



Thin copper phosphide films as conversion anode for lithium-ion battery applications

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ABSTRACT

Air stable copper phosphide of thicknesses (0.2, 0.4 μm) was synthesized over copper plates (of 10 mm diameter) by hybrid electrochemical deposition and low temperature solid-state reaction. Stoichiometric amount of red phosphorus (P) were sprayed over electrodeposited copper and followed by annealing at 250 °C under inert gas atmosphere for different durations (5 h, 7 h and 12 h). During this process, phosphorus particles diffuse by excavating into the copper deposits, producing holes, where the Cu_3P crystallites nucleate and lead to conglomeration of several agglomerates and hence resulted in non-homogeneous morphology. A small extend of Cu_3P oxidation occurs over the film's top surface. X-ray diffraction (XRD) patterns confirm that the layer to be pure Cu_3P . Scanning electron microscopy (FEG-SEM) reveals a porous microstructure consisting of agglomerated particles with $\sim 10 \mu\text{m}$ size. The as-prepared carbon-free Cu_3P electrodes exhibited significantly improved capacity retention and rate capability characteristics over 40 cycles when electrochemically tested against lithium at constant 20 $\mu\text{A}/\text{cm}^2$ rendering it as possible negative electrode for high energy density lithium-ion battery (LiB) applications.

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1. Introduction

Electric energy is required for several day to day applications and hence considered as bloodline for sustaining this modern society. Though, electricity could be generated by both renewable and non-renewable sources, the challenge lies on its storage [1]. Apart from myriad applications, stored form of this energy is essential for portable electronic devices and visualizes long run electric vehicles (EVs) [2–5] due to fast consumption of fossil fuels. For this application, electrochemical devices like battery and supercapacitor were best considered. Since the introduction of rechargeable lithium batteries in early 80's, lithium-ion batteries (LiBs) have undergone several developments in all aspects, and are now regarded as "Heart" for modern electronics due to its high power/energy density [1,4].

Today's immerse research on LiBs are devoted towards material chemistry [6] in discovering the best combination of anode and cathode as a replacement for commercialized graphite and LiCoO_2 , which is based on intercalation–deintercalation mechanism [7,8]. Their performances are limited due to structural inability involving only 0.5Li^+ transfer during cycling. High energy LiBs are foreseen using Sn, Si, Zn etc. as negative electrodes whose capacities are 3 to 10 times higher than graphite. Huge volume change occurs during cycling, limits these materials from being commercialized [8].

The discovery of conversion reaction involving reversible reaction of 2 or more e^- of metal oxides with lithium [9], prompt the exploration for other Metal–X compounds with $X = \text{O}, \text{N}, \text{F}, \text{S}, \text{P}$ and even H [9–23] as possible negative electrodes for high energy density lithium-ion battery (LiB) applications. A typical conversion reaction equation could be given as: $M_aX_b + (b-n)\text{Li} \rightarrow aM + b\text{Li}_nX$. The possible explanation for reversibility of conversion reaction depends on the formation of metal nanoparticles over lithium binary compound (Li_nX) matrix upon complete reduction and the former being very active due to possession of large amount of interfacial surface helps in decomposition of Li_nX matrix when reverting the polarity of the circuit. This nanometric character of the metal nanoparticles has shown to be maintained over several redox cycles [8,9,21].

The major limitations of conversion reactions are poor kinetics, marked by large hysteresis in voltage between charge and discharge and poor capacity retention upon cycling [8,11]. Therefore, for its effective utilization in practical cells, it is imperative to reduce this hysteresis which limits LiB's energy efficiency and power capabilities. From several literatures, it is noted that the polarization (ΔV) decreases from fluorides ($\Delta V \sim 1.1\text{V}$) to oxides ($\Delta V \sim 0.9\text{V}$), sulfides ($\Delta V \sim 0.7\text{V}$) and phosphides ($\Delta V \sim 0.4\text{V}$) [7,8,21]. This is due to the fact that the redox centres are not exclusively located on the transition metal, but electron transfer also occurs into the bands that have a strong anion contribution. It was shown that the actual potential at which conversion occurs depend on both the transition metal and the anionic species, so that, in principle, its reaction potential could be tuned to the required application [8].

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Apparently, metal phosphides may be an option as anodic materials [19–22] for LiB applications for above reasons. Phosphorus forms solid compounds with nearly all the elements in the periodic table, but its presence are less known unlike others [24]. However, the syntheses of all these materials is usually complicated as these requires the use of special devices, such as vacuum sealed tubes and have to be handled and stored under inert atmospheres and hence prevent it from realization for industrial preparation. Metal phosphides (M_xP_y) could be synthesized viz., high temperature solid state technique [25,26], ball milling [27,28] and low temperature hydro- and solvo-thermal methods [29–31].

Copper forms three phosphorus compounds (Cu_3P , CuP_2 and Cu_2P_7) according to Cu–P phase diagram [24]. Among them, only Cu_3P is air stable and already presents industrial applications as a kind of fine solder and as an important alloying addition [31]. Copper phosphide (Cu_3P) presents good qualities as negative electrode. Since no Li–Cu compounds have been reported in the corresponding phase diagram, the reaction in which the maximum lithium uptake of the elements is admitted could be: ($Cu_3P + 3Li \rightarrow 3Cu + Li_3P$). Though, gravimetric capacity of Cu_3P (377 mA h/g) is close to that of graphite (372 mA h/g), but its volumetric capacity (2778 Ah/L) is almost four times higher than that of graphite (800 Ah/L) [19,26,29,32].

