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

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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 MnCO3 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 MnCO3 nuclei instantaneously form and subsequently grow into hierarchical microspheres. The high dispersivity of MnCO3 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, MnCO3 is regarded as promising anode material for high-performance LIBs [1,2]. On the other hand, MnCO3 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 MnCO3 micro-/nanostructures with increased porosity and specific surface area [5–8]. In comparison, however, there lacks the consideration on how well the MnCO3 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 MnO2 active material is plated. For example, Sun et al. fabricated a porous electrode by growing MnO2 on a skeleton of Ni foam. Similarly, MnO2 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 MnCO3 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 MnCO3 microspheres.

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2. Experimental procedure

The procedure of hybrid fabrication of MnCO3 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 KNO3 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 Kα 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, yMn) with the main diffraction peaks of (111), (200), and (220). In the XRD pattern after dealloying (Fig. 2b), rhombohedral phase of MnCO3 with the space group of R-3c was determined to be the major component (JCPDS No. 44-1472), although a minute amount of Cu2O was also found in the dealloyed film. The sharp and narrow peaks in the XRD pattern indicate the abundance of well crystallized MnCO3 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 2p1/2 and Mn 2p3/2 were centered at 652.6 eV and 640.8 eV with a spin energy separation of 11.8 eV, which is characteristic of MnCO3, 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 MnCO3 microspheres, with their diameters ranging from 5 to 10 μm. 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 MnCO3 (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 MnCO3 microspheres at the interface with the substrate, indicating that the MnCO3 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 MnCO3 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 MnCO3 microspheres are to be further studied in the future.

Based on the microstructure observation, we suggest that the formation of MnCO3 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 Mn2+, which immediately react with CO3²⁻ to form MnCO3 nuclei. CO3²⁻ is suggested to originate from CO2 dissolved in the electrolyte. For example, Hu et al. [14] also used the CO2 in the atmosphere as the source of carbonate ions to fabricate MnCO3 hierarchical superstructures. Thus, the formation of MnCO3 nuclei goes through the following reactions:

$$\text{Mn} \rightarrow \text{Mn}^{2+} + 2e^-$$

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_3^{2-} + 2\text{H}^+$$

$$\text{Mn}^{2+} + \text{CO}_3^{2-} \rightarrow \text{MnCO}_3$$

Due to the crystal nature of the rhombohedral structure of MnCO3, the initial MnCO3 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 unfavorable 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...
the precursor alloy for subsequent electrochemical process.

4. Conclusions

In summary, we have fabricated highly-dispersed substrate-bonded MnCO₃ microspheres with hierarchical structure through a hybrid method involving laser cladding of Cu-Mn alloy precursor coupled with a dealloying process. The Cu-Mn alloy precursor by laser cladding formed a single phase and possesses large electrochemical potential difference between the two constituent elements, satisfying the prerequisites for a successful dealloying process that followed. During dealloying, the nucleation of MnCO₃ began by the reaction between Mn²⁺ and CO₃²⁻ in the initial stage, and took the form of nanosheets. Then, the MnCO₃ nuclei aggregated to form microspheres, which increased in size through further coalition, and eventually resulted in highly-dispersed regularly-shaped microspheres solidly attached to the substrate. The fabricated structure can serve as ready templates for further fabrication of other important electrode materials, e.g. manganese oxides, in which the advantages of high specific surface area and low interface resistance can be easily retained.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2016.07.075.

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