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# Laser-hybrid fabrication of highly-dispersed substrate-bonded manganese carbonate microspheres

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## ARTICLE INFO

## Article history:

Received 9 December 2015

Received in revised form

5 July 2016

Accepted 16 July 2016

Available online 18 July 2016

## Keywords:

MnCO<sub>3</sub>

Microsphere

Laser processing

Dealloying

Energy storage and conversion

## ABSTRACT

Development of binder-free electrode materials tightly bonded to current collector effectively improves the performance of energy conversion and storage devices. In this letter, we report the fabrication of highly-dispersed MnCO<sub>3</sub> microspheres directly grown out of a laser cladded substrate through dealloying process. First, laser cladding of Cu and Mn powder mix creates a layer of single-phase Cu–Mn alloy on a stainless steel substrate. Next, during dealloying, Mn is preferentially oxidized on the surface of the Cu–Mn alloy layer where the MnCO<sub>3</sub> nuclei instantaneously form and subsequently grow into hierarchical microspheres. The high dispersivity of MnCO<sub>3</sub> microspheres signifies a large specific surface area, which is highly desirable as an electrode material. Additionally, our unique hybrid fabrication approach eliminates the need for adhesive between the electrode material and its supporting substrate, and thus minimizing the interface resistance.

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## 1. Introduction

The ever-growing energy consumption demands highly efficient energy conversion and storage devices. Electrochemical capacitors (ECs) and lithium-ion batteries (LIBs) are such examples. Tremendous efforts have been put in developing improved electrode materials, which is important to achieve higher energy/power densities, improved safety and longer cycle life.

Owing to its outstanding capacity, low costs, natural abundance and environmentally friendliness, MnCO<sub>3</sub> is regarded as promising anode material for high-performance LIBs [1,2]. On the other hand, MnCO<sub>3</sub> is usually used as a typical and solid precursor in the preparation of manganese oxides, which are important electrode materials for ECs [3].

The performance of the electrodes is largely determined by two factors, i.e. the morphology of the electrode material, and the quality of grafting of the electrode material onto the supporting current collector [4]. During the past years, most effort has been focused on the fabrication of MnCO<sub>3</sub> micro-/nanostructures with increased porosity and specific surface area [5–8]. In comparison, however, there lacks the consideration on how well the MnCO<sub>3</sub> micro-/nanostructure joins the supporting current collector. Conventionally, the electrodes are obtained by mechanically pressing a mixed paste of pre-made electrode material powder, conductive additive and polymer binder onto metallic current collectors. The

drawbacks of these powder electrodes lie in two folds: a) the mixed composite paste lacks well interconnected pore structures, which undesirably reduces the specific surface area of the electrode; and b) mechanical bonding results in abrupt discontinuity between the mixed composite paste and the current collector, which compromise the performance of the electrode.

Approaches to address these issues primarily involve creating nanoscaled skeleton, on which MnO<sub>2</sub> active material is plated. For example, Sun et al. fabricated a porous electrode by growing MnO<sub>2</sub> on a skeleton of Ni foam. Similarly, MnO<sub>2</sub> has also been fabricated on Au skeletons, such as Au nanoporous film [9]. These approaches successfully achieved high capacitive properties due to the increase in active surface area of electrode and the reduction of interface resistance. However, it is not easy to achieve a high loading mass of the active electrode materials using nanoscaled skeletons, compromising its prospect in real applications.

Herein, we present a novel laser-hybrid approach for fabricating electrodes, i.e. laser cladding of Cu–Mn alloy layer on a substrate followed by selective electrochemical etching (or dealloying) to form highly-dispersed MnCO<sub>3</sub> microspheres as the electrode material, resulting in a large specific surface area and direct attachment to the current collector. The as-fabricated structure can also be applied as the precursor for fabrication of manganese oxides, which will inherit the above-mentioned advantages. We introduce the fabrication method as well as propose the formation mechanism of MnCO<sub>3</sub> microspheres.

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## 2. Experimental procedure

The procedure of hybrid fabrication of MnCO<sub>3</sub> microspheres is illustrated in Fig. 1. First, a mixture of Cu and Mn powder (40 at% Cu and 60 at% Mn) was deposited on a high-purity stainless steel substrate, and laser-cladded with a fiber laser (IPG YLS-6000) to form a 1-mm-thick film of Cu-Mn alloy. During laser cladding, a laser beam with a power of 2200 W scanned over the Cu-Mn powder-covered substrate at the speed of 4 mm/s, while argon was used as the protective gas. The resulting Cu-Mn alloy film was metallurgically bonded to the substrate, and served as the precursor for dealloying. Next, the Cu-Mn alloy film was used as the working electrode in a three-electrode cell (Bio-Logic VMP3) with 0.5 M KNO<sub>3</sub> electrolyte, where a saturated calomel electrode and a platinum sheet were used as the reference and counter electrodes, respectively. The dealloying process was conducted at 298 K with an electrode potential of 0.5 V for an hour.

To analyze the composition of the fabricated samples, X-ray diffraction (XRD) patterns were first recorded by an X-ray diffractometer (D8 Advance, Cu target). Surface analysis was also carried out by X-ray photoelectron spectroscopy (XPS) using an X-ray photoelectron spectrometer (PHI 5300) with a monochromatic Al K $\alpha$  source and a pass energy of 30 eV and a step size of 0.05 eV. The fabricated samples were examined with a field-emission scanning electron microscope (FE-SEM, Quanta 650 FEG) and a transmission electron microscope (TEM, JEOL JEM-2100) equipped with energy dispersive spectroscopy (EDS).

