Journal of Electroanalytical Chemistry 688 (2013) 103–112

Contents lists available at SciVerse ScienceDirect

Journal of Electroanalytical Chemistry

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

Lithiation of amorphous carbon negative electrode for Li ion capacitor

Gerald Gourdin [a], Patricia H. Smith [b], Thomas Jiang [b], Thanh N. Tran [b], Deyang Qu [a,*]

[a] Department of Chemistry, University of Massachusetts Boston, Boston, MA 02125, United States
[b] Naval Surface Warfare Center, Carderock Division West Bethesda, MD 20817, United States

ARTICLE INFO

Article history:
Available online 13 September 2012

Keywords:
Asymmetric supercapacitor
Lithiation
SEI layer
Amorphous carbon electrode

ABSTRACT

Electrochemical double-layer capacitors (EDLCs) are well suited to time-dependent electrical power output, but in terms of their overall energy density, these devices are much more limited in comparison to Li ion batteries. However, asymmetric supercapacitors that utilize a lithiated negative electrode and a high surface area positive electrode can result in significant improvements in the overall energy density of the device. Key to the development of a Li_xC_6 asymmetric supercapacitor, or Li ion capacitor, is the preparation of the lithiated negative electrode. A common method of accomplishing this is to allow Li ions to intercalate into the carbon material under a spontaneous potential gradient. However, the insertion process can be very slow and may take several hours to reach equilibrium. However, an electrochemically driven lithiation process could significantly decrease the electrode preparation time, which would have great benefits for the development of these devices. Three methods for the insertion of Li into activated carbon electrodes were evaluated in this work that examined the examined the effect of electrochemically-driven lithiation of an activated carbon powder electrode as it may compare to unaided lithiation. In addition, in one of the configurations, the sacrificial Li metal electrode faced the 'back' side of the carbon electrode, which provides the advantage in that the cell would not have to be disassembled and re-assembled to evaluate the completed Li capacitor cell, since the positive electrode could readily be added to the cell during the initial assembly. During the lithiation process, the current flow and total charge passed were monitored and an electrochemical impedance analysis was performed to gain insight into the formation of the SEI layer on the carbon surface during the Li insertion process.

1. Introduction

There is a growing need for specialized electrochemical energy storage technology that can partly be met by electrochemical double-layer capacitors (EDLCs) or supercapacitors. The power delivery performance of an EDLC fills the gap between dielectric capacitors and traditional batteries, which makes them well adapted to time-dependent high-power applications [1], such as memory backup [2], cold-start vehicle assist [3], and solar cell or wind-generated electrical power storage [4]. The energy storage mechanism of EDLCs derives from the formation of an electric double layer at the electrode/electrolyte interface, which provides the high power and high cyclibility rate of these devices. However, as a consequence of the nature of reversible electrostatic charging, EDLC systems suffer from a more limited energy density when compared to typical batteries [2,5]. This is especially true when that comparison is made to Li ion batteries, which exhibit significantly higher energy densities due to the exceptional capability of the electrode materials to irreversibly store Li. However, high energy density batteries (e.g. Li ion batteries) are intended to be charged/discharged over much longer time scales and are designed primarily as energy storage devices; their power capability is a secondary consideration [6].

As a consequence of these disparities, there has been a push to significantly improve the energy density of EDLCs and several methods of accomplishing this are actively being explored. These areas of active research have generally been confined to three approaches: (1) improving the capabilities of the symmetric capacitor through the use of pseudo-capacitive electrode materials (transition metal oxides, conductive polymers, etc.) [7], (2) modifying the porous structure of the activated carbon electrodes [8,9], and (3) the development of asymmetric capacitors, where both electrodes are not of the same material design [9]. Asymmetric capacitors differ from symmetric capacitors (i.e. double layer capacitors) in that the material of one of the electrodes is replaced with materials possessing more faradaic or pseudo-capacitive properties [10]. Among the most the various types of alternative materials, most notable are lithiated transition metal oxides [8,11], modified carbon blacks [12], and lithiated graphite [13].

As opposed to amorphous carbons, the use of graphite as the negative electrode gives rise to other concerns that may be of

---

* Corresponding author. Tel.: +1 617 287 6035.
E-mail address: deyang.qu@umb.edu (D. Qu).

1572-6657/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jelechem.2012.08.029

greater significance for the use in an asymmetric capacitor. The slow intercalation of Li ions into the graphite matrix can impact the high rate operation of an electrochemical capacitor [14], and graphitic carbons are more amenable to the co-intercalation of solvent molecules between the graphene layers, which can result in increased reactions of the solvent to form a thicker, and more resistant, SEI layer [15,16]. Conversely, work has been shown that amorphous carbons are more resistant to structural changes that arise out of ion intercalation [17]. One possible way to address these inadequacies is to use an amorphous carbon that possesses some graphitic character as the negative electrode. If necessary, partial graphitization of amorphous carbons can be induced through both thermal and chemical means [18,19]. The development of asymmetric capacitors that utilize a lithiated negative electrode, prepared from an amorphous carbon with some graphitic character, and a high surface area positive electrode can result in significant improvements in the overall energy density of an electrochemical capacitor.

