Fabrication of Lithium Titanate/Graphene Composites with High Rate Capability as Electrode Materials for Hybrid Electrochemical Supercapacitors

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Abstract

A lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$)/graphene composite (LTO/graphene) is fabricated with a one-pot sol-gel method. Graphite oxide is dispersed in an aqueous solution of lithium acetate and tetrabutyl titanate followed by heat treatment in H_2/Ar . The LTO/graphene composite with reduced aggregation and improved homogeneity is investigated as an anode material for electrochemical capacitors. Electron transport is improved by the conductive graphene network in the insulating $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. The charge transfer resistance at the particle/electrolyte interface is reduced from $83.1\ \Omega$ to $55.4\ \Omega$. The specific capacity of LTO/graphene composite is $126\ \text{mAh g}^{-1}$ at $20\ ^\circ\text{C}$. The energy density and power density of a hybrid electrochemical supercapacitor with a LTO/graphene negative electrode and an activated carbon positive electrode are $120.8\ \text{Wh kg}^{-1}$ and $1.5\ \text{kW kg}^{-1}$, respectively, which is comparable to that of conventional electrochemical double layer capacitors (EDLCs). The LTO/graphene composite fabricated by the one-pot sol-gel method is a promising anode material for hybrid electrochemical supercapacitors.

Keywords: composite materials; sol-gel growth; electrochemical techniques; electrochemical properties

1. Introduction

Supercapacitors are excellent power sources for electronic devices because of their unique properties including high safety, high charging-discharging rates, and high power density (10^3 - 10^4 W kg⁻¹) [1]. Electrochemical double-layer capacitor (EDLC) with activated carbon (AC) electrode is a widely used energy storage device. However, it is admitted that EDLC cannot satisfactorily meet the requirement to the performances for some important applications. For example, the relatively lower energy density hinders its application as energy storage devices [2]. In order to overcome this drawback, many studies have been undertaken to develop hybrid electrochemical supercapacitors, including redox-active materials (*e.g.*, graphite [3], metal oxides [4, 5], conducting polymers [6, 7])/AC supercapacitors.

Recently, the spinel Li₄Ti₅O₁₂ (LTO) has been found to be a highly promising anode material for both hybrid electrochemical supercapacitors and lithium ion batteries (LIBs) [8, 9]. The spinel LTO exhibits a constant and comparatively safe Li insertion potential (1.55 V vs. Li/Li⁺), which is above the potential range where most electrolytes or solvents are reduced [9]. Furthermore, LTO with zero-strain spinel structure exhibits a good reversibility and structural stability in the charge-discharge processes [10]. All of these merits make LTO more competitive as a safe negative electrode material for hybrid electrochemical capacitors and an anode material for high power LIBs. However, the major obstacle to the practical applications of LTO is its intrinsically poor electronic conductivity ($<10^{-13}$ S cm⁻¹), which seriously limits its high rate capability [11].

In order to overcome the low electrical conductivity of LTO, much effort has been made, such as reduction of particle size [12], surface coating with conductive material [8], doping with aliovalent metal ions [11] and preparation of composites with some excellent conductive components [13-17]. Among these methods, preparation of LTO-based composites using high conductive and low-cost carbon materials by a facile route is practicable and economical for large-scale industrialization.

Due to their superior electrical conductivity, large surface area and great mechanical strength, graphene nanosheets can be used as a useful platform to immobilize LTO [13-15, 18-20]. The composite combining LTO and graphene can provide a shorter path for lithium ion and electron transport, resulting in improved kinetic performance. In addition, graphene produced by the chemical reduction of graphene oxide has abundance functional groups on the surface, such as carboxyl and hydroxyl groups, and thus may provide a better connection with LTO to form a homogenous composite during preparation [13, 15]. As a consequence of the enhancement of their electrical conductivity and structural stability upon their hybridization with graphene, LTO-anchored graphene cannot only increase electrical conductivity, but also improve the electrochemical activity [13-15, 18-20].

Several methods have been reported for the fabrication of LTO/graphene composites. LTO/graphene composites were fabricated by direct crystal growth of LTO on the surface of reduced graphene oxide (RGO) nanosheets in an aqueous colloidal suspension [19]. However, the weak thermal stability of the RGO colloidal nanosheets prevents the optimization of the electrode performance of the LTO/graphene composites by heat treatment at high temperature. Another fabrication method of LTO/graphene composites is

prepared lithiation of metal oxide-graphene nanocomposite [15, 20]. LTO/graphene composites were also prepared by direct immobilization of pre-synthesized lithium titanate composites on the surface of RGO nanosheets [14, 18].

