



Deconvolving double-layer, pseudocapacitance, and battery-like charge-storage mechanisms in nanoscale LiMn_2O_4 at 3D carbon architectures

Jesse S. Ko^a, Megan B. Sassin^b, Debra R. Rolison^b, Jeffrey W. Long^{b,*}

^a Naval Research Laboratory, National Research Council Postdoctoral Associate, USA

^b U.S. Naval Research Laboratory, Surface Chemistry Branch (Code 6170), Washington, D.C., 20375, USA

ARTICLE INFO

Article history:

Received 15 February 2018

Received in revised form

20 April 2018

Accepted 21 April 2018

Available online 23 April 2018

Keywords:

Pseudocapacitance

Double-layer

Impedance

Voltammetry

Manganese oxide

Lithium spinel

Nanostructured

ABSTRACT

Lithium manganese spinel, LiMn_2O_4 (LMO), is a well-established active material for batteries, in which charge is stored via a two-stage insertion of Li^+ that manifests with coupled current peaks or voltage plateaus under voltammetric or galvanostatic conditions, respectively. The charge–discharge kinetics for LMO are significantly enhanced when the oxide is expressed in a nanoscale form, for example as an ultrathin coating of nanocrystallites at the surfaces of a 3D carbon substrate, such as fiber paper–supported carbon nanofoams (CNFs). In addition to expressing well-defined “battery-like” Li^+ -insertion peaks between -0.6 and 1 V vs. Ag/AgCl when cycled in aqueous lithium sulfate, LMO@CNF electrodes exhibit a pseudocapacitance envelop at more negative potentials (~ 0.2 – 0.6 V). The pseudocapacitive character of LMO@CNF is further verified when cycled in aqueous sodium sulfate, where a broad capacitance envelop dominates the voltammetric response over the entire potential range at a current density an order of magnitude greater than expected for double-layer capacitance. Thus, the LMO@CNF electrode provides a prime example where multiple distinct charge-storage mechanisms are expressed in a single material. Herein, we apply voltammetry and impedance-based methods to deconvolve the respective contributions of double-layer capacitance, surface-based pseudocapacitance, and battery-like Li^+ insertion. The use of power-law analysis provides a general assignment of transport dynamics, while projecting impedance data as 3D Bode-style representations provides key mechanistic information regarding the time/frequency–potential response of LMO@CNF electrodes.

Published by Elsevier Ltd.

1. Introduction

Charge-storing materials that offer both high capacity and high rate are critical to advance electrochemical energy storage (EES) to next-generation performance [1]. Among the many different materials investigated for EES, lithium manganese spinel (LiMn_2O_4 , LMO), has been successfully deployed as a high-performance positive electrode material in Li-ion batteries that incorporate organic electrolytes [2–5], and more recently the study of LMO has extended to Li^+ -containing aqueous electrolytes [6–13]. Lithium manganese spinel stores charge via two-stage Li^+ insertion/deinsertion into the tetrahedral sites of the spinel crystal structure, resulting in two reversible redox peaks in cyclic voltammetry or

two voltage plateaus in galvanostatic mode [14–16]. Such energetically defined electrochemical signatures are typical of “battery-like” electrode materials [17].

While inherently providing high capacity and desirable redox potential, research to further improve the rate capability of LMO has focused on reducing particle size [10,11,18], altering morphology at the nanoscale [12,13,19–21], or redesigning the electrode architecture [14–17,22–24]. For example, the charge–discharge kinetics for LMO are significantly enhanced when the oxide is expressed as an ultrathin coating of nanocrystallites bonded to the surfaces of a 3D carbon substrate, such as carbon nanofoams (CNFs) [15,25], an electrode design that we here designate as “LMO@CNF”. Our previous report demonstrated that LMO@CNF exhibits the typical battery-like Li^+ -insertion peaks, but does so at time scales that begin to approach the fast response expected for materials used for aqueous-electrolyte electrochemical capacitors [15].

