M LiPF₆ | Li/Li⁺ cell is more than that of charge capacity. This kind of remarkable changes is may be due to the metal complex action on electrochemical performance. Even though the redox current of curcumin coin cell is high, Cu-(curc)₂ is preferred as cathode material as its coin cell has high discharge capacity than curcumin coin cell.

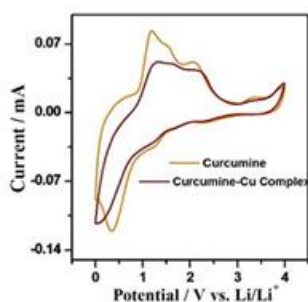


Fig (8) : Cyclic Voltammogram of Curc and Cu-(Curc)₂ complex recorded in 2M LiPF₆ electrolyte.

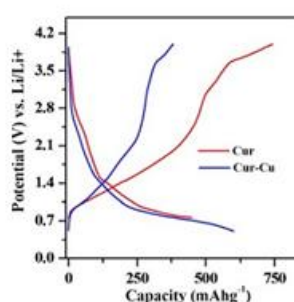


Fig (9) : GCPL profile of Curc and Cu-(Curc)₂ complex.

Electrochemical Characterization of Cu-(curc)₂ complex in aqueous system

The cv profile of Cu-(curc)₂ in aqueous medium was recorded using sat Li₂SO₄ as electrolyte, Lithium Manganous oxide (LiMnO₂) as cathode in a three electrode cell system .The CV is as shown in the **Figure 10a**. From the figure it is clear that the cell has delivered very high redox current compared non aqueous system.

Cu-(Curc)₂| Sat. Li₂SO₄ | LiMnO₂ displayed very less charge and discharge capacity that is of about only 1.2 mAh/g determined by GCPL studies. This result is not appreciable to carry further studies on it. Hence only non-aqueous studies of curcumin and its copper and metal complex is done

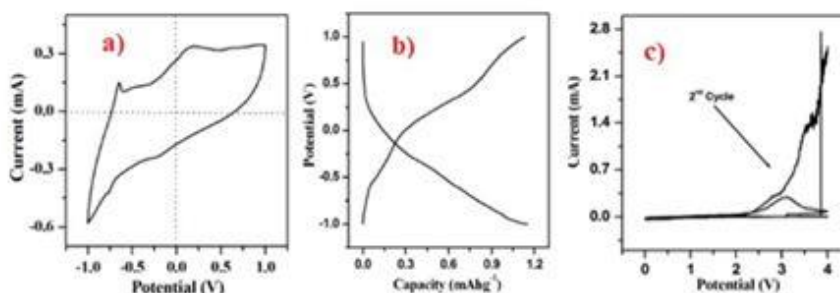


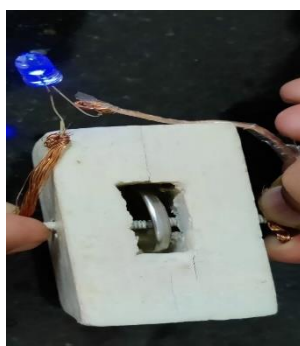
Fig 10 : (a) Cyclic voltammogram of Cu-(Curc)₂ at the scan rate of 0.5mV/sec in Sat. Li₂SO₄ Verses SCE b) GCPL profile of Curcumin – Cu complex aqueous coin cell c) Inappropriate Cyclic Voltammogram of Curcumin-Fe complex recorded at 0.5 mV/sec in 2M LiPF₆ electrolyte.

Conclusion

This study was carried out to develop a Li ion battery using curcumin, a constituent of Turmeric powder. Curcumin, Copper, and Iron complexes were used to fabricate the Li-ion CR 2032 coin cell, and subjected to battery studies in both aqueous and non-aqueous systems. The manufactured Cu-(Curc)₂ | 2M LiPF₆ | Li/Li⁺ coin cell had E_{oc} of 3.223V greater than that of Li ion CR 2032 coin cell (LiCoO₂ electrode material) that are marketed.

The fabricated cell using curcumin and copper curcumin metal complex as electrode material were tested by subjecting to charging and discharging. The fabricated coin cells were charged at 0.05mA for 10hrs followed by subjecting to discharge to glow 0.05W LED bulb. The LED bulb has glowed continuously for 8hrs with Curc | 2M LiPF₆ | Li/Li⁺ coin cell and 10hrs with Cu-(Curc)₂ | 2M LiPF₆ | Li/Li⁺ coin cell.

The GCPL studies result confirms that Copper curcumin complex in non-aqueous system has high discharge capacity and can be utilized to manufacture Li-ion batteries. The fabricated coin cells may be used to power a variety of small electronic devices, including



watches, calculators, hearing aids, etc. Finally, curcumin copper chelated complex, a safer, more affordable, and greener chemical, may be able to successfully replace lithium metal oxides thus lowering the manufacturing cost.

Scope for Future work

The study revealed that curcumin and its metal complexes can be effectively used as electrode material in fabrication of rechargeable Li⁻ion coin cells. Cu-curcumin complex coin cell efficiency is matching with that of marketed LiCoO₂ coin cell hence it can be upgraded to pouch cell, cylindrical cell, prismatic cells etc.. These upgraded batteries can be subjected to prototype testing for their effective use in electronic devices and vehicles. These present studies can be taken further by replacing lithium metal with the emergent sodium, Magnesium and Fluoride battery studies.

Further, curcumin can be derivatized with conjugated organic moieties or can be converted into nanocomposites by conjugation with highly conducting materials example metal/metal oxide nanoparticles (like Cu, Zn, Ni etc.) graphene, reduced graphene, Polyaniline, polythiophene etc., to achieve better battery performance.

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