However, fabrication of LTO/graphene composites is still a challenge because when a conventional synthesis route is employed it requires a tedious process of reducing graphite oxide (GO) to graphene, which increases the manufacturing cost. Besides, no investigations have been carried out for applying LTO/graphene composites as anode materials of hybrid electrochemical supercapacitors.

In the present study, we develop a practical and efficient strategy for synthesizing LTO/graphene composites. A LTO/graphene composite was fabricated with a one-pot sol-gel method. GO was dispersed in an aqueous solution of lithium acetate and tetrabutyl titanate, which was followed by heat treatment in H_2/Ar . LTO is anchored on conductive graphene, forming a LTO/graphene composite which is consisted of uniform particles with nano-size. The LTO/graphene composite is proved to be an ideal negative electrode material due to its smaller particle size for rapid ion diffusion and the formation of highly conductive network for fast electron transition. The electrochemical measurements demonstrate that LTO/graphene composite exhibits high rate performance. Furthermore, the LTO/graphene composite prepared by this method was applied as negative electrode material for hybrid electrochemical supercapacitors.

2. Experimental

2.1 Preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composites

All the reagents were of analytical grade purity and used as received. Graphite oxide (GO) was synthesized from natural graphite powders by Hummers method [1]. The LTO/graphene composite was prepared by a facile sol-gel method with GO, lithium acetate (LAC, CH_3COOLi) and tetrabutyl titanate (TBT, $\text{Ti}(\text{OC}_4\text{H}_9)_4$) as precursors. The fabrication procedures of LTO/graphene composites are schematically illustrated in Fig. 1. For a typical synthesis, the GO powder (260 mg) was sonicated in ethanol for 30 min, subsequently TBT (18 mL) was added under vigorous stirring to obtain solution A. Then, an ethanol solution containing 4.68 g LAC and an ethanol solution containing 6.86 g oxalic acid were added drop-by drop into solution A to obtain a clear solution (solution B), followed by the addition of 5.0 mL H_2O at pH 6.0 which was adjusted with ammonia. The suspension was magnetically stirred for 5 h to obtain a gel. The resulting gelatin was dried at 60 °C for 12 h to extract out excess ethanol and yield organic precursor. Finally, the as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -precursor anchored on graphene was calcinated at 800 °C for 10 h in a 5 wt% H_2/Ar to obtain a crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite. The process for preparing pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is similar to that for preparing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composites, except no addition of GO in the first step. For comparison graphene was obtained by calcination of GO at 800 °C for 10 h in a 5 wt% H_2/Ar .

2.2 Sample characterization

The crystal structures of the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composites were characterized by X-ray diffraction (XRD) (D/MAX2500VB2+PC, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation. The structures of the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composites were characterized by field emission scanning electron microscopy (FESEM, S-800, Hitachi Ltd., Japan) and transmission electron microscopy (TEM, JEOL JEM-2100F). Raman spectra were collected using a Senterra Raman Scope system with a 532 nm wavelength incident laser light. The amount of graphene in the LTO/graphene was measured by thermogravimetry at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in air from $40\text{ }^\circ\text{C}$ to $1000\text{ }^\circ\text{C}$ by Netzsch STA 449C.

2.3 Electrochemical experiments:

The electrochemical characteristics were evaluated using a half-cell and a hybrid electrochemical supercapacitor system.

For half-cell testing of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene anode, CR2032-type coin cells were used with lithium metal foil as the counter electrode and Celgard2400 membrane as separator. The working electrode was prepared as follows: first, active material (80 wt%), acetylene black (10 wt%) and polyvinylidene fluoride (PVDF) (10 wt%) were mixed with N-methyl pyrrolidinone (NMP) and ground to form a uniform slurry, then the slurry was coated uniformly on an aluminum foil and dried under vacuum at $100\text{ }^\circ\text{C}$ for 12 h. Test cells were assembled in an argon-filled glove box with less than 1 ppm oxygen and H_2O . The electrolyte employed was 1 mol L^{-1} LiPF_6 solution in a mixture of ethylene carbonate

(EC) and dimethyl carbonate (DMC) (1:1 in volume). The coin cells were galvanostatically charged-discharged at different current densities over a potential range of 1.0 and 2.5 V (vs. Li/Li⁺) at room temperature with a cell test instrument (Neware Electronic Co., China). Cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS) tests were performed with Princeton PAR2273. CV tests were carried out from 1.0 to 2.5 V at scanning rates of 0.2 mV s⁻¹. EIS was carried out in the frequency range 10⁻²-10⁶ Hz with a potential perturbation of 5 mV. All the results of the measurements mentioned above are based on the total mass of active material.

