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Comparison of copper compounds on copper foil as current collector for fabrication of graphene/polypyrrole electrode

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ABSTRACT

Finding new materials for supercapacitors with the aim of improving their energy density and performance has been recently considered. Herein, a novel current collector material for graphene/polypyrrole electrodes using different copper compounds is introduced.

In this study, nanowire-like $Cu(OH)_2$ arrays, urchin-like microsphere CuO, and leaf-shaped hydrophobic STA-CuO were directly synthesized by a simple and cost-effective liquid–solid reaction method. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM) were used for the analysis of prepared samples. XRD and FTIR analysis confirmed the formation of CuO, $Cu(OH)_2$ and STA-CuO on the copper foil. FESEM results showed the formation of copper compounds with different morphologies. The specific capacitance achieved for $Cu(OH)_2$, CuO, STA-CuO electrode were 200, 55, 30 Fg^{-1} at the scan rate of 10 mVs^{-1}. In the next step, the graphene, polypyrrole and graphene/polypyrrole composite were deposited on $Cu(OH)_2$/Cu-foil as a supercapacitor electrodes. XRD and FTIR analysis confirmed the formation of polypyrrole on graphene sheets. The best specific capacitance was achieved for graphene/polypyrrole/$Cu(OH)_2$ equal to 311 Fg^{-1} at a scan rate of 10 mVs^{-1}. Therefore, the graphene/polypyrrole/$Cu(OH)_2$ electrode showed the best supercapacitive performance.

1. Introduction

In recent years, supercapacitors have attracted considerable attention because of their high power density, fast charge/discharge rate, and low cost. They have been widely used in various applications such as electric vehicles, industrial equipment and energy production. Electrochemical capacitors have different parts: electrodes, separator and electrolyte. Electrode is an important part of a supercapacitor [1–4]. Each electrode consists of several parts including an electroactive material layer, a bonding layer, and a current collector.

Different materials such as carbon-based material, conducting polymers, and metal oxides have been used for supercapacitor fabrication. But each of them has some advantages and disadvantages. Carbon materials have good mechanical properties and long cycle life, but their specific capacitance is low. Metal oxide electrodes show high specific capacitance, but they have low electrical conductivity and instable structure. Conducting polymers show high specific capacitance, but their cycle life still needs to be improved [5–7]. In addition, electrodes are usually fabricated by casting electrode slurry on a current collector such as nickel foam (NF). Electrode slurry is prepared by stirring a mixture of active materials, conductive agents, and binders. Binders play roles of binding active material and conductive agent together and also cohering with current collector, to avoid active materials falling off during the electrode working, but binders cover some surface areas or pores of active materials and increase resistance of electrode.

Moreover, the current collector is another important part of the electrode, which guarantees the active material polarization through its electronic conductivity. Using low cost material for the current collector is also essential for supercapcitors commercialization [8].

Therefore, to fabricate low cost supercapcitors with high electrochemical properties and low resistance, it is necessary to design a new electrode. To do so, it is possible to combine carbon materials with metal oxides or conducting polymers, design of binder-free electrode to prevent the “dead surface” in electrode and using low cost current collector with good electrical conductivity.

Among carbon materials, graphene is a more attractive option because of its unique morphology, chemical stability, and good electrical conductivity. Recently, a large number of studies have been conducted with the aim of improving the properties of graphene electrodes by fabricating a binary graphene/polypyrrole composite [9–11]. Recently, polypyrrole (PPy) has become very important because of their good

