FABRICATION AND CHARACTERIZATION OF NICKEL-COATED POLYETHYLENE TEREPHTHALATE SUPPORTED MANGANESE DIOXIDE THIN-FILM ELECTROCHIMICAL CAPACITOR PROTOTYPES

Wee Boon Hong

Master of Science
2011
FABRICATION AND CHARACTERIZATION OF NICKEL-COATED POLYETHYLENE TEREPTHALATE SUPPORTED MANGANESE DIOXIDE THIN-FILM ELECTROCHEMICAL CAPACITOR PROTOTYPES

WEE BOON HONG

A thesis submitted
in fulfillment of the requirement for the Degree of
Master of Science
(Physical Chemistry)

Faculty of Resources Sciences and Technology
UNIVERSITI MALAYSIA SARAWAK
2011
Acknowledgements

First and foremost, I wish to express my deepest gratitude to my research mentor, Associate Professor Dr. Pang Suh Cern for his near-infinite patience throughout the course of my study. Without his endless encouragement, meticulous guidance and generous financial support, this research project – a brainchild of his works related to energy storage devices, would not have gained much recognition both locally and internationally. My warmest thanks also go to the only member of my advisory committee, Dr. Chin Suk Fun for her invaluable technical inputs and suggestions for which much of unnecessary duplication of effort was avoided during my research works. Much of technical data particularly SEM and TEM micrographs presented in this dissertation were beautifully taken thanks to Madam Ting Woei, scientific officer at Faculty of Resource Science and Technology, despite being committed to her tight and painstaking schedule.

Besides being a postgraduate student, I am also a full time chemist attached to the Malaysian Department of Chemistry (Bintulu Laboratory) which travelling on and off to Physical Chemistry Laboratory (UNIMAS) monthly was required during the first two years of my research. Those were indeed the bumpiest and most tiring throughout the whole duration my study having to travel a total of 1,282 kilometres to and forth by bus. Without the kindness help and support from all my friends in preparing necessary documents to gain access to the laboratory, I would not have easily completed my research which I had ever contemplated of giving up. My perseverance nonetheless kept me on track. To all my friends – Chen Lim, Chian Ye, Miss Tay, Sze Yun and Wai Hwa, your caring and supportive gestures as well as the joyful moment together are greatly appreciated and missed.
During the course of my study, my frequent absence especially in festive occasions was reluctantly acquiesced by my family particularly my soul mate for which I am very much obliged. I am greatly indebted for their unconditional love and support which has been the mainstay that have encouraged me to the completion of my study.
Abstract

Energy deficiency has always been a pressing global concern especially during the midst of the ditch of the world’s oil reserve meagrely supplying 80% to 90% of the current worldwide energy consumption. The increasing demand of fossil fuels at the turn of the millennium can be incontrovertibly associated with the exponential growth of human population resulted in the worrying surge of oil’s price where in search of replacement for this finite resources is direly needed. In today’s society, dramatic advancement in modern electrical technologies which we are heavily dependent on has altered the globe’s energy requirement to cheaper, cleaner, durable, efficient and sustainable energy resources. In respond to the paradigm-shift, concerted efforts are being focused on the development of high performance energy-storage systems that are capable of meeting the ever increasing energy demand of various device applications. As such, our present study entails the fabrication of manganese dioxide (MnO2) thin film electrochemical capacitor prototypes via novel prototyping process (Patent Pending PI 20094040) of core interest focused predominantly on utilizing ubiquitous and environmentally benign materials, optimizing electrode configuration and nanostructuring of electroactive material (MnO2).