The hybrid electrochemical supercapacitors were assembled in CR2032-coin cell shells with Li₄Ti₅O₁₂/graphene negative electrodes and AC positive electrodes. The weight ratio of the active material in the positive and negative electrode was close to 3:1. Commercial carbon (Kuraray Chemical Corp.) was used as active material in the positive electrodes. AC electrodes were prepared using polytetrafluoroethylene (PTFE) as binder. A paste, prepared by mixing 85 wt% AC, 10 wt% acetylene black and 5 wt% PTFE was spread onto a current collector of steel mesh. The electrodes were also dried in vacuum at 100 °C prior to use. Other conditions were identical to those for the half-cell. Charge-discharge tests were performed under constant current mode between 1.0 and 3.0 V. For comparison, we assembled and tested a normal non-aqueous EDLC cell with AC as positive and negative electrode materials and 1.0 M tetraethylammonium tetrafluoroborate (TEABF₄) solution in PC as electrolyte.

The energy density E (Wh kg⁻¹) and average power density P (W kg⁻¹) of the electrochemical capacitor were determined by means of galvanostatic charge-discharge

cycles as follows [21]:

$$E = C \frac{V_{max}}{m_{total}}$$

$$P = V_{max}I$$

where C is the capacity on charge (Ah), V_{max} is the potential at the end of charge (V), m_{max} is the active mass of the two composite electrode (kg) and I is the applied current (A).

3. Results and discussion

3.1 Synthesis and Characterization of $Li_4Ti_5O_{12}$ and $Li_4Ti_5O_{12}$ /graphene composites

The crystal structures of GO, LTO and LTO/graphene are identified using X-ray diffraction (XRD) patterns (Fig. 2). An intense peak at 11.5° appears on the XRD pattern of GO (Fig. 2A), which corresponds to the (002) diffraction peak of GO. The interlayer spacing (0.77 nm) derived from this angle was much larger than that of pristine graphite (0.34 nm), which was lead to by the introduction of oxygen-containing functional groups on the graphite sheets. In Fig. 2B, all the diffraction peaks ascribed to the pure phase of well-crystallized LTO can be observed. A 84% yield of the LTO/graphene was obtained as grey powders by this one-pot sol-gel method. The weight percentage of graphene in the composite measured by TG in air atmosphere is about 5%. In Fig. 2C XRD peaks identical to those of the as-prepared LTO are observed for LTO/graphene, indicating the negligible influence of the graphene on the crystal structure of spinel LTO. In addition, the typical diffraction peak of GO disappears, which indicates that the GO is transformed to graphene after heat treatment in H_2/Ar . There are no obvious diffraction peaks of graphene observed in the XRD pattern of LTO/graphene, implying that the graphene sheets are homogeneously

dispersed in or coated on LTO particles [13].

That LTO/graphene fabricated via the sol-gel process and subsequent heat treatment is further characterized by Raman spectra. The Raman spectrum of the LTO/graphene composite and graphene is shown in Fig. 3. For LTO/graphene composite, the peaks at 227, 404 and 682 cm^{-1} are attributed to the vibrations of titanium and oxygen ions in the spinel lithium titanate lattice [18]. In addition, two peaks appearing at higher frequencies ($\sim 1340 \text{ cm}^{-1}$ and $\sim 1592 \text{ cm}^{-1}$) are assigned to the D and G peaks of graphene, confirming the dispersion of the graphene sheets in the final LTO/graphene composite [14]. For the H_2 -reduced LTO/graphene, the residual oxygenated groups are important in determining the value of I_D/I_G ratio. The D-peak is caused by the presence of structural defects within the material [22]. These defects become notably heightened in intensity after the oxidation of graphite to GO and can persist to a significant degree in the subsequent reduction. The D+D' peaks for LTO/graphene and graphene present at $\sim 2,910 \text{ cm}^{-1}$ are influenced by the presence of structural defects [23].

