Journal of Power Sources 294 (2015) 354–359

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Two-dimensional titanium carbide electrode with large mass loading for supercapacitor

Shuang-Yan Lin, Xitian Zhang*

Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of Physics and Electronic Engineering, Harbin Normal University, Harbin 150025, PR China

HIGHLIGHTS

- Ti_3C_2 electrodes with different mass loading have been investigated.
- Large mass loading electrode retains high specific capacitance and cycling stability.
- Possible mechanism for the high capacitive performance was proposed.
- The intercalation pseudocapacitance occurred in the Ti_3C_2 materials.

ARTICLE INFO

Article history:
Received 29 April 2015
Received in revised form
10 June 2015
Accepted 15 June 2015
Available online xxx

Keywords:
Supercapacitor
MXene
Titanium carbide
Mass loading
Cycling stability
Intercalation pseudocapacitance

ABSTRACT

Layered titanium carbide (Ti_3C_2) has been synthesized by exfoliation of ternary carbides Ti_3AlC_2 and evaluated as working electrodes with different mass loading from 1.8 mg to 7.6 mg. The effect of mass loading on the electrochemical properties of Ti_3C_2 electrodes was studied by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and impedance spectrum test. With increasing of Ti_3C_2 mass from 1.8 to 7.6 mg/cm^2 in electrode, the specific capacitance calculated from the CV curves at 2 mV/s decreases at first from 117 to 78 F/g then maintains at 76 F/g, while areal capacitance increases from 211 to 579 mF/cm^2. Moreover, both electrodes with low mass loading (1.8 mg) and large mass loading (7.6 mg) have delivered good cycling performances with capacitance retention of 97% and 98% after 10000 cycles. These results indicate that large mass loading electrode retains high specific capacitance and good cycling stability, due to the excellent electronic conductivity and layered structure of Ti_3C_2.

1. Introduction

The growing energy demands and worsening global issues call for urgent development of clean alternative energies as well as advanced energy storage devices [1–3]. Electrochemical capacitors, also known as supercapacitors, have drawn intensive research attention as ideal energy storage devices due to their significant advantages of high power density, long cycle-life and safety tolerance to high rate charge and discharge [4–6]. Supercapacitors can be classified as two types according to the energy stored mechanism, namely the electrical double-layer capacitor and the pseudocapacitor [7–9]. The capacitance of the former arises from an electrical double layer at the interface between electrode and electrolyte, carbon materials are typical example [10]. The capacitance of the latter is due to fast and reversible Faradic reactions, transition metal oxides are notable pseudocapacitive materials [11]. Specially, intercalation pseudocapacitance occurs when ions intercalate into the tunnels or layers of a redox-active material accompanied by a faradaic charge-transfer with no crystallographic phase change [12,13]. The mechanism is advantageous for thick electrodes, offering the promise of exploiting high-rate charge-storage devices. Notably, the heart of a supercapacitor device is electrode materials, which directly determine the performance of supercapacitors. Therefore, tremendous efforts have been focused on the development of advanced electrode materials, with the aim of fabricating novel electrodes for next generation high performance supercapacitors.

For the purpose of practical application, the importance of high mass loading of active materials and electrode microstructure for the fabrication of supercapacitors has been highlighted [14,15].

* Corresponding author.
E-mail address: xtzhangzhang@hotmail.com (X. Zhang).

http://dx.doi.org/10.1016/j.jpowsour.2015.06.082
0378-7753/

However, the increase in material loading usually leads to increased resistance and reducing specific capacitance, due to close-packed structures resulting in a limited electrochemically active surface area, so only ultrathin layers of active materials can deliver specific capacitances [16,17]. In despite of the promising performance, the electroactive material is generally too low to meet their practical applications [18,19]. Therefore, increasing the utilization efficiency of electroactive material at large mass loading is still a challenge.

Recently, a new family of 2D transition metal ternary carbides – labeled MXenes—was synthesized by exfoliation of ternary carbides MAX phases [20–23]. MXenes have attracted increasing attention due to the quite unique combination of excellent mechanical properties, hydrophilic surfaces and metallic conductivity. Both theoretical calculation [24–26] and experiment results [27] have proved that MXenes are promising candidates for electrodes in lithium (Li)-ion batteries and supercapacitors. Among MXenes, titanium carbide (Ti_3C_2) electrodes have been shown to have high volumetric capacitances. M. R. Lukatskaya et al. reported that the flexible Ti_3C_2 films show a volumetric capacitance of over 300 F/cm^3 at scan rate of 2 mV/s and excellent cycling stability [27]. L. Zheng et al. demonstrated that Ti_3C_2/polymer composites exhibit an impressive volumetric capacitance of ~530 F/cm^3 at 2 mV/s [28]. M. Ghidiu et al. fabricated additive-free films of Ti_3C_2 'clay' by an easier method, and the films have volumetric capacitances of up to 900 F/cm^3 at 2 mV/s [29]. M.-Q. Zhao et al. demonstrated a significant improvement in volumetric capacitance (390 F/cm^3) and excellent rate performance of the sandwich-like $Ti_3C_2T_x$/CNT electrodes [30]. Nevertheless, the effect of Ti_3C_2 mass loading on electrochemical performance has remained unexplored.

