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Comparative study of electroless nickel film on different organic acids modified cuprammonium fabric (CF)

Hang Zhao, Yinxiang Lu*

Department of Materials science, Fudan University, Shanghai, 200433, China

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ABSTRACT

Nickel films were grown on citric acid (CA), malic acid (MA) and oxalic acid (OA) modified cuprammonium fabric (CF) substrates via electroless nickel deposition. The nickel films were examined using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Their individual deposition rate and electromagnetic interference (EMI) shielding effectiveness (SE) were also investigated to compare the properties of electroless nickel films. SEM images illustrated that the nickel film on MA modified CF substrate was smooth and uniform, and the density of nickel nuclei was much higher. Compared with that of CA modified CF, the coverage of nickel nuclei on OA and MA modified CF substrate was very limited and the nickel particles size was too big. XRD analysis showed that the nickel films deposited on the different modified CF substrates had a structure with Ni (1 1 1) preferred orientation. All the nickel coatings via different acid modification were firmly adhered to the CF substrates, as demonstrated by an ultrasonic washing test. The result of tensile test indicated that the electroless nickel plating on CF has ability to strengthen the CF substrate while causes limited effect on tensile elongation. Moreover, the nickel film deposited on MA modified CF substrate showed more predominant in EMI SE than that deposited on CA or OA modified CF.

1. Introduction

Nonconductive nature of regenerated cellulose fibers brings about inevitable drawbacks such as static charge accumulation and transmission of the electromagnetic waves in apparel, biomedical or industrial textiles (building, automotive, filtration, etc.). Accumulation of static charge beyond a certain level may cause electric spark and lead to fire hazard. Transmission of electromagnetic waves may cause electromagnetic interference (EMI) which is undesirable for electronic equipments and as well as harmful to human body [1–4]. To overcome these problems, many researches have been carried out to impart electrical conductivity in them. Incorporation of metal fibers or metal powders during spinning processing, inserting metal wires in textile structure, selecting intrinsically conductive polymers (polypyrrole, ployaniline, etc.) for spinning, etc. [5–8], are common technologies of manufacturing conductive textiles. However, those aforementioned methods are always sophisticated and high-cost. An efficient and simplified method is urgently required to impart electrical conductivity to textiles. Electroless plating is also one of the most frequently adopted industrial processes for metallization due to its low cost, inherent selectivity and simplicity of processing. In a typical electroless plating process, metal coating was directly formed on the substrate, which would transform the textile from insulative to conductive. As with electroless plating, the first issue to be resolved is the poor adhesion of insulative substrate to metals due to its chemically inert nature [9]. Various pretreatment methods have been adopted to improve metal adhesion to the regenerated cellulose fiber substrate, such as plasma treatment [10–12] and etching with vigorous mineral acid [13]. As we known, those treatments always generate adverse effect on the substrate's mechanical property. Consequently, with the aim to circumvent this difficult problem, finding a moderate treatment to strengthen metal layer to substrate, chemical modification technique was selected in this paper. Chemical modification technique allows one to grow thin organic films uniformly on solid surfaces. Organic thin film can serve as a modification layer and modify surface properties. Organic polyatomic acids, which have been used for modification, are expected to produced carboxylic (–COOH) on the surface of cellulosic (Ce–OH) fabrics. After the surfaces have been treated with organic polyatomic acids (i.e. citric acid (CA), malic acid (MA), oxalic acid (OA)), the original chemically inert hydroxyl surfaces are functionalized with –COOH groups via ester bond with cellulosic (Ce–OH) fabrics [14]. The adventitious –COOH groups on

* Corresponding author. Tel.: +86 21 55665059; fax: +86 21 55665059.
E-mail address: yxlu@fudan.edu.cn (Y. Lu).

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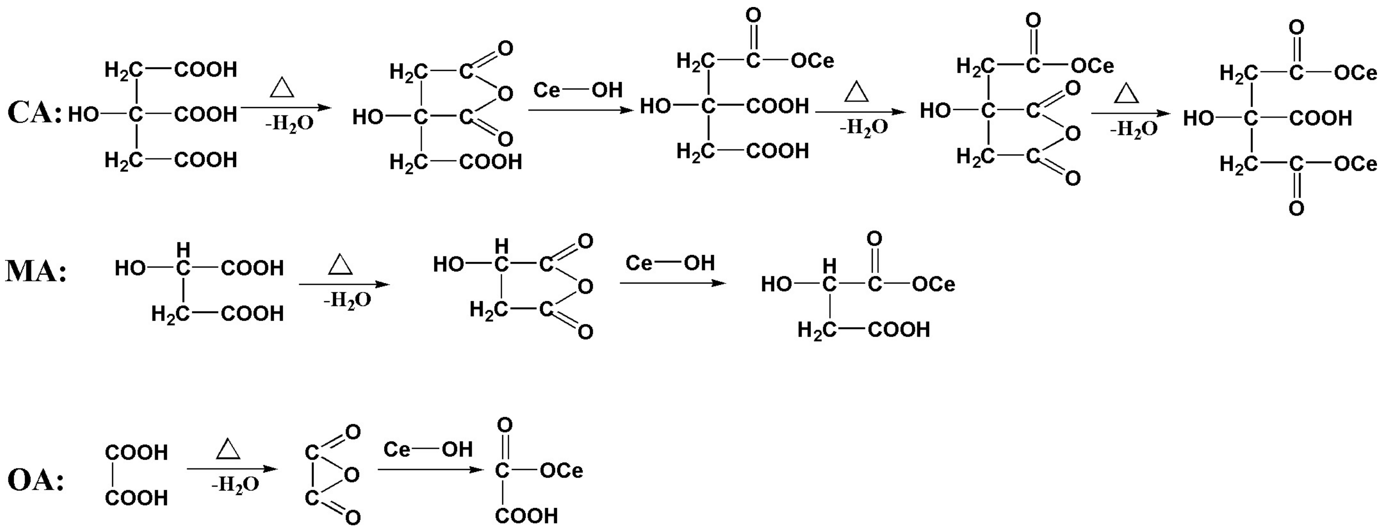

