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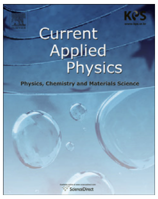

Charge storage performance of lithiated iron phosphate/activated carbon composite as symmetrical electrode for electrochemical capacitor

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ABSTRACT

In this study, a symmetric electrochemical capacitor was fabricated by adopting a lithium iron phosphate ($LiFePO_4$)-activated carbon (AC) composite as the core electrode material in 1.0 M Na_2SO_3 and 1.0 M Li_2SO_4 aqueous electrolyte solutions. The composite electrodes were prepared via a facile mechanical mixing process. The structural properties of the nanocomposite electrodes were characterised by scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) analysis. The electrochemical performances of the prepared composite electrode were studied using cyclic voltammetry (CV), galvanostatic charge–discharge (CD) and electrochemical impedance spectroscopy (EIS). The experimental results reveal that a maximum specific capacitance of 112.41 F/g was obtained a 40 wt% $LiFePO_4$ loading on an AC electrode compared with that of a pure AC electrode (76.24 F/g) in 1 M Na_2SO_3. The improvement in the capacitive performance of the 40 wt% $LiFePO_4$–AC composite electrode is believed to be attributed to the contribution of the synergistic effect of the electric double layer capacitance (EDLC) of the AC electrode and pseudocapacitance via the intercalation/extraction of H^+, OH^-, Na^+ and SO_3^{2-} and Li^+ ions in $LiFePO_4$ lattices. In contrast, it appears that the incorporation of $LiFePO_4$ into AC electrodes does not increase the charge storage capability when Li_2SO_4 is used as the electrolyte. This behaviour can be explained by the fact that the electrolyte system containing SO_4^{2-} only exhibits EDLC in the Fe-based electrodes. Additionally, Li^+ ions that have lower conductivity and mobility may lead to poorer charge storage capability compared to Na^+ ions. Overall, the results reveal that the AC composite electrodes with 40 wt% $LiFePO_4$ loading on a Na_2SO_3 neutral electrolyte exhibit high cycling stability and reversibility and thus display great potential for electrochemical capacitor applications.

1. Introduction

Recently, electrochemical capacitors have been of great interest in the development of new energy storage systems due to their potential to be applied in power electric vehicles, hybrid electric vehicles and renewable energy systems [1]. Commercial electric double-layer capacitors (EDLCs) are mainly based on a symmetric configuration of two porous activated carbon (AC) electrodes immersed in a non-aqueous electrolyte. The charge is stored in the double layer, building up at the interface of porous electrodes and the electrolyte upon polarisation. Because the charge storage mechanism of EDLCs is based solely on reversible ion adsorption on the surface of porous electrodes, the charging process is fast and allows for high-power applications. However, EDLCs cannot store as much charge as batteries because the charge storage process is limited to the surface of the active material [2]. Due to these properties, EDLCs are characterised by a low specific energy (less than 10 Wh/kg) and a high specific power (above 10 kW/kg) [3]. In contrast, secondary batteries are electrochemical energy storage

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devices capable of delivering a high specific energy of up to 250 Wh/kg but a rather low specific power compared with electrochemical capacitors, which typically does not exceed 1 kW/kg [3].

Recent studies have demonstrated that the energy density can be increased significantly through the development of a lithium ion capacitor (LIC), which utilises both high-surface-area AC and a lithiated compound in a lithium-based non-aqueous electrolyte [4]. The concept of a non-aqueous LIC was first introduced by Amatucci and co-workers in 2001 [5]. The hybrid system was constructed with a nanosized $Li_4Ti_5O_{12}$ negative electrode and an AC positive electrode in a non-aqueous electrolyte, achieving a specific energy of more than 20 Wh/kg with 85% capacity retention after 5000 cycles. The high working voltage in a non-aqueous LIC causes an electrolyte depletion problem during the charging process, which may adversely affect the safety and long-term stability of the LIC [6]. Thus, Wang and co-workers (2005) developed a new concept hybrid electrochemical capacitor technology constructed with a $LiMn_2O_4$ positive electrode and an AC negative electrode in a mild Li_2SO_4 aqueous electrolyte [7]. This new state-of-the-art hybrid aqueous electrochemical capacitor can provide promising solutions for the major problem of electrolyte depletion observed in conventional non-aqueous hybrid capacitors. The results indicate that the use of an aqueous electrolyte can overcome the drawbacks of safety hazards arising from the use of highly toxic and flammable solvents in an organic electrolyte. Similarly, another aqueous-based asymmetric system has been successfully synthesised in which acid-treated $LiMn_2O_4$ was used as the positive electrode in combination with AC operating as the negative electrode in 1 M Li_2SO_4, resulting in a specific capacitance of 60 F/g. The capacitive performance can potentially be improved by acid treatment of the $LiMn_2O_4$ compound, which could lead to the perseverance of the $LiMn_2O_4$ structural framework as well as the oxidation of manganese from Mn^{3+} to Mn^{4+} after lithium-ion removal [8]. Recently, nanosized $LiFeO_2$ has been explored as a potential electrochemical capacitor electrode material in Li_2SO_4. This novel electrode material is able to achieve a stable capacitance of 50 F/g in the neutral electrolyte. The Li^+ ions with the smaller unhydrated radii may reversibly intercalate/de-intercalate in the $LiFeO_2$ lattices, resulting in pseudocapacitance [9].

