

UNIVERSITI TEKNOLOGI MARA

**ELECTROCHEMICAL STUDIES OF
CARBON NANOTUBE-REDUCED
GRAPHENE OXIDE WRAPPED
IRON COBALTITE FOR ALL-SOLID-
STATE ASYMMETRIC
SUPERCAPACITOR**

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ABSTRACT

Supercapacitors employing transition metal oxide electrodes exhibit larger specific capacitances and energy densities. However, transition metal oxides have smaller surface area, which limit the kinetic in redox reaction. Performance enhancement of the transition metal oxide electrodes can be achieved by incorporation of carbonaceous materials, to form composite electrode. However, incorporation of carbonaceous materials during the synthesis process can alter the morphology properties of the transition metal oxides. Iron cobaltite, FeCo_2O_4 with nanosheets morphology (FCO) was synthesized by hydrothermal method. It exhibits large specific surface area and pore volume, which enhances the loading and diffusion of ions within the electrode. Herein, we designed composite electrodes made up of FCO, reduced graphene oxide (rGO) and functionalized multi-walled carbon nanotubes (f-MWCNTs) while retaining the high specific surface area of the FCO nanosheets. The composite electrodes were prepared by a two-step hydrothermal process. The prepared composite electrodes were characterized for their structural, morphological, and electrochemical properties. The composite electrodes maintained the flower-like nanosheet structure of the pristine FCO. The electrochemical properties of FCO and its composites were examined by cyclic voltammetry (CV), galvanostatic charge discharge (GCD), and electrochemical impedance spectroscopy (EIS). At 3 A g^{-1} , the composite electrode exhibits specific capacitance, C_{sp} of 1797 F g^{-1} as compared with 943 F g^{-1} of the pristine FCO. The higher C_{sp} of composites as compared to FCO is because high conductive f-MWCNT and rGO help in reducing the internal resistance of the electrode. However, excessive loading of f-MWCNT and rGO bring adverse effect to the C_{sp} performance. This is because when f-MWCNT and rGO are in excess, the porous structure of FCO can be further closed up, which is supported by the Barrett-Joyner-Halenda (BJH) analysis. Used in an asymmetric supercapacitor, the composite electrode demonstrates maximum energy density of 34 Wh kg^{-1} , maximum power density of 4479 W kg^{-1} and 92 % rate capability after 5000 cycles. In contrast, the pristine FCO retains only 70 % capacitance after 3000 cycles. The performance of supercapacitors in this work is comparable with other published works.

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CHAPTER ONE

INTRODUCTION

1.1 Research Background

Energy storage device is aggressively developing in these recent years. This is due to the high demand of electric energy in science and technology industries. Many researchers devoted attention in the studies and development of supercapacitors. Supercapacitors store charge by ion adsorption or fast redox reaction to achieve higher capacitance compared to conventional capacitor (S. S. Shah et al., 2021). The advantages of supercapacitors are high power density, long cycle life, environmental friendliness, light weight and small in size (Xiang Zhang et al., 2017).

Supercapacitors can be classified into electrochemical double layer capacitors (EDLCs) and pseudocapacitors, based on the electrode materials employed and their storage mechanism. The electrode materials of EDLCs are made from carbon materials such as graphene and carbon nanotube. Carbon materials are used because they have high specific surface area, good electrical conductivity and good stability (Rajagopal, Pulapparambil Vallikkattil, Mohamed Ibrahim, & Veleev, 2022). However, carbon materials suffer from low specific capacitance and low energy density (J. Yu et al., 2019). The charge storage mechanism in EDLCs is non-Faradaic. There is no charge transfer between the electrode and electrolyte but based on the charge accumulation at the electrode-electrolyte interfaces (Mitra, Shukla, & Sampath, 2001). An “electrical double layer” is formed between the electrodes and the electrolyte as a result of charge accumulation.

On the other hand, the charge storage mechanism in pseudocapacitor is Faradaic, which involves the transfer of charge between electrode and electrolyte such as oxidation-reduction, and intercalation. Pseudocapacitive materials such as metal oxides, metal hydroxides and metal selenides are used as the electrode materials. Pseudocapacitors with transition metal oxide electrodes such as MO_2O_4 ($M = Li, Mn, Ni, Cu, Zn$) possess high specific capacitance and high specific energy (W. Xu et al., 2018). However, transition metal oxides suffer from poor cycling stability due to their poor conductivity (Xinyang Zhang et al., 2018).