MODELING OF ELECTRIC DOUBLE LAYER CAPACITOR

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Dedicated to my beloved parents

Mohd Pabli bin Ismail & Maharani binti Husain

Siblings

Nur Izzati binti Mohd Pabli

Ahmad Akram bin Mohd Pabli

Fatin Amieza binti Mohd Pabli

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and

All my friends in UTM Skudai

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ABSTRACT

Electric double layer capacitor (EDLC) is an energy storage device that fills the gap between battery and conventional capacitor. One way to understand EDLC's charge storage mechanism is through its equivalent circuit analysis. Nonetheless, most of existing equivalent circuits proposed in the past researches are not capable in justifying DC characteristics of the EDLC and hence, prevent the discovery of the technology's full potential. The project focuses on evaluating electrochemical characteristics of EDLC and proposes a new equivalent circuit model that capable of not only illustrating the charge storage mechanism but also justifying the DC characteristics of the EDLC. Electrochemical impedance spectroscopy (EIS) measurement was carried out on two commercially available EDLCs with the capacitance of 300 and 400 Farad using an electrochemical measuring system. With the aid of EIS Spectrum Analyzer software, the test results were analyzed and a new equivalent circuit was proposed. The impedance spectrum and equivalent circuit model designed from the two samples were compared and their characteristics and electrical behavior were analysed to justify DC characteristics of the samples.

ABSTRAK

Electrik kapasitor dua lapisan (EDLC) adalah alat penyimpanan tenaga yang mengisi jurang antara bateri dan kapasitor konvensional. Salah satu cara untuk memahami mekanisme penyimpanan caj EDLC adalah melalui analisis litar setara. Namun begitu, kebanyakan litar setara yang sedia ada yang dicadangkan dalam kajian lepas tidak mampu dalam mewajarkan DC ciri-ciri EDLC dan dengan itu, menghalang penemuan potensi penuh teknologi ini. Projek ini memberi tumpuan kepada ciri-ciri penilaian elektrokimia pada EDLC dan mencadangkan satu model litar setara baru yang mampu bukan sahaja menggambarkan mekanisme penyimpanan caj tetapi juga mewajarkan ciri-ciri DC daripada EDLC. Pengukuran elektrokimia impedans spektroskopi (EIS) telah dijalankan ke atas dua EDLC yang boleh didapati secara komersial dengan kapasitan 300 dan 400 Farad menggunakan sistem pengukur elektrokimia. Dengan bantuan perisian EIS Spectrum Analyzer, keputusan ujian telah dianalisis dan litar setara baru telah dicadangkan. Spektrum impedans dan model litar setara yang direka daripada kedua-dua sampel telah dibandingkan dan ciri-ciri mereka dan tingkah laku elektrik akan dianalisis untuk mewajarkan ciri-ciri DC pada sampel.

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LIST OF ABBREVIATIONS

EDLC	-	electric double layer capacitor
EIS	-	electrochemical impedance spectroscopy
EC	-	electrochemical capacitor
ECPA	-	electrochemical proximity assay
UPS	-	uninterruptable power supply
SWG	-	signal waveform generator
PG	-	potentiostat / galvanostat
CE	-	counter electrode
WE	-	working electrode
RE	-	reference electrode
NHE	-	normal hydrogen electrode
RHE	-	reversible hydrogen electrode
SCE	-	saturated calomel electrode
AC	-	alternating current
DC	-	direct current
ANN	-	artificial neural network
PDE	-	potential difference equation
ESR	-	equivalent series resistance
CPE	-	constant phase element
Al	-	alluminium
Ta	-	tantalum
H_2SO_4	-	sulfuric acid
Ni-Cd	-	nickel- cadmium
Ni-MH	-	nickel- metal hydride
Li-ion	-	lithium-ion

