



Aqueous energy-storage cells based on activated carbon and LiMn_2O_4 electrodes



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HIGHLIGHTS

- Asymmetric lithium ion capacitors are presented.
- The positive electrode was based on a LiMn_2O_4 spinel.
- They operate between 0 and 1.5 V in neutral aqueous solutions.
- They exhibit better rate capability and cycle life than batteries.
- These hybrid capacitors can exhibit energy density of 14 Wh Kg^{-1} .

ARTICLE INFO

Article history:

Received 18 January 2017

Received in revised form

21 March 2017

Accepted 10 April 2017

Keywords:

Li-ion capacitors

Hybrid capacitors

LiMn_2O_4 (spinel)

Aqueous electrolyte

ABSTRACT

In recent years, there has been an increasing need for rechargeable energy-storage devices of many kinds. There are some applications for which energy density is important, whereas for others rate capability (high-power density) and prolonged durability are essential. Batteries address the need for high energy density, while electrochemical capacitors, so called, supercapacitors, can be relevant for the high power density purpose. In between these two kinds of devices, it is possible to develop hybrid systems which possess intermediate properties between supercapacitors and batteries, and which contain both a capacitive or pseudocapacitive electrode and a battery type electrode. With a good selection of electrodes, it is possible to achieve high-rate capability and durability, and also enhanced specific energy density compare to standard supercapacitors. This paper describes the development and study of Li-ion-based hybrid capacitor based on a carbon-based capacitive negative electrode, LiMn_2O_4 spinel as positive electrode and aqueous solutions with Li_2SO_4 salt as the electrolyte ($\text{pH} = 7.5$). Here, we demonstrate full hybrid devices as a proof of concept.

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1. Introduction

Scientific and industrial developments in recent years have focused on the need for rechargeable energy-storage devices that can provide both high-energy and high-power densities [1]. However, the demand for high-energy density may bring with it drawbacks in terms of safety, durability (limited cycle life) and high costs. There are applications, such as load leveling, for which energy density is not at all essential, but durability, safety and cost are critically important. Electrochemical capacitors, so-called

supercapacitors, that are mostly based on capacitive charge storage provide very high power density, and demonstrate excellent durability and safety features [2]. Capacitive electrodes are usually composed of highly porous carbons, such as activated carbons, which maximize specific ion-adsorption processes [3]. Further developments of pseudo-capacitive electrodes include specific transition-metal oxides or nitrides for which the electrochemical signature is similar to the capacitive one but result from fast and reversible surface red-ox reactions [4]. Another approach that can couple all the interesting properties of supercapacitors with improved energy density combines a capacitive electrode and a faradaic electrode, *i.e.* a battery type electrode, in a single device, thereby promoting the development of so-called hybrid capacitors [5]. It is important to note that all kinds of capacitors, including

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asymmetric and hybrid systems, cannot compare to batteries in terms of energy density. Moreover, using electrodes with red-ox properties may limit durability, worsen safety and increase cost, compared to standard supercapacitors [6]. Hence, only by a very carefully selection of the components there is a chance to maintain the advantages and minimize the drawbacks of energy-storage devices that combine capacitive and faradaic electrodes. This work includes attempts to optimize the selection of components for the design of hybrid capacitors using aqueous electrolyte solutions in order to maximize their specific capacitance, their rate capability, their good safety and low cost. Such devices possess high-power density, very good durability and excellent safety features. They are supposedly cheap due to the different components that are implemented and provide higher energy density than symmetric supercapacitors. In this study, aqueous Li-ions based hybrid capacitors were studied because aqueous Li-salt solutions may possess relatively wide electrochemical windows compared to other aqueous systems [7]. Given that the energy and power density of capacitive devices are proportional to the square of the voltage applied, the relatively wide electrochemical window of the electrodes in the solution we use is important. Also, there is a plethora of Li-insertion electrode materials that work well in aqueous solutions [8–13]. Indeed, in recent years, there have been many reports in the literature on attempts to develop aqueous Li-ion batteries [14]. Here, we describe the study of an aqueous lithium-ion capacitor (ALIC) which is composed of a spinel LiMn_2O_4 positive electrode and an activated carbon negative electrode [15], [16]. An obvious difference between the work described herein and previous works in this field relates to the use of reasonable mass loading here (7 mg cm^{-2}) whereas most previous papers present much lower mass loading, sometimes of few hundred of micrograms of active materials per cm^2 . Compared to aqueous Li-ion batteries, ALIC may have advantages in terms of applied cell voltage and durability. Note that the electrodes relevant to aqueous Li-ion batteries belong to the 3–4 V (vs. Li^+/Li) class of cathode materials only [17]. Therefore, there are not too many attractive combinations of Li-insertion electrodes available for aqueous Li-ion batteries.