* Corresponding author.

E-mail address: jeffrey.long@nrl.navy.mil (J.W. Long).

In the potential range outside that for battery-like Li^+ insertion, LMO@CNF electrodes also exhibit a pseudocapacitive response [15]. Pseudocapacitive charge-storing materials, in particular manganese oxides, have an electrochemical signature reminiscent of a capacitive electrode (*i.e.*, linear charge–potential dependence), yet the nature of charge storage originates from faradaic mechanisms [26,27]. Such processes for manganese oxides are generally associated with $\text{Mn}^{\text{III/IV}}$ redox reactions [28–30], accompanied by proton and/or alkali metal insertion at near-surface sites in the oxide [28–31]. For electrode architectures of high surface area, contributions from the electrical double layer, which is based on the electrostatic accumulation of ions/molecules at the interface of the electrode (non-faradaic), will also contribute to the electrochemical signature [32].

The expression of both pseudocapacitive character (box-like voltammetric signatures) and well-defined redox peaks (yet responding at fast time scales) make LMO@CNF a prime example of a class of emerging electrode materials that inherently blur the distinction between traditional capacitor and battery functions [27,32–38]. Herein, we use LMO@CNF electrodes as a test case with which to explore the use of voltammetry- and impedance-based electroanalytical methods to deconvolve the double-layer, pseudocapacitive, and battery-like contributions to overall charge-storage characteristics. Power-law analysis of voltammetric data identifies the rate-limiting step for charge storage in terms of transport dynamics (surface-confined vs. finite diffusion vs. semi-infinite diffusion). We find that a more insightful mechanistic assessment can be made by extracting frequency-dependent information on charge-storage dynamics from impedance measurements. Motivated by the theoretical treatment for expressing impedance data in the form of three-dimensional (3D) Bode plots, as previously reported by Bai and Conway in the early 1990s [39,40], we apply such analysis to map out the complex electrochemical response of LMO@CNF electrodes as a function of potential, frequency, and capacitance (or phase angle), clearly distinguishing double-layer, pseudocapacitive, and battery-like processes [41].

2. Experimental

2.1. Materials

All chemicals used in the preparation of the lithium manganese spinel-coated carbon nanofoam electrodes were used without modification: Resorcinol (“R”; Aldrich), formaldehyde (“F”, 37%, Aldrich), sodium carbonate (“C”; Aldrich), sodium sulfate (Aldrich), lithium sulfate (Aldrich), and sodium permanganate monohydrate (Aldrich). All aqueous solutions were prepared with ultrapure water ($>18 \text{ M}\Omega \text{ cm}$) from an in-house purification system.

2.2. Preparation of LMO@CNF

Carbon nanofoams (RF 40 R/C 500) were fabricated following a published procedure [42,43]. In brief, carbon fiber paper (Lydall Technimat) was exposed to an air/ice plasma for 45 min and then vacuum infiltrated with oligomerized RF sol for 1 min; the paper was flipped and vacuum infiltrated for an additional minute. The RF-infiltrated carbon fiber paper was sandwiched between two glass slides and secured with mini binder clips on all four sides. The glass slide assembly was wrapped in duct tape and placed in an Al foil pouch with $\sim 2 \text{ mL}$ of water and cured at 25°C for 12 h. The Al pouch was placed in a pressure cooker (Nesco 3-in-1, steam setting) and “cooked” on the “slow” setting for 9.5 h followed by the “warm” setting for 14.5 h. The polymer-filled carbon fiber paper was removed from the glass slides, soaked in water for 1 h, acetone

for 1 h, and then dried under ambient laboratory conditions. The polymer-filled carbon fiber paper was pyrolyzed at 1000°C under Ar to create carbon fiber–supported nanofoam (CNF) paper.