LIST OF SYMBOLS

ΔE	-	peturbing signal
$Z(\omega)$	-	complex impedance
$E(\omega)$	-	complex energy
$i(\omega)$	-	comple current
Z_{re}	-	real impedance
Z_{im}	-	imaginary impedance
v	-	volume
V	-	voltage
I	-	current
E	-	energy
P	-	power
Q	-	electric charge
C	-	capacitance
F	-	farad
C_{dl}	-	double layer capacitance
C_H	-	compact/Stern layer capacitance
C_{diff}	-	diffuse/Gouy-Chapman layer capacitance
$C_{f\pm}$	-	faradaic capacitance
$R_{f\pm}$	-	faradaic resistance
Z_F	-	faradaic impedance
R_{CT}	-	charge transfer resistance
C_P	-	capacitance
Θ	-	saturation inclusion
R_S	-	ESR
ε_0	-	permittivity

ε_r	-	relative permittivity
τ_S	-	relaxation time
P_{max}	-	maximum power

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

Brief discussion on the research project is presented in this chapter. The first section explains about the project overview and the brief history of the project research and development. The second section discusses about project motivation and problem statements. Consequently, the next section consists of objectives, scope, and limitations involved in the project. The thesis outline is also clearly stated at the end of this chapter.

1.1 Project Overview

After the age of Tesla and Edison in 1800s, electrical energy has become fundamental in everyday life [1]. The world has become energy dependent that even a few seconds of outage would stunt the life routine. Almost all works require electrical energy to run. So, energy storage is very important to create sustainable energy systems in order to undergo 60% of the diverse applications continuously such as lighting, computing, telecommunication, transportation, industry, and home appliances [1]. To achieve such energy systems, energy storage development has become an important topic for the industry to keep up with the world demand. An energy storage device is a device with the ability to store energy in different forms, depending on the means of the storage medium [1]. Till date, various energy storage devices are invented and further innovate to satisfy markets need.

1.1.1 State of The Art of Energy Storage Technology

An energy storage device is a device with the ability to store energy in different forms, depending on the means of the storage medium. It is a passive dynamic one terminal electric device that consists of two types of energy storage which are direct and indirect electrical energy storage device [1]. A direct energy storage device such as capacitors and inductors stores energy in electromagnetic field in a defined volume, v without converting the energy form [1]. So, it does not need energy conversion process and hence gives rapid usage. Indirect energy storage device stores energy in several form of energy such as mechanical and chemical energy and need to convert the energy to the electrical energy first before usage. The examples of indirect electrical energy are batteries, flywheel, pumped hydro, heat, compresses air, and hydrogen. Giving rapid process of storage, inductors and capacitors is more convenient compared to the indirect electrical energy storage [1]. It can be used in most applications, provided that it can provide sufficient energy needed in the respective application. It is the most suitable technology to cover those applications requiring the management of rapid power variations [2]. Hence, a capacitor with a large energy capacity is developed and researched, namely as Supercapacitor.

Supercapacitor consists of three groups which is electric double layer capacitor (EDLC), pseudocapacitors, and high voltage ceramic capacitors (Figure 1.1). In many past to current researches, researchers address pseudocapacitors as electrochemical double layer capacitor which is also shortly called EDLC. So, to avoid confusion, the author will refer EDLC for electric double layer capacitor only while for electrochemical double layer capacitor will be called pseudocapacitors throughout the project. EDLC is one of the latest energy storage devices that need a lot of research to satisfy the market request. There is currently rapid growth in EDLC demand as the trend has become the limelight in energy storage technology. Hence, the strong demand for surface-mounting design with size reduction and higher reliability towards solid electrolyte material [3]. The skyrocketing demand of EDLC is because of the high power density to produce fast charging and discharging process, but with the ability to hold 100 times more electrical charge quantity than the conventional capacitor. EDLC is also said to have longer cycle life than other types of supercapacitor, with simple and cheaper materials used that make this device as currently the most developed and used supercapacitors [2]. EDLC usually comes in low voltage with the rated of 2.3V, 2.5V, and 2.7V as the capacitance can go from the range 10F to 3000F. Higher voltages can be achieved by connecting many cells in series like other polarized devices [4] [5]. It is very advantages for applications that require rapid but large power variations such as in transportation, backup in power failure, and backup sources of energy in power system. Hence, this project will focus on EDLC only. In research and development of EDLC, there are various problems and issues arise that will be discussed in detail in the next chapter.