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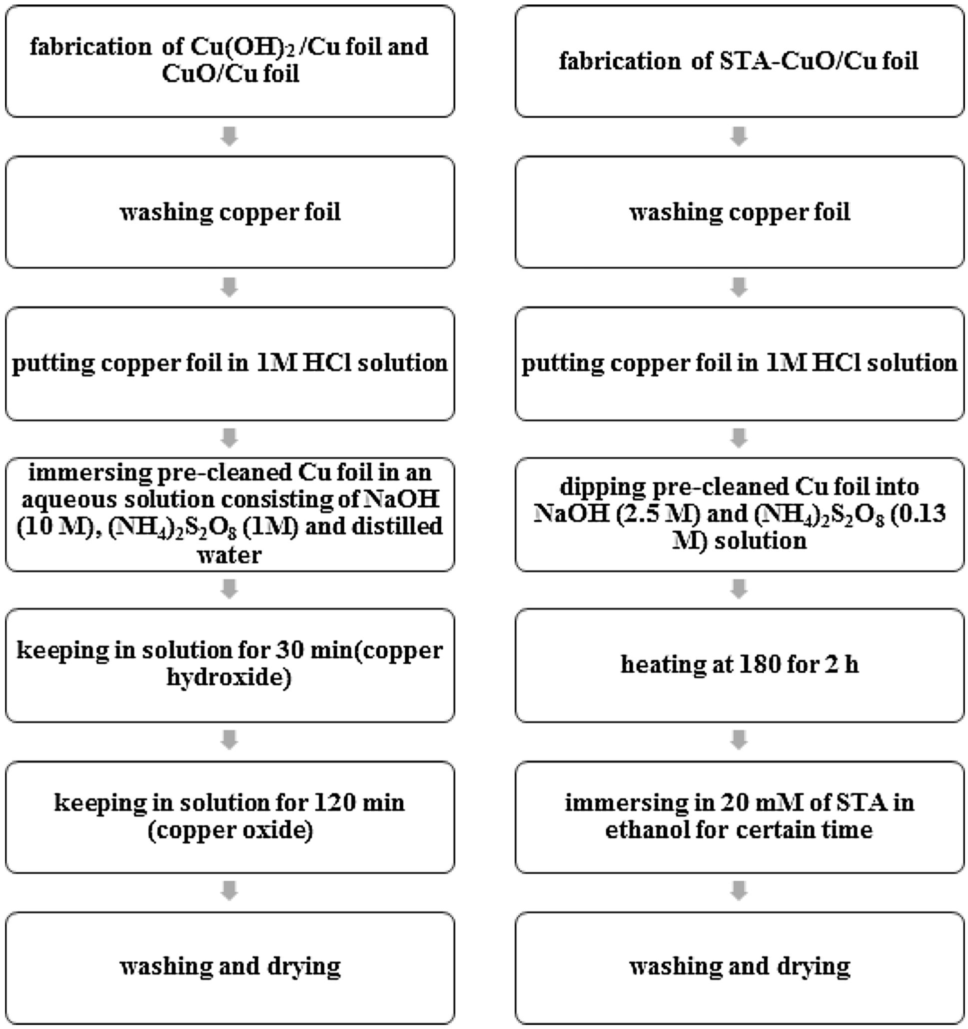

Fig. 1. Flowchart of fabrication steps of copper compounds.

electrical conductivity, facile synthesis process and their cost. PPy has the potential to improve the capacitance through faradic reaction, which can enhance the overall capacitance of the nanocomposite.

In addition to the use of new electroactive material, some researches have investigated different current collectors for fabrication of low resistance and low cost electrode. Shi et al fabricated free binder polypyrrole electrode by polymerization of pyrrole in an aerogel-based current collector composed of crosslinked cellulose nanocrystals (CNCs) and multiwalled carbon nanotubes [12], Yang et al also investigated aerogel Cellulose nanocrystals (CNCs) current collector for fabrication of binder free PPy-CNT electrode [13]. Using these new current collectors, the researchers succeeded in making electrodes with appropriate electrochemical and mechanical properties. Furthermore, different metal current collector such as nickel foam, copper, aluminum or stainless steel have been used as a current collector, among which, nickel foam is expensive, and aluminum and stainless steel have lower electrical conductivity. Therefore, copper is the ideal metal electrode substrate with its low cost, low resistance, and good electrical conductivity. However, copper is very sensitive and it is hard to prevent the copper oxidation and corrosion during cycling. Hence, to use copper as the current collector, it is necessary to protect the copper surface from oxidation and corrosion [14].

Different strategies, such as cathodic protection [15], corrosion inhibitors [16], self-assembly monolayers (SAM) [17], inorganic coatings [18], conducting polymeric coatings [19], organic–inorganic coatings [20], or any combination thereof, have been developed to address the growing need of copper corrosion inhibition in aggressive aqueous solutions. However, all of these methods are subject to certain limitations, such as the high cost and hydrogen embrittlement of cathodic protection, the environmental toxicity of organic inhibitors [21], poor durability and limited corrosion resistance of SAMs [22], poor adhesion and water permeability of conducting polymer coatings [23]. Therefore, an alternative strategy is desirable to provide effective and long-term protection for copper corrosion.

Recently, significant efforts have been devoted to low-cost synthesizing of copper oxide (CuO), copper hydroxide ($Cu(OH)_2$), and hydrophobic copper compounds on copper substrates to protect them from corrosion. The common synthetic methods of CuO and $Cu(OH)_2$ nanostructures are thermal oxidation, liquid-solid reaction, electrodeposition and hydrothermal synthesis [14,24–30], among which, liquid-solid reaction (immersion solution) has a simple procedure for fabricating copper oxide and copper hydroxide. In addition, in the research conducted by Panpan Xu et al. [24], copper compound were bonded electroactive material to current collector in addition of working as protection layer, so with this method it is possible to fabricate binder- free electrode with high utilization of the active material and conductivity.

In this study, we selected copper foil as a current collector and for protecting the copper surface from oxidation and corrosion, at first, $Cu(OH)_2$, CuO, and hydrophobic STA-CuO were directly grown on copper foils with a simple and facile method. Then, graphene/PPy powder was synthesized by the in-situ polymerization method. Finally, the