Lithium manganese spinel (LiMn_2O_4 , LMO) coatings were deposited at carbon nanofoams as described previously [15]. Briefly, CNF papers were vacuum infiltrated with 0.1 M Na_2SO_4 for 20 h, followed by soaking in 0.1 M $\text{NaMnO}_4 \cdot \text{H}_2\text{O}$ in 0.1 M Na_2SO_4 under vacuum for 20 h to produce birnessite-type MnOx -coated CNFs [44,45]. These nanofoams were then removed from the MnO_4^- solution, rinsed with water, and soaked for 1 h in water under vacuum; the process was repeated twice more. After drying at 50°C under N_2 , the MnOx -coated CNFs were soaked for 24 h in 1 M LiNO_3 , rinsed with water and soaked in water under vacuum for 1 h; the rinse/soak step was repeated once to produce Li-MnOx CNFs. The conversion from Li-MnOx to LiMn_2O_4 to produce LMO@CNF electrodes was completed through thermal treatment at 300°C under Ar for 4 h, followed by thermal treatment in air at 200°C for 6 h.

2.3. Materials characterization

Samples of native CNF and LMO@CNF were analyzed using a Rigaku SmartLab X-ray diffractometer equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$). Scans were recorded from 10 to $70^\circ 2\theta$ with a 0.02° step size and an integration time of 1 s per step. Scanning electron micrographs were acquired with a Leo Supra 55 at an accelerating voltage of 20 keV by adhering the LMO@CNF electrode onto an aluminum stub with conductive carbon tape. Elemental maps were acquired via Oxford Aztec energy dispersive spectroscopy detector attached to the scanning electron microscope. Pore size distribution (Barrett-Joyner-Halenda, BJH model) and Brunauer-Emmett-Teller (BET) surface area were measured with a Micromeritics ASAP 2020 N_2 -sorption porosimeter where prior to analysis, the sample was degassed at 150°C under N_2 for 10 h.

2.4. Electrochemical characterization

All electrochemical measurements (cyclic voltammetry, AC impedance, and galvanostatic cycling) were performed using a Gamry Reference 600 potentiostat. The charge-storage properties of LMO@CNF were assessed using a three-electrode configuration. The working electrode was prepared by adhering a 0.29 cm^2 ($0.54 \times 0.54 \text{ cm}^2$) piece of LMO@CNF ($\sim 4\text{--}5 \text{ mg cm}^{-2}$ with $\sim 36 \text{ wt}\%$ mass loading of LMO) onto a $0.6 \times 0.6 \text{ cm}^2$ nickel foil flag using conductive carbon glue (DAG EB-020A). These electrodes were baked at 150°C for 10 min to cure the carbon adhesive. For the preparation of powder-composite electrodes using commercial nanoscale LMO (Altair-nano, $\sim 70 \text{ nm}$), the active material was ground using an agate mortar and pestle with conductive carbon (Super P) and a polymeric binder (Kynar HSV 500) using N-Methylpyrrolidine (Aldrich, 97%) as the solvent in a ratio of (75/15/5) for 15 min. This carbon slurry was pasted onto the nickel flag, dried under ambient temperature overnight, and then dried at 100°C overnight. A platinum coil and a Ag/AgCl (3 M KCl) served as the counter and reference electrodes, respectively; all potentials are reported relative to Ag/AgCl . A CNF control was tested in 1 M Na_2SO_4 and LMO@CNF was cycled in both 1 M Na_2SO_4 and 1 M Li_2SO_4 electrolytes. The electrochemical cells were purged with N_2 for 30 min before each measurement.

For voltammetric measurements, CNF and LMO@CNF electrodes were cycled between 0.2 and 1.1 V from 2 to 100 mV s^{-1} . The specific voltammetric capacity was calculated as the average of the integrated current of both the anodic and cathodic branches of redox peaks and normalized to the total electrode mass and LMO

Download English Version:

<https://daneshyari.com/en/article/6602936>

Download Persian Version:

<https://daneshyari.com/article/6602936>

[Daneshyari.com](https://daneshyari.com)