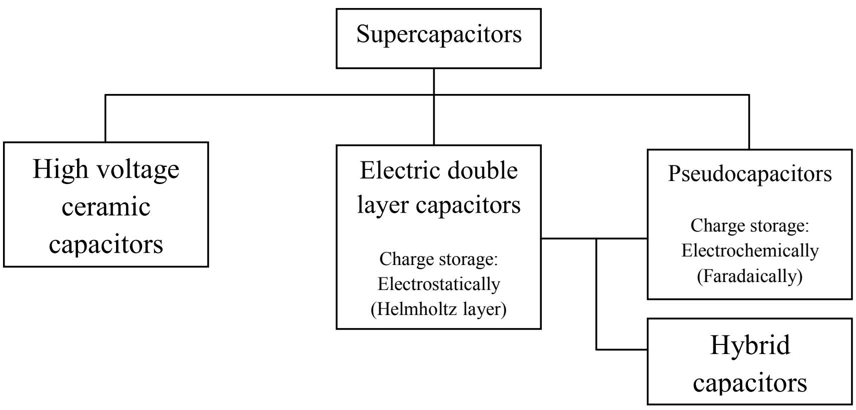

Figure 1.1: Taxonomy of the Supercapacitor in general terminology [6]

1.1.2 Project Motivations

There are many advantages when using supercapacitor such as EDLC in power system. Not only has it provided high specific energy and specific power, but also high efficiency, cycling capability over 500 000 cycle, wide range of operating temperatures, and also semi permanent life [7]. However, based on the literature review studied, it is shown that the characteristics study and design process of EDLC is hardly done. It is difficult to build an accurate model for supercapacitors due to the complexity of the electrochemical characteristics [8]. The data provided in the datasheet does not represent the detail information and electrical behavior of the energy storage system and further control of the design cannot be carried out. Many researchers working on modeling the EDLC in various ways such as electrochemical models, equivalent circuit models and artificial-neural-network-based (ANN-based) models [7]. From overall review, electrochemical models can achieve high accuracy once their parameters are precisely identified, but the usage of partial differential equations (PDEs) contributes to large number of difficultly calibrated parameters, unacceptable computational loading and large memory requirement [7]. For ANN-based model, an accurate dynamics data of the EDLC can be extracted, but it relies heavily on the amount and quality of the training data [7].

Equivalent circuit model is the most widely used model in the literature with a simple structure and reasonable accuracy in the delimitation of the dynamic behavior of a supercapacitor [7]. The equivalent circuit model consists of three types of model which are series, branch, and dynamic model that can be implemented for ease in design process and characterization study. An innovative model is essential to identify the parameters faster and also minimize the number of parameters. Different modeling will also produce different ability to represent a wide working frequency range that permits to characterize correctly the EDLCs electrical behavior in their typical working conditions. However, most of EDLC modeling that were published till date seldom justifies the DC characteristics of the model. There is also another factor that contributes to EDLC behavior which is charge residual [9]. This phenomenon occurs during charging and discharging process that is rarely considered [9]. Hence, the project proposes an efficient electrical circuit modeling of an EDLC to investigate the electrical behavior of an EDLC and to achieve several objectives.

1.2 Project Objectives

The project is developed following four main objectives:

- To study the AC characteristics of an EDLC.
- To carry out AC impedance measurement on EDLC using electrochemical impedance spectroscopy (EIS).
- To propose an electrical circuit model that can illustrate the charge storage mechanism of an EDLC using EIS Spectrum Analyser.
- To justify the DC characteristics of an EDLC based on the proposed electrical circuit model.