Of all electroactive materials, manganese dioxide is specially selected as it not only fulfills the basic criteria for electrode materials as being cheap and toxicologically harmless, but also exhibits superior capacitive behaviour comparable to that of ruthenium dioxide. Ruthenium dioxide despite being regarded as the quintessential electrode material to date, its potential applications are commercially unviable where the limiting factor mainly lies in the expensive cost of production. The rapid prototyping process which we have developed entails the deposition of manganese dioxide thin films on metallized poly(ethylene terephthalate) substrate.
using the novel horizontal submersion approach. Interdigitated array (IDA) electrodes of different configurations were generated using a computer interfaced cutting plotter. Subsequently a conformal agar-based gel electrolyte layer containing dissolved Na₂SO₄ salt was deposited by solution casting directly onto the IDA electrodes. These prototypes of different IDA electrode configurations were studied using various established characterization techniques. Both electrochemical and material characterizations of the thin-film MnO₂ electrochemical capacitor prototypes showed promising electrochemical properties with excellent capacitive performance and cycling reversibility. Morphological characterizations showed that the deposited manganese dioxide thin films were largely nanoparticulate in nature and possess high electrochemically active surface area. Noticeable morphological changes of MnO₂ film were observed during voltammetric cycling in which the film was slowly transformed into a well-organized and interconnected petal-like microstructure. As a result, MnO₂ electrodes of enhanced cycling stability and capacitive behaviour were obtained. However, the physicochemical mechanisms that governed the observed morphological changes which led to the formation of foregoing microstructure remained unclear. Much research on the synthesis of nanomaterials is imperatively necessary to better understand the myriad of fundamental interactions at nanoscale level. Electrodes of desired microstructures can therefore be finely architectured to obtain enhanced capacitive performance.

Cyclic voltammetry studies on MnO₂-based electrochemical capacitors with dual planar IDA electrode configurations showed that the capacitive performance is more superior compared with ECs of conventional parallel electrode configuration in terms of the specific capacitance, cycling stability and coulombic efficiency. Electrochemical impedance spectroscopy provides complimentary data to that obtained by cyclic voltammetry. The impedance characteristics of
MnO₂-based electrode were measured at predetermined frequency range and amplitude of alternating/direct current potential. A Nyquist plot of MnO₂-based electrochemical capacitors with IDA electrode configurations indicated distinctive impedance responses which include: 1) a nearly pure capacitive behaviour represented by vertical plot of phase angle approximate to at low frequencies, 2) a diffusion controlled behaviour represented by inclined plot of phase angle approximate to π/4 at intermediate frequencies, and 3) a purely resistive behaviour represented by depressed semicircular arc at high frequencies. The exceptional capacitive performance of EC prototypes of IDA electrode configuration could be attributed to the enhanced ionic conductivity associated with the shorter ionic diffusion path length and utilization of electroactive materials. The major advantage of IDA electrode configuration is that each pair of electrode array can be potentiostated individually and hence resulted in a higher reaction kinetic by providing a shorter diffusion path length between adjacent electrodes for redox electroactive species.

Despite its long-standing merits as the cathode electrode of commercial batteries, the MnO₂-based electrode is currently being extensively studied for electrochemical capacitor applications. The functionalities of MnO₂-based electrodes have inspired an attempt to fabricate novel hybrid energy storage prototype which comprises a battery and an electrochemical capacitor being integrated as a single embodiment. It is denoted as the Hybrid Batt-EC prototype which consists of two MnO₂-based EC prototypes with IDA electrode configuration 2, and a piece of galvanized zinc inserted between these IDA EC prototypes. Chronopotentiometry evaluation of this hybrid device showed encouraging results with energy density of 1.17 x 10⁻³ Ah or 1.17 mAh could be obtained at a discharge current of 0.01 mA.
It is envisaged that nanostructuring of electroactive materials offers a more accurate and precise control on the microstructures and porosity (uniform distribution of pores) of desirable electrochemical characteristic. It is recommended that future works should address the effect of microstructural parameters, namely film thickness and homogeneity, grain size, porosity and electrochemically active surface area, and optimized interdigitated array (IDA) electrode configurations.
FABRIKASI DAN PENCIRIAN PROTOTAIP KAPASITOR ELEKTROKIMIA FILEM NIPIS
MANGAN DIOKSIDA YANG DISOKONG OLEH POLIETILENA TEREFTALAT
BERSALUTAN NIKEL