Fig. 1. Thermo-chemical reaction of cellulosic (Ce-OH) fabrics with citric acid (CA), malic acid (MA) and oxalic acid (OA).

Table 1
Formulations and operation conditions of electroless nickel plating bath.

Formula	Amount
Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	25 g/L
dimethylamine-borane (DMAB)	1.5 g/L
sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	25 g/L
$NH_3 \cdot H_2O$	To adjust pH 12
Temperature (°C)	50
Time (h)	0.5

the surface of the as-modified substrate can facilitate the dative adsorption with noble catalytic metal nanoparticles and the subsequent adhesion of metal layer to substrate. Hence, the organic acids modification could enhance the adhesive strength of metal layer and substrate by chemical sorption, instead of the physical sorption in the conventional plasma treatment or vigorous acid etching.

In the present work, comparative study of electroless nickel film on different organic acids modified cuprammonium fabric was conducted to find out the prime modifying agent among CA, MA and OA. Herein, cuprammonium fabric (CF) is a kind of man-made cellulosic (Ce–OH) fabrics, and was selected as the substrate for electroless nickel plating due to its considerably light-weight and acceptable biodegradability [15]. In order to understand the interaction mechanism between the CF substrates and the organic acid molecules, Infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) studies were conducted. The surface morphology and crystal structure of the resultant nickel plated CFs were detected by scanning electron microscopy (SEM) and X-ray diffractometer (XRD) measurements. Surface resistance (R_s) was measured by the four probe method described in ASTM F 390. R_s is considered to be the resistance of a square sample, and unit of R_s is expressed as Ω/sq. Electromagnetic interference (EMI) shielding effectiveness (SE) of the resultant nickel plated CFs was measured by using a Spectrum analyzer with a scattering parameter test set over a frequency range of 0.3–1000 MHz. Ultrasonic washing test and tensile test were utilized to evaluate the reliability of the obtained nickel coated cuprammonium textile composites.

2. Experimental

2.1. Materials

The CFs (45 × 45 count/cm^2, 8 mg/cm^2) used were man-made cellulosic (Ce-OH) fabric purchased from Taicang Biqi Novel Material Co., Ltd, the area of CFs was precisely cut into 5 cm × 5 cm patch before experiments. Citric acid (CA), malic acid (MA) and oxalic acid (OA) were obtained from Sinopharm Chemical Reagent Co., Ltd. All the other chemicals used were of analytical grade.

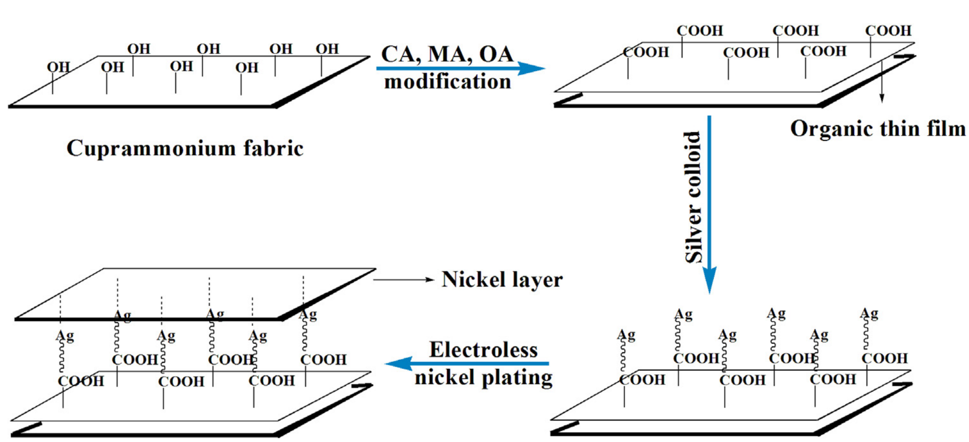

Fig. 2. Procedures for the manufacture of nickel coated cuprammonium fabric (CA, MA and OA are the abbreviation of citric acid, malic acid and oxalic acid, respectively).