1.3 Project Scopes and Limitations

There are wide ranges of analysis for supercapacitor such as thermal model, frequency related losses, and charging or discharging losses, but the EDLC equivalent circuit modeling is focused on the study of charge storage mechanism of EDLC only. Analysis on the charge storage mechanism is important for power and energy density improvements. A charge storage mechanism is a physical phenomenon that can be simply described by the typical scheme of the EDLC as in Figure 1.2 below. There are also various types of test method that can be held for an EDLC such as charge discharge method, cyclic voltammetry curve method, AC impedance method, and galvanostatic method [10] [11] [12]. The project focused on modeling the equivalent electrical circuit for EDLC using measured AC impedance data that are further explained in Chapter 3. Then, the project analyses the accuracy and efficiency of the circuit model, together with justification of DC properties of EDLC based on proposed electrical circuit model. The simulation of the model is made using EIS Spectrum Analyser.

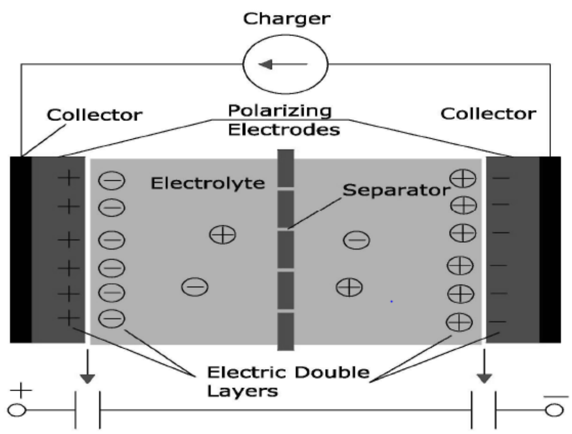

Figure 1.2: Typical configuration of an EDLC cell [38]

1.4 Thesis Outline

The thesis documentation is divided onto 5 chapters, which are described briefly as follow.

Chapter 2 discusses an overview of capacitor technology in detail in terms of historical overview, current research and development, and applications to compare current energy storage devices. The author describes about conventional capacitor, electrolytic capacitor, and electrochemical capacitor to overview about supercapacitors technology. Then, the author goes more detail on the project sample which is the constructions of EDLC. After that, the electrochemical measurement techniques, EDLC test method, and equivalent circuit overview is described in detail to understand the modelling of EDLC.

Chapter 3 of methodology part describes about the steps by steps taken towards carrying out the project. This part describes in detail about the test procedure and data collection carried out throughout the project. After that, an overview on equivalent circuit design is also discussed in project simulation. Then, the author describes about the software used for EDLC equivalent circuit modelling and data fitting.

In Chapter 4, the author shows and discusses the results obtained from the experiment test procedure and data fitting procedure. The comparison is made between the 300 farad and 400 farad EDLC in two states which is at no charge state and full charge state. The relationship between the charge storage behaviour and the equivalent circuit designed based on data fitting is also analysed and further discussed. Hence, the AC and DC characteristics of the sample are analysed.

Lastly, in Chapter 5 for conclusion, the proposed equivalent circuit design is verified and the pro and cons is discussed. The result and analysis is summarized and all the problems and errors when running the procedure are also described. Further improvement of the project is then discussed to improve the modelling of EDLC.

REFERENCES

[1] Peter J. Grbovic, 2014. "Ultra-capacitors in Power Conversion Systems; applications, analysis and design from theory to practice", Huawei Technologies Dusseldorf GmbH, Energy Competence Center Europe, Germany,

[2] Alberto Berrueta, Idoia San Martín, Andoni Hernández, Alfredo Ursúa, Pablo Sanchis, 2014, "Electro-thermal modelling of a supercapacitor and experimental validation", Journal of Power Sources 259 (2014) 154-165

[3] Atsushi Nishino, 26 December 1994, "Capacitors: operating principles, current market and technical trends", Journal of Power Sources 60 (1996) 137-147

[4] Nathalie Devillers, Samir Jemei, Marie-Cécile Péra, Daniel Bienaimé, Frédéric Gustin, 2014, "Review of characterization methods for supercapacitor modeling", Journal of Power Sources 246 (2014) 596e608, Journal of Power Sources