Abstrak

Kekurangan sumber tenaga merupakan isu global yang membimbangkan terutamanya semasa sumber minyak asli yang semakin merosot dan hanya mampu membekal sebanyak 80% hingga 90% kepada penggunaan sumber tenaga dunia. Peningkatan populasi manusia secara langsung mengakibatkan permintaan yang mendasar ke atas minyak asli dan akibatnya harga minyak asli mencatat peningkatan yang tidak terkawal menyebabkan pencarian sumber tenaga alternatif amat diperlukan. Pada zaman sekarang, peralatan elektrik berteknologi moden akan memerlukan sumber tenaga yang lebih murah, bersih, tahan, cekap dan mampan. Dengan itu, usaha pembangunan sistem penyimpanan tenaga sedang giat dijalankan untuk memenuhi keperluan tenaga yang semakin meningkat. Projek penyelidikan ini adalah berkaitan dengan fabrikasi prototaip mangan dioksida (MnO2) kapasitor elektrokimia filem nipis melalui proses fabrikasi (Hak Cipta PI 20094040) yang menggunakan bahan mentah yang murah dan mesra alam, konfigurasi elektrod yang paling optimum dan penstrukturan bahan elektroaktif nano.

Daripada kesemua bahan elektroaktif, mangan dioksida telah dipilih dalam penyelidikan ini kerana ia bukan sahaja memenuhi segala kriteria-kriteria sebagai bahan elektrod yang murah dan tidak bertoksik, ciri-ciri kapasiti yang bagus juga setanding dengan ruthenium dioksida (RuO2). Walaupun RuO2 telah dikenalpasti sebagai bahan elektrod yang paling bagus dalam penghasilan elektrod tetapi kosnya adalah sangat mahal. Proses penghasilan prototaip yang vii
diciptakan ini merangkumi penghasilan filem nipis mangan dioksida pada permukaan substrak polietilen tereftalat (PET) dengan menggunakan teknik rendaman mendatar (horizontal submersion). Elektrod interdigitated array (IDA) telah dihasilkan menggunakan pisau plotter yang dikawal oleh sistem komputer. Selepas itu, lapisan elektrolit gel agar yang mengandungi garam terlarut Na₂SO₄ dibentukkan di atas permukaan elektrod IDA melalui teknik solution casting. Kemudian, prototaip-prototaip yang mempunyai konfigurasi elektrod IDA berlainan akan diuji dengan menggunakan teknik-teknik tertentu.

Kapasitor elektrokimia MnO₂ mempamerkan ciri-ciri elektrokimia dan bahan yang memberangsangkan dengan prestasi kapasiti dan kestabilan mengitar yang bagus. Lapisan nipis mangan dioksida yang dibentuk terdiri daripada partikal nano yang mempunyai permukaan elektrokimia yang tinggi. Perubahan morfologi yang ketara semasa voltammetric cycling melibatkan transformasi partikal nano tersebut ke rangkaian struktur mikro seperti kelopak yang teratur. Akibat daripada struktur mikro yang terbentuk tersebut, kestabilan mengitar dan kapasiti elektrod mencatatkan peningkatan. Namun demikian, mekanisma-mekanisma yang menyebabkan perubahan morfologi tersebut adalah tidak diketahui. Oleh itu, penyelidikan ke atas sintesis bahan nano adalah penting untuk dikaji supaya lebih memahami interaksi-interaksi asas pada tahap berskala nano. Dengan pengetahuan tersebut, elektrod yang mempunyai struktur mikro yang diperlukan dan elektrod yang berkapasiti lebih tinggi boleh dihasilkan.