Key to the development of a Li_xC_6 asymmetric supercapacitor, or Li ion capacitor (LIC), is the preparation of the lithiated negative electrode. During the initial charge/discharge cycle of a Li ion capacitor or Li ion battery, a significant portion of the Li ions present in the system is used in the formation of the SEI layer. The major components of this layer arise from electrolyte decomposition products reacting with the Li to form ionic lithium compounds (e.g. lithium carbonates and lithium alkyl carbonates). With a non-lithiated negative electrode, it is the Li ions from the electrolyte that are consumed to form the SEI layer, as illustrated in Fig. 1a. Although other factors may also contribute, such as reactions with surface functional groups on the carbon matrix [20], it is the development of the SEI layer that is the most significant contributor to the irreversible capacity [21]. However, pre-lithiation of the negative electrode would allow for the Li salt concentration in the electrolyte to not diminish during the first initial cycles as a stable SEI layer is formed, as illustrated in Fig. 1b. The SEI layer will be formed during the initial pre-lithiation of the electrode using a piece of sacrificial Li metal to supply the Li ions, so that adequate electrolyte conductivity can be maintained after the initial formation cycles. Although a portion of the anions from the electrolyte may undergo reactions to form part of the SEI layer, it is a small fraction and is not considered to be significant.

A simple method for accomplishing this pre-lithiation step would be to allow Li ions to insert unaided into the carbon matrix under the potential difference that spontaneously develops when Li metal and a carbon electrode are combined in a cell. That potential difference is proportional to the energy (ΔG) that drives the chemical lithiation process. Yet, when this method is applied to high surface area carbon materials, the Li insertion process can be very slow and may take several hours to reach equilibrium (or maximum Li loading). Furthermore, since the negative electrode is typically coated on Cu foil, after the lithiation process has completed the cell would then have to be disassembled to insert the

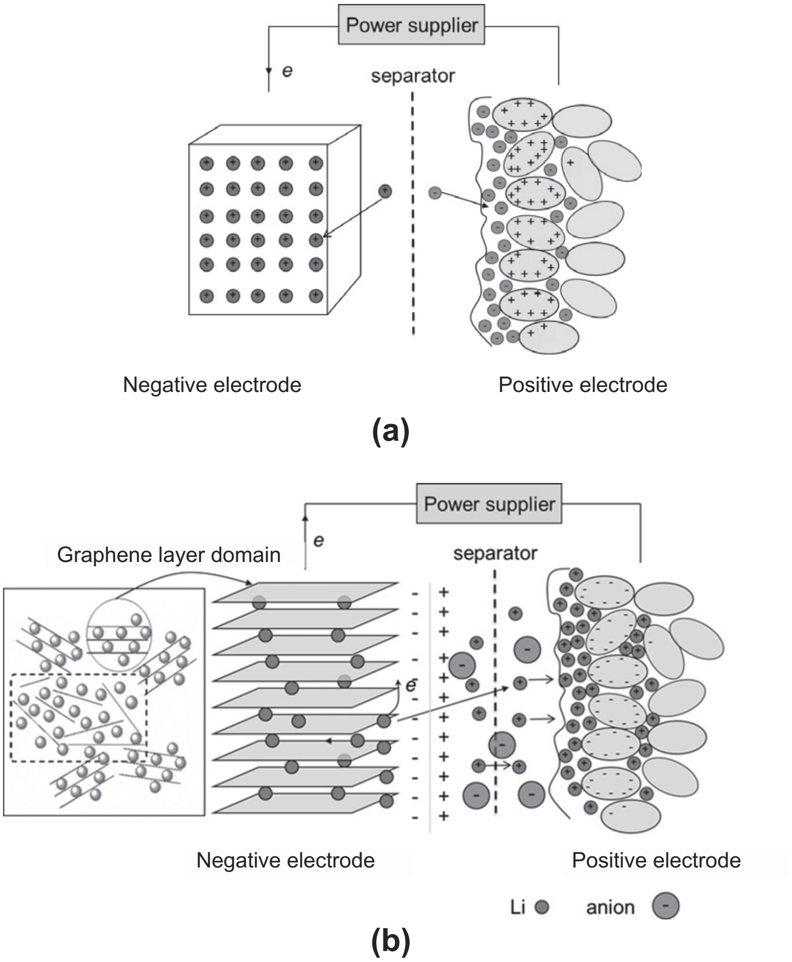

Fig. 1. Charge and discharge mechanisms. This figure illustrates the different mechanisms for the two types of lithium ion capacitors. Li ions from the electrolyte are consumed to form the SEI layer when a non-lithiated negative electrode is used (a) but the Li salt concentration in the electrolyte is not diminished during SEI layer formation when a pre-lithiated negative electrode is used (b).