Unconventional Electrochemical Characterization of Nanocomposite Supercapacitor Electrode with High Energy Density

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A supercapacitor electrode was fabricated from a nanocomposite consisting of multiwall carbon nanotubes and titanium oxide nanoparticles. Conventional electrochemical characterizations cyclic voltammetry and galvanostatic charge-discharge in a lithium-based electrolyte gave a specific capacitance of 345 F/g at a current density of 0.1 A/g. Unconventional electrochemical characterization techniques that allow one to obtain the peak capacitance associated with intercalation and to distinguish between electrostatic and faradaic charge storage are described and applied to the electrode measurements. The advantages of the unconventional techniques are shown by comparison to the conventional ones. Finally, the maximum energy density obtained was 31 Wh/kg.

I. Introduction

Supercapacitors, also called ultracapacitors or electrochemical double layer capacitors (EDLCs), bridge the gap between batteries and conventional dielectric capacitors [1, 2]. The most common electrode material is carbon-based and include activated carbon [1, 3, 4], carbon nanotubes [5–11], and graphene [12, 13]. To go beyond electrostatic charge storage in the double layer, pseudocapacitive and faradaic components (faradaic components henceforth) such as conducting polymers and metal oxides were incorporated into supercapacitors [3, 14–16]. Two ways of incorporating the faradaic material have been employed, both in an asymmetric (or hybrid) configuration where: (1) a carbon electrode and a faradaic electrode form the two electrodes of a supercapacitor [17–21]; (2) at least one of the electrodes is a composite material that combines advantages of electrochemical double layer charge storage as well as surface redox or intercalation charge storage [22–24].

Carbon nanotubes (CNT) have a high aspect ratio and form porous networks with good conductivity. As such, they have been implemented as supercapacitor electrodes in many instances in the literature [1, 3, 5, 7–11, 27, 28]. Titanium oxide is a versatile compound and can be found in several energy harvesting and energy storage applications, namely photocatalysis, secondary batteries, and supercapacitors [29]. Three polymorphs exist at room temperature and atmospheric pressure: rutile, anatase, and brookite. The crystal structure of anatase can accommodate the most Li+ per TiO$_2$ unit and is an attractive energy storage material due to its Li-intercalation capabilities and cycle life [30]. TiO$_2$ nanowires have been synthesized by hydrothermal methods in a couple of studies, functioning as the anode of a supercapacitor with carbon nanotubes acting as the cathode [19, 20]. These are type (1) asymmetric supercapacitors.

In this study, the application of a nanocomposite containing TiO$_2$ nanoparticles and multiwall carbon nanotubes in a single supercapacitor electrode is reported. Such a nanocomposite have been synthesized by sol-gel method [31], hydrothermal treatment [32, 33], electrodeposition [34], and layer-by-layer assembly [35] for photovoltaics, photocatalysis, and hydrogen peroxide sensing applications. As a supercapacitor electrode, its performance is rarely reported in the literature. Here, results from conventional as well as unconventional electrochemical characterization are reported to show the various aspects of the energy storage mechanism in the electrode. The unconventional techniques are described in detail, their main advantage resting in their ability to extract parameters pertaining to the amount of charge stored electrostatically and faradaically. The results show that the combination of double layer and faradaic capacitance leads to high energy density and good power density in a single electrode.

II. Experimental Section

A. Synthesis of CNT-TiO$_2$ nanocomposite

TiO$_2$ (anatase) nanoparticles were synthesized [36] and dispersed in ethanol with a concentration of 2 mg/mL. Multiwall carbon nanotubes (MWNT) along with polyvinylidene fluoride (PVDF) in a 1:1 weight ratio were also dispersed in ethanol using the same concentration. A mixture containing 80 wt. % TiO$_2$, 10 wt. % MWNT, and 10 wt. % PVDF was bath-sonicated for half an hour and heated on a heat plate until most of the ethanol had evaporated away. The remaining slurry was drop cast onto half of a stainless steel current collector 1 cm wide and 2 cm long so that the area of the electrode is 1 cm$^2$. The electrode was heated in an oven at 80 C overnight to evaporate the remaining solvent.
B. Conventional Electrochemical Characterization

Cyclic voltammetry (CV) as well as galvanostatic cycling (GC) were performed on the CNT-TiO$_2$ composite electrodes. Cyclic voltammetry of the composite electrode at various scan rates was measured in 1 M LiClO$_4$ in propylene carbonate with lithium metal sheets as the reference electrode and counter electrode, shown in Figure 1. The voltage window was 1 V to 2.6 V vs. Li/Li+. A series of galvanostatic measurements were performed, two of which are shown in Figure 2. The abrupt change in the slope of the chronopotentiometric curve at low current densities indicates that the intercalation potential is about 1.9 V. At high current densities, the change in the shape of the discharge cycle is more pronounced than the change in the shape of the charge cycle.