LiMn_2O_4 (spinel structure) is an attractive cathode material for Li-ion batteries because it undergoes fully reversible Li-ion insertion/de-insertion processes at relatively high and constant potential (around 4 V vs. Li^+/Li). The high-rate capability due to the unique three-dimensional structure [18] of LiMn_2O_4 (spinel) allows very fast insertion and removal of Li^+ ions. The good voltage regulation due to the character of the red-ox processes of this material (first-order phase transitions that occur at nearly constant potentials) during cycling, the relatively low cost, the excellent electrochemical reversibility and the fact that this material can be considered to be environmentally friendly, makes LiMn_2O_4 an attractive cathode material for aqueous Li-ion batteries [19], [20]. Furthermore, its electrochemical properties, such as high voltage, high rates and fully reversible behavior in aqueous media, make LiMn_2O_4 a good cathode material for ALIC. The choice of electrolyte solutions deserves further discussion. In order to ensure high specific capacity and fast rates we have chosen to work with 2 M Li_2SO_4 aqueous solutions. Despite their limited electrochemical stability, aqueous solutions may have significant inherent advantages over organic electrolyte solutions for capacitive energy storage and conversion: high ionic conductivity, low cost, non-flammability and environmentally friendly properties. They can be electrochemically stable with carbon electrodes up to a 2 V potential window. Usually, aqueous-based electrolytes are limited by oxygen evolution. The thermodynamic voltage range of stability of water is 1.23 V. Supercapacitors based on KOH or H_2SO_4 aqueous electrolyte solutions are limited to 1 V and 0.8 V, respectively

[7,21,22]. By using neutral aqueous electrolyte solutions that contain sulfates, we can reach wider electrochemical windows, up to 2 V, without oxygen or hydrogen evolution reactions due to high over-potential for the gas evolution reactions [23].

2. Experimental details

Activated carbon powder was obtained from EnerG2 Corporation. The separators were purchased From NKK (Japan). Super P carbon black from Timcal (Switzerland) is used as an electrically conductive additive for the composite electrodes. Electrodes are prepared with two types of binders: Teflon and Polyvinylidene difluoride (PVDF) dissolved in of 1-Methyl-2-Pyrrolidinone (NMP). Teflon emulsion (60%) was obtained from Sigma-Aldrich. PVDF and NMP solutions were purchased from Sigma-Aldrich. LiMn_2O_4 from Yunan Yuxihuilong Technology Co. Ltd is used. Electrodes are prepared by two procedures:

1. Mixing active materials with carbon black and PVDF binder (in NMP) and then spreading the slurry on nickel-mesh current collectors.
2. Mixing the active materials and carbon black (CB) with a Teflon emulsion, thereby forming a slurry, and then spreading the mixture on a current collector and calendaring it to the desired thickness.

All the electrochemical measurements were performed using potentiostatic or galvanostatic computerized instruments from Bio-Logic Inc. For galvanostatic prolonged cycling, a multi-channel battery analyzer from Arbin Inc. was used.

A FEI Magellan 400L high-resolution scanning microscope (FEI Company, USA) was used for electrode-surface imaging. Gas adsorption properties are studied using a San Autosorb-1 MP (Quantochrome, Florida USA). The specific surface area of the electrode materials was calculated using the BET model.

Electrochemical measurements were performed in three-electrode cells with saturated calomel reference electrodes (SCE). The stable potential difference between the SCE and standard hydrogen electrode (SHE) is +0.242 V. Argon was bubbled through the cells to avoid undesirable reactions with dissolved oxygen. The electrolyte solution was 2 M Li_2SO_4 at pH = 7.5. At this concentration, the conductivity is the highest (See supporting information Fig. S1).

Electrochemical characterization of the LiMn_2O_4 electrodes was carried out in three-electrode cells. Ni mesh (from Dexmet Corporation) was found to be the most suitable current collector for these electrodes in the aqueous media used here. Ni-mesh samples were coated with a slurry comprising 80% LiMn_2O_4 , 10%CB, and a 10% binder. The counter-electrodes were composed of Pt mesh and the reference electrodes were SCE. A typical cyclic voltammetric response of Ni mesh electrodes vs. SCE in the solutions we use (2 M Li_2SO_4 , pH = 7.5) is presented in Fig. S1 at the supporting information and demonstrates the required stability, which justifies the use of this current collector for the LiMn_2O_4 electrodes.

Model ALIC devices were prepared in 2325 coin-cell configuration with composite electrodes. The LiMn_2O_4 positive electrodes had the following composition: 80 wt% active mass, 10 wt% carbon black and 10 wt% binder with mass loading of 7 mg cm^{-2} , while the activated carbon negative electrodes comprised 87 wt% activated carbon, 5 wt% carbon black and 8 wt% Teflon binder with a mass loading of 6 mg cm^{-2} . Electrode balancing (weight/area) for each set of negative and positive electrodes was maintained, to ensure good charge distribution between the electrodes. The specific capacity of the positive LiMn_2O_4 spinel electrodes used for calculation was about 100 mAh g^{-1} , corresponding to about 360 C g^{-1} (Q_+).

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