Lithium iron phosphate ($LiFePO_4$) is a promising lithium metal oxide that exhibits high capacity stability during prolonged cycling, good rate performance, environmental friendliness, low cost and safety [10]. Composite electrodes consisting of both this material and AC, which offers low cost and an excellent cycle life and fast charge capability, appears as one of the most viable strategies to develop electrochemical capacitors with high performance without significant safety concerns. Although several papers have focused on $LiFePO_4$ as a potential electrode material for non-aqueous Li-ion capacitors [10,11], few studies have evaluated the electrochemical performance of $LiFePO_4$-based electrode materials in mild aqueous electrolytes. Moreover, to the best of our knowledge, no research has been reported on symmetric composite electrodes assembled using $LiFePO_4$ and AC for Li-ion capacitors. Hence, in this work, we undertake a detailed evaluation of the electrochemical performance of $LiFePO_4$/AC composite electrodes in neutral Na_2SO_3 and Li_2SO_4 aqueous electrolytes. The composite material is prepared via simple facile mechanical mixing in a dispersive solvent followed by the intercalation of electrolyte ions. The problem associated with the commonly reported poor electric conductivity of $LiFePO_4$ could be overcome by the incorporation of a predetermined amount of carbon black into the system, which can significantly improve the electrochemical performance of oxide-based composite electrodes.

2. Materials and methods

2.1. Preparation of electrodes

The active core materials were prepared by adding various compositions of $LiFePO_4$ with a BET surface of approximately 12.87 $m^2\ g^{-1}$ (RHE Resources, Malaysia) to AC with a BET surface of approximately 1716 $m^2\ g^{-1}$ (RHE Resources, Malaysia) to form the composite electrodes containing carbon black (Ketjen black, EC-600JD from Akzo Nobel, surface area of approximately 1400 $m^2\ g^{-1}$) and polytetrafluoroethylene (PTFE 60% dispersion in H_2O, Sigma Aldrich) as the polymer binder in the weight ratio of 80:15:5. Six different electrode compositions were evaluated in this study, as listed in Table 1. The mixture was dissolved into a 1:1 mixed solution of distilled water and isopropanol by mechanical mixing and stirring. The mixtures in dough form were then cold-rolled into 0.8-mm-thick films. The electrodes were punched into coin-shaped electrodes of 2 cm^2 and were dried in a vacuum oven at 80 °C for 45 min to ensure that the isopropanol solvent was evaporated completely. After being immersed overnight in 1 M Na_2SO_3, the discs were then sandwiched together with aluminium current collectors in a Teflon cell for electrochemical measurements. All of the electrochemical measurements were performed with a two-electrode Teflon cell via the screw-fitting plug method.

2.2. Structural analysis

The microstructure and surface morphology of the $LiFePO_4$/AC composite electrodes were observed using a field-emission scanning electron microscope (FESEM, FEI, Quanta 400 F). The crystal structure of the composite electrodes was determined using Pan analytical X-ray diffraction (XRD) analysis. The detected diffraction angle (2θ) was scanned in the range of 20–70° using Cu-Kα radiation with a wavelength of 1.5418 Å. The physical adsorption of N_2 at the normal boiling point (−195.875 °C or 77 K) was performed over a range of N_2 pressures below 1 atm to characterise the specific surface area of composite electrodes from a five-point surface area measurement using the Brunauer–Emmett–Teller (BET) equation with a Micromeritic ASAP 2020 surface area analyser.

2.3. Electrochemical characterisation

Electrochemical tests, including cyclic voltammetry (CV), charge–discharge testing (CD) and electrochemical impedance spectroscopy (EIS), were performed using a Metrohm Autolab PGSTAT128N potentiostat equipped with a FRA2 frequency response analyser module and FRA software. In this study, all of the electrodes were tested in 1 M Na_2SO_3 and 1 M Li_2SO_4. All of the data presented here were obtained from a real two-electrode system. The CV curves were scanned from 0 to 1 V at a voltage ramp rate of 10 mV/s. Galvanostatic CD was conducted at a constant current of 20 mA. EIS was conducted using a sinusoidal signal with a mean voltage of 0 V and an amplitude of 10 mV over the frequency range of 100 kHz to 10 mHz.

Table 1
The composition of various active compounds in the electrodes.

Electrode material	$LiFePO_4$ (wt %)	Activated carbon (wt %)	Carbon black (wt %)	PTFE (wt %)
AC	0	80	15	5
4 LFP	4	76	15	5
20 LFP	20	60	15	5
40 LFP	40	40	15	5
60 LFP	60	20	15	5