



Research papers

Lithium-ion adsorption on surface modified porous carbon

Bincy Lathakumary Vijayan^{a,b}, Amina Yasin^{a,b}, Izan Izwan Misnon^{a,b}, Chelladurai Karuppiah^c, Chun-Chen Yang^c, Rajan Jose^{a,b,*}

^a Center for Advanced Intelligent Materials, Universiti Malaysia Pahang, 26300 Kuantan, Malaysia

^b Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, 26300 Kuantan, Malaysia

^c Battery Research Center of Green Energy, Ming Chi University of Technology, New Taipei City 24301, Taiwan, ROC



ARTICLE INFO

Keywords:

Electrochemical capacitors
Supercapacitors
Porous carbon electrodes
Materials sustainability
High voltage capacitors

ABSTRACT

Lithium-ion storage in porous carbon electrodes offers challenges due to poor electrode kinetics and limited storability. In this article, we demonstrate improved lithium-ion storage kinetics and rate capability in carbon electrode with appropriate surface or void modifications. The surface of porous carbon is modified by developing a thin film of either a metal oxide (Mn_2O_3) or a metal (cobalt) or the large voids in them are filled using hierarchical MnCo_2O_4 or TiO_2 nanoflowers. Lithium-ion capacitors are fabricated in the Carbon//LiPF₆//Li configuration and evaluated their lithium storage performance using cyclic voltammetry, galvanostatic charge discharge cycling, and electrochemical impedance spectroscopy. While the surface or void modification nominally increased the specific capacitance, the potential window and rate capability of the resulting devices remarkably increased. Among all the tested devices, the MnCo_2O_4 flowers filled electrode showed the largest capacitance and capacity retention, which are ascribed to its lower lithium transfer resistance.

1. Introduction

Electrical energy storage devices and fuel cells have received significant attention recently than ever before, owing to the efforts to decarbonize the energy sector, where the former become increasingly popular because of their many levels of evolution after its market entry in the form a dry cell delivering 1.5 V by the National Carbon Company in 1896. [1,2] Currently, rechargeable batteries in two storage modes are commercial, viz. lithium-ion batteries (LIBs) and electrochemical capacitors (ECs; synonymously supercapacitors), with significantly differing performance indicators arising from the differences in their storage mode. Batteries store electrolyte charges in their electrodes via (i) a redox reaction, (ii) alloying reaction or (iii) charge intercalation whereas ECs do it via (i) charge accumulation at the pores, known as electric double layer (EDL) formation, (ii) a redox reaction limited to a few layers in the surface, known as pseudocapacitance, (iii) charge intercalation. [3–7] The storage process can be a combination of two or more above mechanisms, known as the hybrid capacitors. [8] Fundamentally, both LIBs and ECs store electrical charge from an electrolyte on positive and negative electrodes and give rise to a voltage; readers are referred to a few in-depth articles on the charge storage in batteries and ECs and their differences. [9–11]

Considering sustainability of electrical energy storage devices, ECs are preferred over batteries at least for two reasons. First is that the electrode materials in batteries are earthborn, which are mined and processed as specialty materials; the processing is highly energy intensive and adds significant amount of carbon emission. [12,13] On the other hand, electrode materials of ECs could be sought from biomass although the current commercial ECs are made from carbons of traditional sources such as coal and pitch. The biomass carbon offers many advantages in terms of sustainability and economy; [14] a few are (i) the precursors are carbon negative as the carbon in biomass are obtained from the atmospheric carbon dioxide via photosynthesis, (ii) low embodied energy and low environmental footprint, and (iii) sustainable. Secondly, the charge storage in EC is via a non-faradic ion adsorption process, thereby giving chargeability at any voltage within the electrochemical stability window of the electrolyte. [15] On the other hand, battery storage is via faradic reaction through either alloying or intercalation or redox reactions or their combinations, thereby requiring certain energies for charging. [16,17] These two advantages make the ECs to be an intensive research topic recently.

Although EDLC-type charge storage is commonly explained as an electrolyte ion adsorption in the pores of the electrode under an applied potential, recent studies have shown that such a simple model is not the

* Corresponding author at: Center for Advanced Intelligent Materials, Universiti Malaysia Pahang, 26300 Kuantan, Malaysia.

E-mail address: rjose@ump.edu.my (R. Jose).

<https://doi.org/10.1016/j.est.2023.108221>

Received 30 March 2023; Received in revised form 16 May 2023; Accepted 28 June 2023

Available online 4 July 2023

2352-152X/© 2023 Elsevier Ltd. All rights reserved.