As mentioned earlier, like other metal phosphides, Cu_3P powders/films were synthesized by similar techniques [25–31] and subsequently, its electrochemical cycling were tested. The main drawbacks of these methods were requirement of (1) absolute inert atmosphere due usage of air sensitive chemicals and (2) high temperature (400–900 °C) for solid state synthesis. After these careful considerations, herein, we presented a hybrid technique to produce carbon-free Cu_3P thin films over Cu current collector and firstly, reported the effect of various film thicknesses and annealing time on its electrochemical reactivity against lithium.

2. Experimental

A typical hybrid electrochemical deposition and low temperature solid state synthesis were employed to envision the product, Cu_3P . This section would elaborate on material synthesis and details of instrumentation for materials characterization.

2.1. Synthesis of Cu_3P material over Cu plate

2.1.1. Electrochemical deposition of copper

Pulse electrodeposition (using AUTOLAB, PGSTAT 302N, Metrohm) was carried out in a 50 mL capacity cell from an alkaline electrolyte [10,11] consisting of 100 g/L $CuSO_4 \cdot 5H_2O$ (Sigma Aldrich), 20 g/L $(NH_4)_2SO_4$ (Sigma Aldrich) and 80 mL/L diethyl-tri-amine (DETA, Sigma Aldrich) to electrodeposit copper of various thickness (2.5, 1.5, 0.8, 0.4, 0.2 μm). Prior to electrodeposition, the Cu plates (of 10 mm diameter) were polished following these successive steps, with 800, 1200 and 2400 grit sand paper and then with 6, 3, 1 and 0.25 micron diamond suspension using a polishing cloth. After this last step, copper disc surfaces exhibited a mirror look meaning that an object is perfectly reflected without any deformation. Copper deposits were obtained by electrodepositing for appropriate duration (using Faraday's I law of electrolysis) while assuming 99% electrolyte's current efficiency. All electrodeposition experiments were carried out at room temperature (30–32 °C).

2.1.2. Low temperature solid state synthesis

Firstly, calculated stoichiometric amount of red phosphorus (Spectrochem Pvt. Ltd., Mumbai) for each deposit were dispersed in acetone using ultra-sonicator and were uniformly sprayed over, respective, electrodeposited copper plates. Each set of samples

were heated at 1 °C/min in tubular furnace (Thermo Scientific, Lindberg Blue M) under an inert (N_2 gas) atmosphere at constant 250 °C for different durations like 5 h, 7 h and 12 h. The samples were collected after cooling to room temperature (32 °C) and the same were characterized for phase composition, morphology and electrochemical studies against lithium.

2.2. Phase composition and morphology characterization of copper phosphide films

X-ray diffraction (XRD) measurements were performed with X'PERT PRO PANalytical (Model: PW3040 160 X'Pert PRO, Netherlands) equipped with Cu K_α radiation. XRD patterns were compared with JCPDS data to identify the phase of each samples.

Field Emission Gun – Scanning Electron Microscope (FESEM) (JOEL, Model: JSM-7600F, Japan) coupled with energy dispersive X-ray (EDX) was used to characterize the surface morphology and compositional analysis of copper phosphide films. The instrument was operated at 0.1–30 kV.

2.3. Electrochemical behaviour with lithium

Swagelok-type cells were assembled in an argon-filled dry glove box (Mbraun, MB10 compact) using the Cu_3P thin films as the positive electrode and the Li metal as the negative electrode. Both positive and negative electrodes were electronically separated by a Whatman GF/D borosilicate glass-fibre sheet saturated with 1 M $LiPF_6$ electrolyte solution (in EC:DMC/1:1 in mass ratio) purchased from Merck. Unless it is specifically stated, otherwise, the cells were galvanostatically cycled (in Arbin Instrument's BT2000) between 0.01 V and 2.5 V at constant 20 $\mu A/cm^2$. In-situ impedance spectroscopy at various potentials during first discharge-charge cycle were measured using Biologic Science Instruments (Model: VMP3; S/n: 0398) between 0.1 MHz to 10 mHz under AC stimuli with 5 mV of amplitude.

3. Results and discussion

Fig. 1 shows the overall morphology of the electrodeposited copper over Cu plates/discs. These deposits were obtained at constant current densities of -2 and -30 mA/cm². The latter have well-defined grain boundary and adherent/compact deposits [33] as compared to former conditions. The deposits obtained at -2 mA/cm² were utilized for rest of the experiments since it would permit the fast reactivity and P diffusion while heating to form Cu_3P thin films.

Preliminary experiments were made at various temperatures between 250 °C to 400 °C for constant 5 h duration. To the surprise, pure Cu_3P phase was obtained at minimum temperature of 250 °C while distinct Cu oxidation to cuprous oxide and sublimation of P occurs at elevated temperatures. Hence, the temperature was fixed at 250 °C and thereon, studied the effect of heating time which would play a vital role in the conversion of Cu deposits of different thicknesses to copper phosphide which in turn would determine the kinetics between the active materials (Cu_3P) and Cu current collector [10,11].

3.1. Phase and compositional analysis

Fig. 2 shows the different XRD patterns obtained for the Cu–P discs, heat treated at 250 °C for various time 5 h, 7 h and 12 h, respectively. With the exception of the reflections owing to metallic copper of the substrate, the XRD pattern of the heat treated copper deposits reveal Bragg peaks which can all be indexed on the basis of a hexagonal cell with the following lattice parameters: $a = 6.992$ Å and $c = 7.170$ Å, and $P\bar{3}c1$ space group (JCPDS No.: 74-1067). XRD

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