The capacitance of the electrode can be obtained by dividing the charge accumulated by the voltage range $C = \frac{Q}{\Delta V}$. The specific capacitance is given by $C_{sp} = \frac{C}{M}$, which is a measure of the amount of charge that can be stored per amount of active material. The storage capacity of the composite electrode decreases with increasing current but approaches a constant value, shown in Figure 3 along with the coulombic efficiency. The departure of the coulombic efficiency from a value of unity is not a violation of the law of charge conservation but is an indication that the charge accumulation/depletion processes lack time reversal symmetry.

C. Unconventional Electrochemical Characterization

The galvanostatic charging for a given current $I$ is described by

$$V = \frac{I}{C} t + IR_s$$

where $C$ is the capacitance of the electrode and $R_s$ is the internal resistance. The quantity $IR_s$, denoted by $V_d$, is the voltage drop at the beginning of charging cycles and discharging cycles. The temporal slope $dt/dV$ plotted as a function of the potential is shown in Figure 4. These plots will be called temporal slope voltammograms (TSVs) in this article.

Similar to CVs, the anodic peaks (Li extraction) and cathodic peaks (Li insertion) become more separated as the applied stimulus increases. In cyclic voltammetry, this is due to $R_s$ and mass transfer limitations. The true potential at the electrode deviates from the applied potential by an amount $IR_s$, and this deviation increases with scan rate as the current increases with scan rate. Moreover, the increasing prominence of the mass transfer current and the double layer charging current causes the faradaic/intercalation peaks to flatten as the scan rates increase. The broadening
FIG. 2: Galvanostatic measurements of CNT-TiO$_2$ composite electrode with applied currents densities 0.7 A/g and 4 A/g.

FIG. 3: (a) Specific capacitance vs. current density. (b) Coulombic efficiency.

of the peaks adds uncertainty to the determination of the peak potential $V_p$. TSVs, however, are free from such difficulties. The temporal slope peaks remain sharp even for large current densities.

As shown in Figure 5a, as $V_d$ vanishes, both anodic and cathodic peak potentials approach the same value, the standard potential for the intercalation reaction. Besides determining the true peak potential, TSVs also allow one to obtain the peak capacitance. A plot of the temporal slope peaks versus $I^{-1}$ shows a linear relationship (Figure 5b). Linear regression gives the peak capacitances at $V_p$: 2410 F/g for Li extraction and 1450 F/g for Li insertion. As a point of reference, the theoretical specific capacitance of TiO$_2$ assuming one Li$^+$ ion per TiO$_2$ molecule is 2295 F/g, calculated using the formula $FV_p/\rho_{TiO_2}$, where $F$ is the faraday constant and $\rho_{TiO_2}$ is the TiO$_2$ molar mass. The peak capacitance at the standard potential of the faradaic reaction could be an important figure of merit in characterizing
FIG. 4: Temporal slope voltammograms were constructed from galvanostatic measurements. Similar to cyclic voltammograms, the separation between anodic and cathodic peaks increases as the current increases.

and optimizing nanocomposites as the mass normalized quantity depends very little on the double layer contributions.

The storage capacity is a measure of the total charge stored, without differentiating between electrostatic and faradaic contributions. The distinction is important because one is often interested in the effect of nanoparticle size on the faradaic reactions and whether the faradaic process involves only surface sites or the bulk [36]. In the electrostatic case, where the capacitance depends only on the geometry and dielectric constant of the capacitor and not the capacitors potential, the state of charge is directly proportional to the potential. A more general potential-dependent capacitance would allow for the possibility that the change in charge stored be caused by a change in potential or a change in the physical characteristics/chemical composition of the charge storage medium itself:

$$dq = C dV + V dC$$

(2)

The first term on the right hand side describes capacitive behavior while the second term describes battery behavior. Charge conservation requires

$$\frac{dq}{dV} = C + V \frac{dC}{dV}$$

(3)

Given this relationship between pseudocapacitance and the potential-dependent capacitance $C$, called supercapacitance in what follows, the charge stored is no longer the integral of $C$ with respect to $V$ but the integral of the right hand side of Eq. (3) with respect to $V$.