As is well known, the two-phonon (2D) Raman scattering of graphene-based materials is a valuable band to identify the layers of graphene as it is highly perceptive to stacking of graphene layers. Generally, a Lorentzian peak for the 2D is broaden and shifted to higher wavenumber in case of multi-layer graphene [24]. In this investigation broaden 2D bands were observed at 2662 and 2684 cm^{-1} for LTO/graphene and graphene respectively. This indicates that both LTO/graphene and graphene have multilayered structure. It is also cleared that the 2D band of graphene is shifted toward higher wavenumber which suggested that the stacking of graphene sheets in pure graphene is more serious compared

with that of LTO/graphene. The reason for the difference of the 2D band position between LTO/graphene and graphene is as follows. First, LTO particles in LTO/graphene act as spacers to prevent stacking of graphene layers due to Vander Waal interactions. Second, after reduction by H_2 , the pristine grapheme is stacking due to less functional groups. Thus LTO prevents the stacking of graphene sheets as demonstrated by 2D bands.

The SEM and TEM images of the LTO/graphene composites compared to that of the pristine LTO is presented in Fig. 4. The pure LTO particles with an irregular polyhedral shape are about 100-500 nm in size and aggregation of the particles occurs, as shown in Fig. 4a and c. Reduced aggregation and improved homogeneity are observed for LTO/graphene composites (Fig. 4b and d). When introducing graphene sheets in LTO, microcrystalline LTO particles are immobilized on the flat surface of the graphene sheets. Because of the existence of functional groups, GO sheets act as anchor sites and consequently lead the attachment of the in situ formed LTO on the surfaces and edges of the GO sheets. The LTO/graphene composites were obtained by heat treatment of the precursors (mixtures of GO, LAC and TBT) in H_2/Ar . Heat treatment leads the in situ formation of LTO and graphene simultaneously, which ensures that LTO are homogeneously anchored on graphene sheets and prevents serious stacking of graphene. Thus loss of active surface area can be lowered. It is seen from Fig. 4d that LTO particles within 200 nm are uniformly attached on the graphene sheets. It should be emphasized that the LTO prepared in the absence of graphene aggregate severely with irregular particles (Fig. 4c) as compared with the LTO/graphene composites (Fig. 4d). The reason for reducing aggregation is that, on the one hand, LTO particles prevent the stacking of graphene sheets, while on the other hand,

the presence of graphene with good electrical conductivity is favorable to improve the dispersion of LTO particles and the electrical conductivity of the composite electrode.

3.2 Electrochemical performances

3.2.1 Half cell system

The electrochemical performance of the LTO/graphene composites was characterized by cyclic voltammograms (CV) within a potential window of 1.0-2.5 V (vs. Li/Li⁺). It is widely known that the shape of redox peaks observed on a CV curve reflect the electrochemical reaction kinetics of Li⁺ insertion/deinsertion. A sharp and well-resolved peak generally signifies fast Li⁺ insertion/deinsertion, whereas a broad peak suggests a sluggish process. From the CV comparison shown in Fig. 5, it is seen that there is a broad peak on the CV curve of LTO while a sharp peak can be observed on the CV curve of the composite with graphene. In addition, the peak current of the LTO/graphene composite is higher than that of LTO, indicating a fast Li⁺ insertion/deinsertion [14].

To elucidate the effectiveness of graphene in improving the rate capability of the electrode, the Li-ion insertion/extraction properties of the LTO/graphene composites and the pristine LTO were investigated, respectively. The charge-discharge curves of the pristine LTO at 0.2 to 10 C are shown in Fig. 6a. The discharge capacity is 169 mAh g⁻¹ at a rate of 0.2 C. At a rate of 10 C, no clear discharge voltage plateau can be observed for the pristine LTO and the capability is only 44 mAh g⁻¹. The greatly improved electrochemical performance of the LTO/graphene is shown in Fig. 6b. The LTO/graphene electrode exhibits a specific capacity of 191 mAh g⁻¹ at 0.2 C (the capacity is calculated based on the

mass of the LTO in the LTO/graphene electrode), and the potential plateau is around 1.55 V, as observed in the case of the pristine lithium titanate [25]. In addition, the discharge capacity of LTO in the LTO/graphene composites is higher than that of the pristine LTO at various rates, indicating that the RGO coupling is effective in improving the electrochemical performance of LTO. Although both the capacity and the cell voltage decrease with increasing current density, a capacity of 126 mAh g⁻¹ is still maintained at 20 C.