Hasil ujian cyclic voltammetry, menunjukkan bahawa prestasi kapasiti dari segi specific capacitance, kestabilan mengitar dan kecepatan coulombic bagi kapasitor elektrokimia MnO₂ yang berelektrod konfigurasi IDA adalah lebih tinggi berbanding dengan kapasitor elektrokimia yang menggunakan elektrod konvensional. Electrochemical impedance spectroscopy membekalkan data tambahan di samping data-data yang diperolehi daripada cyclic
Ciri-ciri rintangan elektrod MnO₂ boleh ditentukan dengan menguji elektrod tersebut pada frekuensi dan amplitud potensi arus terus/ulang-alik yang tertentu. Ciri-ciri utama plot Nyquist untuk kapasitor elektrokimia MnO₂ adalah meliputi: 1) plot menegak yang bersudut π/2 pada frekuensi rendah mewakili ciri-ciri kapasiti yang hampir tulen, 2) plot mencondong bersudut π/4 pada frekuensi pertengahan mewakili ciri-ciri penyebaran, dan 3) *depressed semicircular arc* pada frekuensi tinggi mewakili ciri-ciri perintang yang tulen. Prestasi prototaip EC (elektrod berkonfigurasi IDA) yang memberangsangkan boleh dikaitkan dengan jarak pergerakan ion yang lebih pendek dan penambahbaikan pada penggunaan bahan elektroaktif. Kelebihan utama elektrod berkonfigurasi IDA adalah setiap barisan elektrod boleh *potentiostated* secara berasingan dan menghasilkan jarak pergerakan yang lebih pendek di antara elektrod-elektrod berdekatan. Ini secara langsung meningkatkan tindak balas kinetik pada bahan elektroaktif.

Walaupun MnO₂ sudah lama digunakan sebagai elektrod katod dalam bateri komersial, ia telah dikaji secara meluas sebagai elektrod untuk kapasitor elektrokimia. Disebabkan elektrod MnO₂ yang mempunyai dwifungsi seperti yang dinyatakan, satu prototaip sistem penyimpanan tenaga hibrid telah difabrikasi yang terdiri daripada bateri dan kapasitor elektrokimia yang diintegrasikan dalam satu *embodiment*. Sistem hibrid yang dinamakan prototaip *Hybrid Batt-EC* mempunyai dua prototaip MnO₂ EC yang menggunakan elektrod IDA konfigurasi 2 dan sekeping zink galbani yang diletak di antara prototaip EC tersebut. Ujian *chronopotentiometry* ke atas sistem hibrid tersebut menunjukkan prestasi yang memberangsangkan dengan ketumpatan tenaga sebanyak \(1.17 \times 10^{-3}\) Ah atau 1.17 mAh pada arus discas 0.01 mA.

Ini menunjukkan bahawa kemungkinan besar penstrukturkan bahan elektroaktif nano boleh mengawal struktur mikro dan keliangan dengan lebih jitu dan tepat. Cadangan untuk projek penyelidikan seterusnya harus meliputi kesan-kesan struktur mikro seperti ketebalan dan
kehomogenan filem, saiz butiran, keliangan dan luas permukaan bahan elektroaktif dan elektroda
berkonfigurasi IDA yang optimum.
# Table of Contents

Acknowledgements ............................................. i
Abstract ................................................................ iii
Abstrak ................................................................ vii
List of Tables ......................................................... xv
List of Figures ......................................................... xvii
List of Abbreviations ............................................... xxiv

## Chapter 1: Introduction

1.1 Background ..................................................... 1
1.2 Fundamentals of Electrochemical Capacitors (ECs) .... 3
1.3 Applications of Electrochemical Capacitors (ECs) ....... 5
1.4 Objectives ....................................................... 7
1.5 Goals and Findings ............................................ 8

## Chapter 2: Literature Review

2.1 Electrode Materials for Electrochemical Capacitors (EC) 12
2.2 Electrochemical Performance of Manganese Dioxide Electrode 15
2.3 Electrolyte Materials for Electrochemical Capacitors (EC) 19
2.4 Current Collectors for Electrochemical Capacitors (EC) ..... 22

## Chapter 3: Fabrication of Manganese Dioxide Thin-film Electrochemical

...
Capacitors Prototypes

Abstract

3.1 Introduction

3.2 Materials and Methods

3.2.1 Materials

3.2.2 Preparation of \( \text{MnO}_2 \) sol

3.2.3 Preparation and Characterization of \( \text{MnO}_2 \) Thin Films

3.2.4 Fabrication of EC Prototypes

3.2.5 Electrochemical Evaluation of EC Prototypes

3.3 Results and Discussion

3.3.1 Characterization of \( \text{MnO}_2 \) Thin-film Electrodes

3.3.2 Fabrication of EC Prototypes

3.3.3 Electrochemical Characterization and Evaluation of EC Prototypes

3.3.3.1 Cyclic Voltammetry (CV)

3.3.3.2 Electrochemical Impedance Spectroscopy (EIS)

3.3.3.3 Chronopotentiometry (CP)

3.4 Conclusion

Chapter 4 Characterization and Performance Evaluation of Manganese Dioxide Thin-Film Electrochemical Capacitor Prototypes