For two reacting species in a reversible charge transfer reaction the current associated with the concentration changes at the electrode surface is described by [37]

$$I_F = \frac{(nF)^2}{RT} \delta A \frac{C_0}{C} \frac{e^{F(V^\circ - V)}}{(1 + e^{F(V^\circ - V)})^2} \frac{dV}{dt}$$

(4)

where $F = nF/RT$, $C_0$ and $C$ are the starting and instantaneous ion concentration at the electrode-electrolyte interface, $\delta$ is the width of the diffusion layer, $A$ is the area of the TiO$_2$ nanoparticles, and $V^\circ$ is the standard potential of the reaction. The current associated with the changes in the double layer is given by $I_{dl} = C_{dl} dV/dt$. It follows that the supercapacitance is

$$C(V) = \frac{nF \delta A C_0}{V} \left( \frac{1}{1 + e^{F(V^\circ - V)}} - \frac{1}{1 + e^{F(V^\circ)}} \right) + C_{dl}$$

(5)
FIG. 5: (a) The peak potential is linear in the voltage drop $V_d$. The anodic and cathodic intercepts are both 1.9 V. (b) Temporal slope peaks are linear in $I^{-1}$. The absolute values of the two linear regression slopes are the peak capacitances, 2410 F/g in the anodic case and 1450 F/g in the cathodic case.

and the charge stored is

$$q(V) = nF\delta AC_O^p \left( \frac{1}{1 + e^F(V_o - V)} - \frac{1}{1 + e^FV_o} \right) + C_{dl}V \quad (6)$$

The charge accumulation as a function of potential can be obtained from galvanostatic measurements, as shown in Figure 6, which does not include any charge stored on the electrode at the starting potential. The double layer capacitance can be obtained from the slope of $q(V)$ for sufficiently large potentials, after available TiO$_2$ lattice sites are fully intercalated. When the double layer contribution is subtracted, the resulting intercalated charge versus potential curve has the functional form given by Eq. (6) with $C_{dl} = 0$.

III. Results and Discussion

In a highly cited paper by Conway [38], it was pointed out that battery processes ideally occur at constant potential while supercapacitor processes occur over a range of potentials, the potential being a good indicator of the state of charge. Therefore, batteries and supercapacitors are fundamentally different. However, battery processes can be thought of as a change in the storage capacity at a singular potential. The storage capacity decreases as one phase converts to another during a discharge. In fact, one can model the constant current discharge that is prevalent in the characterization of these energy storage devices with Eq. (6). The equation of interest is

$$t = \frac{q(V)}{I} \quad (7)$$

The discharge profiles $V(t)$ can be plotted for different amounts of faradaic charge, as shown in Figure 7. In the regime where the double layer capacitance is large, the discharge profile is capacitor like. In the regime where the amount of faradaic charge is large, the discharge profile resembles typical battery discharge curves. Perhaps, in the context of mathematical modeling, batteries and capacitors are not as different as once thought.

Supercapacitors bridge the gap between batteries and dielectric capacitors, while nanocomposite electrodes bridge the gap between EDLCs and batteries. The performance of the CNT-TiO$_2$ electrode can be compared to lithium-ion...
FIG. 6: Charge accumulated as a function of potential for a current density of 0.1 A/g.

FIG. 7: Calculated constant current discharge profiles for a composite electrode with a double layer capacitance of 0.02 F. The solid line was calculated using 0.66 micromoles of faradaic charge (capacitor like); the dashed line was calculated using 6.6 micromoles of faradaic charge (battery like).

batteries and other electrochemical capacitors in the form of a ragone chart, shown in Figure 8. The storage capacity and the voltage range can be converted to energy density and power density with the formulas

$$ED = \frac{1}{8} C_{sp} \Delta V^2$$  \quad PD = \frac{\Delta V^2}{8MR_s}$$

The synergy between the two materials gives rise to high energy and good power. From the perspective of the high energy density Li-intercalation material, namely the TiO$_2$ nanoparticles, the addition of carbon nanotubes led to a
IV. Conclusion

A supercapacitor electrode was fabricated from a nanocomposite consisting of multiwall carbon nanotubes and titanium oxide nanoparticles. Conventional electrochemical characterizations cyclic voltammetry and galvanostatic cycling gave a specific capacitance of 345 F/g at a current density of 0.1 A/g. Unconventional electrochemical characterization techniques that allow one to obtain the peak capacitance associated with intercalation and to distinguish between electrostatic and faradaic charge storage are derived from galvanostatic measurements. The unconventional techniques show that most of the charge is stored faradaically, via the intercalation mechanism. The double layer charge storage mainly attributed to carbon nanotubes brought significant improvement in power density to the faradaic material. As a nanocomposite, the CNT-TiO$_2$ combination tested here achieved a maximum energy density of 31 Wh/kg.

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