The rate performances of the LTO/graphene composite and LTO at different rates are shown in Fig. 6c. The discharge capacity of LTO decreases rapidly with increasing the discharge rate, whereas the discharge capacity of the LTO/graphene composite decreases much slower. For LTO/graphene, the capacity decreases from 191 to 126 mAh g⁻¹ with increasing the discharge rate from 0.2 to 20 C. However, the capacity of the pristine LTO decreases quickly from 169 to 44 mAh g⁻¹ with increasing the discharge rate from 0.2 to 10 C. It is note worthy that the capacity (126 mAh g⁻¹) of the LTO/graphene composite at 20 C higher is than that of the pure LTO at 10 C. This result indicates that a significantly improved rate capability is achieved for the LTO/graphene composite, because of the improved electrical conductivity produced by the graphene in the composite [14].

This result of charge-discharge curves agreed well with that from electrochemical impedance spectroscopy (EIS). The electrodes of the LTO/graphene composite and the pristine LTO were evaluated by EIS at ambient temperature, and the typical Nyquist plots are given in Fig. 7. Each EIS curve consists of a depressed semicircle in high-middle frequency region and an oblique straight line in low frequency region. The intercept

impedance on the Z-real axis reflects the Ohmic resistance (R_s) of the electrodes and electrolyte, while the size of the depressed semicircle at high-middle frequency reflects the charge transfer impedance (R_{ct}). The oblique line at low frequency is related with the lithium ion diffusion process [15]. These impedance spectra were fitted to the equivalent circuit shown in the inset of Fig. 7a. Here R_s is the Ohmic resistance of the electrodes and electrolyte, R_{ct} the charge transfer resistance at the electrode/electrolyte interface, and Z_w the Warburg impedance. The low frequency region of the straight line is attributed to the diffusion of lithium ions into the bulk of the electrode material, the so-called Warburg diffusion [26]. Fig 7b illustrates the relationship between the real impedance and the reciprocal square root of the lower angular frequencies. This relationship is governed by Eq. 1. The diffusion coefficient values of lithium ions diffusion into electrode material were calculated by Eq. 2.

$$Z_{re} = R_s + R_{ct} + \sigma_w \omega^{-0.5} \quad (1)$$

$$D = 0.5 \left(\frac{RT}{AF^2 \sigma_w C} \right)^2 \quad (2)$$

$$i^0 = \frac{RT}{nFR_{ct}} \quad (3)$$

where Z_{re} , real impedance; σ_w , Warburg impedance coefficient; ω , regular frequency in the low frequency region; D , diffusion coefficient; R , gas constant; T , absolute temperature; F , Faraday's constant; A , area of the electrode surface, and C , molar concentration of Li^+ ions (moles cm^{-3}). Table 1 shows the fitting results for the impedance parameters.

The obtained impedance parameter results show that the LTO/graphene has lower charge transfer resistance and higher mobility for Li^+ than pure LTO. The charge-transfer

resistance of LTO/graphene composite electrode is 55.4 Ω , which is much lower than that of the LTO electrode (83.1 Ω). The obtained diffusion coefficients showed that LTO/graphene has higher mobility for Li^+ diffusion than LTO. Furthermore, the exchange current density (Eq. 3) [15] of the LTO/graphene electrode is higher than that of the LTO electrode. The lithium insertion reaction of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ follows the next reaction:

This reaction occurs only when equivalent ions and electrons are available simultaneously. The charge-transfer resistance and Li-ion diffusion from EIS results suggest that the higher electrical conductivity achieved by coupling LTO with graphene is mainly responsible for the improvement of the discharge capacity.

Thus, improvement of the rate performance may be ascribed to the following aspects: First, the graphene sheets with a good electrical conductivity resulted in a low charge-transfer resistance; Secondly, the graphene sheets prevent agglomeration and growth of LTO particles during the calcination; Finally, the LTO particles on the surface of graphene sheets prevent the stacking of graphene sheets, leading to a large available surface area for energy storage. Therefore the LTO/graphene composite is favorable for rapid ion diffusion and electronic transitions due to the synergistic effect of both components (*i.e.*, graphene sheets with high conductivity and fine LTO particles with high capacity).