Abstract

4.1 Introduction
4.2 Materials and Methods

4.2.1 Materials 62
4.2.2 Preparation of MnO₂ sol 62
4.2.3 Preparation and Characterization of MnO₂ Thin Films 63

4.3 Results and Discussion

4.3.1 Microstructural Characterization of MnO₂ Thin Films 64
4.3.2 Cyclic Voltammetry (CV) 69
4.3.3 Electrochemical Impedance Spectroscopy (EIS) 72
4.3.4 Effect of Scan Rates 78
4.3.5 Effect of Electrolytes 83
4.3.6 Effect of Electrolyte Concentration 86
4.3.7 Effect of Polarization 88

4.4 Conclusion 94

Chapter 5 Optimization of Manganese Dioxide Thin-Film Electrochemical Capacitor Prototypes

Abstract 95

5.1 Introduction 96

5.2 Materials and Methods

5.2.1 Materials 98
5.2.2 Preparation of Agar-based Gel Electrolyte Films 98
5.2.3 Fabrication of MnO₂-based EC Prototypes of IDA 99

Electrode Configurations  

xiii
5.3 Results and Discussion

5.3.1 Agar-based Gel Electrolyte with Different Na₂SO₄ Electrolyte Concentration

5.3.2 Electrochemical Characterization and Performance Evaluation of EC Prototypes

5.3.2.1 Cyclic Voltammetry (CV)
5.3.2.2 Electrochemical Impedance Spectroscopy (EIS)
5.3.2.3 Chronopotentiometry (CP)
5.3.2.4 Effect of Agar-based Gel Electrolyte Film Thickness

5.3.3 Fabrication and Electrochemical Characterization of Hybrid Energy Storage Device

5.3.3.1 Cyclic Voltammetry (CV)
5.3.3.2 Electrochemical Impedance Spectroscopy (EIS)
5.3.3.3 Chronopotentiometry (CP)

5.4 Conclusion

Chapter 6 Conclusion and Recommendation

6.1 Concluding Remarks

6.2 Recommendation for Future Works

References
List of Tables

Table 3.1 Typical layout dimension of EC prototypes with different electrode configurations.

Table 3.2 Total cost of materials for the production of a functional MnO₂ EC prototype.

Table 3.3 The cycling behavior of EC prototypes of different IDA electrode configurations.

Table 3.4 Capacitance (mF) and Specific capacitance (F/g) values of EC prototypes determined by EIS at different frequency. EC prototypes were evaluated in liquid and agar-based gel electrolytes before (*) and after (†) cyclic voltammetry test.

Table 3.5 Typical galvanostatic charge/discharge behavior for EC prototypes of different IDA configurations at charge/discharge current of 0.08 mA.

Table 4.1 Specific capacitance (F/g) for MnO₂-based electrochemical capacitors calculated from cyclic voltammograms (CVs) at different scan rates and electrochemical impedance spectroscopy (EIS) at the frequency of 10 mHz.

Table 4.2 Specific capacitance (F/g) of MnO₂-based electrochemical capacitors (Configuration 1) in different aqueous electrolytes calculated from cyclic
voltammograms (CVs) at scan rate of 50 mV/s and electrochemical impedance spectroscopy (EIS) within the frequency range of 1 MHz to 10 mHz.

Table 4.3 Activity coefficient of the cation, ionic strength and cation activity.

Table 5.1 Composition of agar-based gel electrolyte films.

Table 5.2 Dimensional properties of the interdigitated array (IDA) electrodes for MnO₂ EC prototypes.

Table 5.3 The capacitive behaviour of EC prototypes of different IDA configurations.