Herein, we carried out a detailed study of the impact of the mass loading (1.8–7.6 mg/cm^2) within a large range of scan rates on the capacitance, in order to evaluate the capacitance of the Ti_3C_2 electrodes. The as-prepared electrodes with large mass loading still exhibit a high specific capacitance, relatively good rate performance and good cycling stability (capacitance retention of 98%). This can be attributed to the excellent electron conductivity and layered structure of Ti_3C_2 that allows a small resistance and facilitates ions and electron transportation. Importantly, the process of intercalation pseudocapacitance occurred in this layered Ti_3C_2 materials is beneficial for thick electrodes.

2. Experimental section

2.1. Materials synthesis

All of the reagents used in the experiment were of analytical grade without further purification. Layered Ti_3C_2 powder was prepared by selective etching the Al layer from Ti_3AlC_2 [20,22]. Briefly, Ti_3AlC_2 powder of 200 mesh was treated with 40% aqueous HF solution at room temperature for 20 h. The resulting suspensions were washed seven times using deionized water and separated from remaining HF by centrifuging until the pH value of the liquid reached around 5. The wet sediment was dried at 80 °C for 10 h in vacuum oven.

2.2. Intercalation of multilayer Ti_3C_2

0.15 g Ti_3C_2 powder was suspended in 5 ml of 5 mol/L KOH aqueous solution. The mixtures were stirred for 24 h with a magnetic stirrer at room temperature. Afterwards, the resulting suspension was washed three times using deionized water and dried at 60 °C for 10 h in vacuum oven.

2.3. Electrode preparation from Ti_3C_2

The working electrodes were prepared with active materials (Ti_3C_2), acetylene black and poly(vinylidene fluoride) (PVDF) binder in a weight ratio of 8:1:1. A small amount of N-methyl-2-pyrrolidone (NMP) solvent was added to the mixture with vigorous stirring and ultrasonic to form homogeneous slurry. The slurry was then coated onto nickel foam (surface area 1 cm^2) and dried in a vacuum oven at 90 °C overnight as working electrodes. The mass loading of electrodes can be controlled by adjusting the concentration of the Ti_3C_2. The obtained electrodes corresponding the mass loading of 1.8, 2.9, 4.1, 6.1 and 7.6 mg/cm^2 were denoted as Ti_3C_2-1.8, Ti_3C_2-2.9, Ti_3C_2-4.1 Ti_3C_2-6.1 and Ti_3C_2-7.6, respectively. Before measurements, the working electrode was immersed within the electrolyte for 1 day to ensure that the electrode material was thoroughly wetted.

2.4. Materials characterization

The morphology and the structure of the electrodes were characterized by FE-SEM (SU70, Hitachi, Japan), and XRD (D/max2600, Rigaku, Japan) using the Cu Ka radiation ($\lambda = 1.5418$ Å).

2.5. Electrochemical measurements

Electrochemical measurements were conducted in an electrochemical workstation (VMP3, France) with a standard three-electrode electrochemical cell. The Pt foil and Ag/AgCl were used as the counter electrode and the reference electrode, respectively. 1 M KOH solution was chosen as electrolyte. The electrochemical performance of the as-prepared electrodes was studied by means of the cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) techniques with the potential window from −0.4 V to −0.9 V. Moreover, the electrochemical impedance spectroscopy (EIS) measurements were performed by applying an alternating-current voltage with 10 mV amplitude in a frequency range from 10 mHz to 200 kHz.

The specific capacitance (Cm) and areal capacitance (Cs) values determined from the CV curves were calculated according to Eqn. (1) and Eqn. (2), respectively.

$$Cm = \frac{\int I dU}{m\nu\Delta U} \tag{1}$$

$$Cs = \frac{\int I dU}{S\nu\Delta U} \tag{2}$$

where Cm (F/g), Cs (F/cm^2), m (g), ν (mV/s), ΔU (V), I (A) and S (cm^2) are specific capacitance, areal capacitance, the mass of active materials, the potential scan rate, the potential window, charge/discharge current, and working electrode area, respectively.

The specific capacitance was also calculated from the GCD curves according to Eqn. (3),

$$Cm = \frac{I\Delta t}{m\Delta U} \tag{3}$$

where Cm (F/g), m (g), ΔU (V), I (A), and Δt (s) are specific capacitance, the mass of active materials, the actual potential window in the discharging process, the applied current, and the discharging time, respectively.