3.2.2 Hybrid electrochemical supercapacitor

Fig. 8a shows the fifth charge-discharge curve of an AC/ (LTO/graphene) hybrid electrochemical supercapacitor at a charge-discharge rate of 5 C. The capacity values

supplied in the figure are calculated based on the total mass of the active materials in the positive and negative electrodes. The charge-discharge process in the hybrid electrochemical supercapacitor involves the electric double-layer electrostatic adsorbing-desorbing PF_6^- in AC and Li-ion insertion-extraction in LTO/graphene. The efficiency over 5 charge-discharge cycles is close to 100%.

Fig. 8b shows Ragone plots of the hybrid electrochemical supercapacitor (AC/(LTO/graphene)). The charge-discharge tests were performed between 1.0 and 3.0 V at various current densities. For comparison, a hybrid electrochemical supercapacitor (AC/LTO) and a conventional EDLC (AC/AC) were assembled. At a low power density of 0.03 kW kg^{-1} , the energy density of the hybrid electrochemical supercapacitor (AC/(LTO/graphene)) reaches 120.8 Wh kg^{-1} , which is superior than the AC/LTO hybrid electrochemical supercapacitor. At a higher power of 1.5 kW kg^{-1} , the energy density of the hybrid electrochemical supercapacitor remains at 36.0 Wh kg^{-1} , which is twice as large as that of the conventional EDLC (AC/AC). So in terms of the large discharge capacity, the LTO/graphene nano-composite is a promising electrode material for hybrid electrochemical supercapacitors.

4. Conclusions

A facile route was developed to fabricate a highly electrically conductive LTO/graphene composite as an anode material for hybrid electrochemical supercapacitors. Lithium and titanium sources were dissolved in a GO colloidal suspension and followed by heat treatment in H_2/Ar . The LTO micro-crystals are immobilized on the surface of the graphene

nano-sheets. Because the synergistic effect of both components (*i.e.*, graphene sheets with high conductivity and fine LTO particles with high capacity), the composites are favorable for rapid ion diffusion and electronic transitions. The LTO/graphene composite exhibits a higher rate capability in comparison to pure LTO. The hybrid electrochemical supercapacitor with LTO/graphene negative electrode and AC positive electrode exhibits much high rate capability. The energy density of the hybrid electrochemical supercapacitor reaches 36 Wh kg⁻¹ at a power density of 1.46 kW kg⁻¹. The LTO/graphene composite is a promising negative electrode material for hybrid electrochemical supercapacitors.

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Table 1 Fitting results of the impedance spectra and the exchange current densities for the electrodes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite.

Materials	R_s	R_{ct}	σ_w	D	i^0
	(Ω)	(Ω)	($\Omega \text{ cm}^2 \text{ s}^{-0.5}$)	($\text{cm}^2 \text{ s}^{-1}$)	(mA cm^{-2})
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	2.2	83.1	28.1	2.00×10^{-12}	0.30
$\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene	1.4	55.4	18.5	4.70×10^{-12}	0.46

Figure captions

Fig. 1: Schematic illustration of the preparation procedure of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composites.

Fig. 2: XRD patterns of (a) graphene oxide, (b) pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (c) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite and spinel (JCPDS No. 49-0207)

Fig. 3: Raman spectra of (a) graphene and (b) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite.

Fig. 4: (a,b) SEM and (c,d) TEM images of (a,c) pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (b,d) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite.

Fig. 5: Cyclic voltammograms of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite at a scan rate of 0.2 mV s^{-1} .

Fig. 6: (a) Charge-discharge curves of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different rates (0.2, 0.5, 1, 3, 5 and 10 C). (b) Charge-discharge curves of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite at different rates (0.2, 0.5, 1, 3, 5 10 and 20 C). (c) Cyclic performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite at different rates.

Fig. 7: (a) AC impedance spectra of the electrodes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite and pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The inset is the equivalent circuit for fitting. (b) Relationship between the real impedance and the low frequencies of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite and pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Fig. 8: (a) Charge-discharge curve of AC/($\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene) hybrid electrochemical supercapacitor at 5 C. (b) Ragone plots of the AC/($\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene) hybrid electrochemical supercapacitor, the hybrid electrochemical supercapacitor (AC/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$) and the conventional EDLC (AC/AC).

Figures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

GRAPHICAL ABSTRACT