Table 5.4 Coulombic efficiency of EC prototypes of different IDA configurations at charge/discharge current of 0.08 mA.

Table 5.5 Current (mA) and specific capacitance (F/g) of the MnO₂-based EC prototype of IDA electrode configuration 2.
List of Figures

Fig. 2.1 Schematic diagram of cyclic voltammetry for a MnO₂-based electrochemical capacitor in aqueous electrolyte.

Fig. 2.2 Schematic diagram of geometries of microelectrodes and microelectrode arrays: (a) microdisk, (b) microring, (c) microdisk array, (d) microband array, (e) microband, (f) single microcylinder fiber, (g) microsphere; (h) microhemishpere; (i) fiber array, (j) interdigitated array. $r$ is the diameter of the microdisk.

Fig. 3.1 SEM micrographs of MnO₂ thin film of 5 coatings: (a) before cycling test (20K magnification); (b) after cycling test (25K magnification). The insets (a-i) and (b-i) are the typical TEM micrographs of dispersed MnO₂ nanoparticles (500K magnification). Inset (b-ii) is the SEM micrograph of the microstructure of MnO₂ thin film after cycling test.

Fig. 3.2 (a) Cyclic voltammograms of the MnO₂ thin film with various numbers of coatings. (b) Effect of number of coating on the capacitance (mF/cm²) and $Q_a/Q_c$ ratio of the MnO₂ thin film.

Fig. 3.3 Layout of the electrode configuration design. The length of electrode (a and d), width of the electrode finger (b), and gap between adjacent electrodes (c) are depicted.
Fig. 3.4  A rapid prototyping process for the fabrication of thin-film electrochemical capacitor (EC) prototypes.

Fig. 3.5  Cyclic voltammograms for ECs prototypes of various configurations in liquid electrolyte (only show the 10th cycle).

Fig. 3.6  Comparison of cyclic voltammograms for solid-state ECs (a) Configuration 1, (b) Configuration 2, (c) Configuration 3, (d) The cycling behaviour of EC prototypes of various configurations.

Fig. 3.7  Nyquist plots of electrochemical capacitors (EC) prototypes of, (a) configuration 1, (b) configuration 2, (c) configuration 3, in liquid and agar-based gel electrolyte; (d) configuration 1, (e) configuration 2, (f) configuration 3, in agar-based gel electrolyte before and after long cycle test; (g) EC prototype in liquid electrolyte prior to cyclic voltammetric test, and (h) EC prototype in agar-based gel electrolyte after cyclic voltammetric test. All EC prototypes were tested at ambient temperature and 100% Relative Humidity (RH) within the frequency range of 1 MHz to 10 mHz.

Fig. 3.8  Chronopotentiogram for electrochemical capacitors (EC) prototypes of different IDA configurations in agar-based gel electrolyte at constant charge/discharge current of 0.08 mA.
Fig. 4.1  TEM micrographs of (a) dispersed MnO₂ nanoparticles (scale bar is 50 nm), inset shows an individual MnO₂ nanoparticle with nanofibrillar structure, (b) aggregated MnO₂ nanoclusters (scale bar is 50 nm), and (c) longitudinal bundles of MnO₂ nanoclusters (scale bar is 0.2 µm).

Fig. 4.2  SEM micrographs of MnO₂ thin film after cyclic voltammetric cycling in 0.2M Na₂SO₄ liquid electrolyte for (a) 0 cycle, (b) 50 cycles, (c) 100 cycles, and (d) 300 cycles.

Fig. 4.3  (a) Cyclic voltammograms of MnO₂ thin film EC prototypes evaluated in 0.2 M Na₂SO₄ aqueous electrolyte upon cycling for up to 300 cycles, (b) Changes in specific capacitance (F/g) as a function of cyclic number.

Fig. 4.4  Nyquist plots of electrochemical capacitors (EC) at different charge/discharge cycle. (Inset shows the Nyquist plots at high frequency region).

Fig. 4.5  (a) Charge-transfer resistance and Warburg resistance at different charge/discharge cycle; and (b) Constant phase element, CPE and frequency power, n at different charge/discharge cycle.