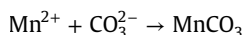
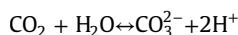
## 3. Results and discussion

Fig. 2 shows the XRD patterns and XPS spectrum of the laser cladded Cu-Mn alloy film before and after dealloying. In the XRD pattern before dealloying (Fig. 2a), sharp peaks were identified as face-centered cubic (fcc) single-phase solid solution (Cu, $\gamma$ Mn) with the main diffraction peaks of (111), (200), and (220). In the XRD pattern after dealloying (Fig. 2b), rhombohedral phase of MnCO<sub>3</sub> with the space group of *R*-3c was determined to be the major component (JCPDS No. 44-1472), although a minute amount of Cu<sub>2</sub>O was also found in the dealloyed film. The sharp and narrow peaks in the XRD pattern indicate the abundance of well crystallized MnCO<sub>3</sub> microspheres. XPS was used to further determine the composition of the dealloyed film (Fig. 2c). The dealloyed film contained Mn, O and C as the main constituents. In the Mn 2p spectrum (Fig. 2c inset), the peaks of Mn 2p<sub>1/2</sub> and Mn 2p<sub>3/2</sub> were centered at 652.6 eV and 640.8 eV with a spin energy separation of 11.8 eV, which is characteristic of MnCO<sub>3</sub>, agreeing with previous literature [10,11].

The morphology of the dealloyed film is shown in Fig. 3. Fig. 3a is the top-view of the FESEM image of the dealloyed structure. The structure consisted of highly-dispersed regularly-shaped MnCO<sub>3</sub> microspheres, with their diameters ranging from 5 to 10  $\mu$ m. At a higher magnification (Fig. 3b), finer substructures can be observed on the surface of the microsphere, which in a TEM image (Fig. 3c) were identified as nanoflakes with a size of hundreds of nanometers. These nano-flake substructures were beneficial to

increase the surface area of active materials. The EDS results confirmed that the nanoflakes mainly consisted of manganese, carbon, and oxygen, a chemical composition that agreed well with the MnCO<sub>3</sub> (Fig. 3d). The presence of modicum of molybdenum was attributed to the supporting film used in TEM. Fig. 3e is a cross section image of MnCO<sub>3</sub> microspheres at the interface with the substrate, indicating that the MnCO<sub>3</sub> microspheres grew directly out of the Cu-Mn alloy layer, which was in solid attachment with the substrate. In contrast to the approach with polymer binder, the space between the microspheres was open and clear, which would effectively enhance electrolyte accessibility for ion transportation when serving as LIB electrodes. The micrographs (Fig. 3) witness that the obtained MnCO<sub>3</sub> microspheres are quite fine-grained and contain, therefore, very developed grain boundaries and free surfaces. It has been recently demonstrated that the physical properties of pure and doped nanograined oxides strongly depend on the presence of defects like interphase boundaries and grain boundaries [12] and on the presence of doping atoms in the amorphous surficial, interfacial and intergranular layers [13]. Therefore, the effects of grain boundaries on MnCO<sub>3</sub> microspheres are to be further studied in the future.

Based on the microstructure observation, we suggest that the formation of MnCO<sub>3</sub> microsphere involves nucleation and subsequent growth of the nuclei during dealloying process. Initially, under the electrochemical conditions, the Mn atoms on the surface of the Cu-Mn alloy film become Mn<sup>2+</sup>, which immediately react with CO<sub>3</sub><sup>2-</sup> to form MnCO<sub>3</sub> nuclei. CO<sub>3</sub><sup>2-</sup> is suggested to originate from CO<sub>2</sub> dissolved in the electrolyte. For example, Hu et al. [14] also used the CO<sub>2</sub> in the atmosphere as the source of carbonate ions to fabricate MnCO<sub>3</sub> hierarchical superstructures. Thus, the formation of MnCO<sub>3</sub> nuclei goes through the following reactions:



Due to the crystal nature of the rhombohedral structure of MnCO<sub>3</sub>, the initial MnCO<sub>3</sub> nuclei take the form of nanosheets. These nanosheets then tend to aggregate into microspheres to overcome high surface energy as shown in Fig. S1 (Supplementary material). Gradually, the smaller and thermodynamically unfavored microspheres further coalesce to form larger ones.

Successful dealloying requires the precursor alloy to be a single phase alloy composed of two alloying components with large electrochemical potential difference [15,16]. The standard reversible potentials of Cu and Mn are 0.342 V and -1.135 V, respectively, (both relative to standard hydrogen electrode (SHE)), and thus have a 1.477 V difference apart from one another, which is distinct enough to achieve selective electrochemical etching of Mn given appropriate conditions. The single Cu-Mn phase, on the other hand, is ensured by the rapid cooling from liquid state during laser cladding according to the Cu-Mn phase diagram, indicating the suitability of the laser cladding approach in producing

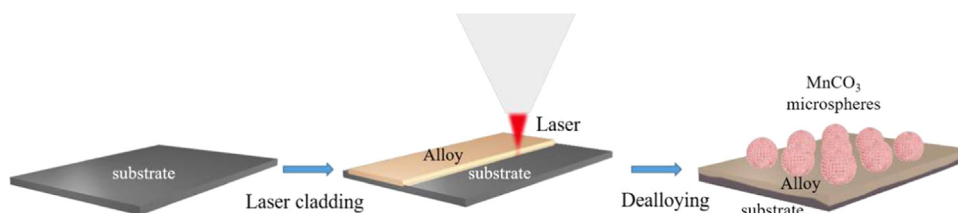


Fig. 1. Schematics of laser cladding-hybrid dealloying method.

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