Fig. 4.6  Cyclic voltammograms at different scan rates (10 to 300 mV/s). Only the 50th cycle of cyclic voltammograms is shown.
Fig. 4.7  The specific capacitance (F/g) of the EC prototypes versus the inverse of CV scan rate (1/scan rate).

Fig. 4.8  Cyclic voltammograms in different aqueous electrolytes at scan rate of 50 mV/s.

Fig. 4.9  (a) Cyclic voltammograms in different Na₂SO₄ electrolyte concentration at scan rate of 50 mV/s, (b) Specific capacitance (F/g) of the EC at different Na₂SO₄ electrolyte concentration, [Na₂SO₄] and cation activity, pNa⁺.

Fig. 4.10  Nyquist plots of MnO₂ EC (the inset shows the Nyquist plots at high frequency region).

Fig. 4.11  The response of current to different operating potentials at frequency from 1 MHz to 10 mHz.

Fig. 5.1  (a) Cyclic voltammograms of EC prototypes of different Interdigitated Array (IDA) configuration (only show 50th cycle); (b) Specific capacitance (F/g) and the ratio of anodic current to cathodic current (Qₐ/Qₖ). (Config x-y, with x represents the prototype configuration and y represents the band width).

Fig. 5.2  Interdigitated array (IDA) electrodes comprising different circuit elements. Electrolyte resistance, Rₑₒᵣ; Double layer capacitance, Cₑₒᵣ; and Dielectric

XX
capacitance, $C_{dl}$. Red line indicates the potential profile across a pair of interdigitated electrode fingers.

Fig. 5.3 Electrolyte Resistance ($R_{seal}$) and Dielectric Capacitance ($C_{dl}$) of Interdigitated Array (IDA) EC prototypes of different configurations. (With $R_2$ and $R_3$ represent Electrolyte Resistance for Configuration 2 and 3 respectively, whereas $C_2$ and $C_3$ represent Dielectric Capacitance for Configuration 2 and 3 respectively).

Fig. 5.4 Typical discharge curve of IDA EC prototypes of different configurations in agar-based gel electrolyte at discharge current of 0.08 mA, (a) configuration 1, (b) configuration 2, and (c) configuration 3.

Fig. 5.5 Coulombic efficiency, $\eta$ (%) of Interdigitated Array (IDA) EC prototypes of different configurations at charge/discharge current of 0.08 mA.

Fig. 5.6 Cyclic voltammograms of IDA EC prototypes of various configurations in (a) 0.2 M Na$_2$SO$_4$ aqueous electrolyte, (b) agar-based gel electrolyte containing 0.2 M Na$_2$SO$_4$.

Fig. 5.7 Capacitive behaviours of EC prototypes of various IDA electrode configurations in agar-based gel electrolyte of various thicknesses.
Fig. 5.8 Nyquist plots of Interdigitated Array (IDA) EC prototypes of different configuration with (a) liquid electrolyte and, (b) agar-based gel electrolyte thin film. Insets show the magnified plots at high frequency region of EC prototypes evaluated with liquid and agar-based gel electrolytes.

Fig. 5.9 Schematic diagram of proposed ionic diffusion pathway between a pair of IDA electrodes in EC prototype.

Fig. 5.10 Schematic diagram of hybrid energy storage prototype with integrated battery and electrochemical capacitor (Hybrid Batt-EC prototype).

Fig. 5.11 (a) Cyclic voltammograms of MnO2-based EC prototypes with IDA electrodes of configuration 2 integrated in Hybrid Batt-EC prototype. With EC 1 and EC 2 represent individual MnO2-based EC prototypes, and EC 1+2 represents both MnO2-based EC prototypes connected in parallel. The changes of current density (A/g) and current (mA) of IDA electrodes with respect to the scanning potential were represented by the solid curves and dotted curves, respectively. (b) Electrical circuit of two MnO2-based EC prototypes, (c) The equivalent circuit of the parallel connection.

Fig. 5.12 Nyquist plots of MnO2-based EC prototypes of IDA electrodes configuration 2 integrated in Hybrid Batt-EC prototype. Inset shows the magnified plots at high frequency region.