[5] Luis Zubieta, and Richard Bonert, "Characterization of Double-Layer Capacitors for Power Electronics Applications", IEEE TRANSACTIONS ON INDUSTRY APPLICATIONS, VOL. 36, NO. 1, JANUARY/FEBRUARY 2000

[6] Beguin F. and Frackowiak E. 2013 "Supercapacitors; Materials, Systems, and Applications" Germany, Wiley-VCH

[7] L. Zhang, Z. Wang, X. Hu, F. Sun, David. G. Dorrell, 2015 "A comparative study of equivalent circuit models of ultracapacitors for electric vehicles", for Journal of Power Sources 274, 899-906

[8] A. Eddahech, O. Briat, M. Ayadi, J. Vinassa, 2014, "Modeling and adaptive control for supercapacitor in automotiveapplications based on artificial neural networks", Electric Power Systems Research 106 (2014) 134– 141

[9] Dimitri Torregrossa, Maryam Bahramipanah, Emil Namor, Rachid Cherkaoui, March 2014, "Improvement of Dynamic Modeling of Supercapacitor by Residual

Charge Effect Estimation", IEEE TRANSACTIONS ON INDUSTRIAL ELECTRON ICS, VOL. 61, NO. 3

[10] Peter J. Mahon, George L. Paul, Sarkis M. Keshishian, Anthony M. Vassallo, "Measurement and modelling of the high-power performance of carbon-based supercapacitors" for Journal of Power Sources 91 2000. 68–76

[11] M. Ayadi, O. Briat, R. Lallemand, A. Eddahech, R. German, G. Coquery, J.M Vinassa, 2014, "Description of supercapacitor performance degradation rate during thermal cycling under constant voltage ageing test", Microelectronics Reliability 54 (2014) 1944–1948

[12] W.G. Pell, B.E. Conway, "Voltammetry at a de Levie brush electrode as a model for electrochemical supercapacitor behavior" for Journal of Electroanalytical Chemistry 500 (2001) 121–133

[13] Beguin F. and Frackowiak E. 2013 "Supercapacitors; Materials, Systems, and Applications" Germany, Wiley-VCH

[14] R. L. SPYKER, R. M. NELMS, "Classical Equivalent Circuit Parameters for a Double-Layer Capacitor", IEEE TRANSACTIONS ON AEROSPACE AND ELECTRONIC SYSTEMS VOL. 36, NO. 3 JULY 2000

[15] Yu A, Chabot V, and Zhang J, 2012 "Electrochemical Supercapacitors for Energy Storage and Delivery; Fundamentals and Applications" New York, CRC Press

[16] Z. Song , H. Hofmann , J. Li , X. Han , M. Ouyang , "Optimization for a hybrid energy storage system in electric vehicles using dynamic programing approach", Applied Energy 139 (2015) 151–162

[17] A. Takshi, H. Yaghoubi, T. Tevi, S. Bakhshi, "Photoactive supercapacitors for solar energy harvesting and storage", Department of Electrical Engineering, University of South Florida, USA, for Journal of Power Sources 275 (2015) 621-626

[18] F. Bensmaine, O. Bachelier, S. Tnani, G. Champenois, E. Mouni, "Modeling and Control of a STATCOM-Supercapacitors Energy Storage System Associated with a Wind Generator", for 978-1-4799-2399-1/14/2014 IEEE

[19] C. J. Donahue and J. A. Exline, April 15, 2014 "Anodizing and Coloring Aluminum Alloys" J. Chem. Educ., 2014, 91 (5), pp 711–715

[20] C. S. Ashley, C. J. Brinker and D. M. Smith, Journal of Non-Crystalline Solids, Volume 285, 2001

[21] Metrohm, 1 july 2011 "Electrochemical Impedance Spectroscopy (EIS) Part 1-6", Autolab Application Note, EIS01

[22] Metrohm, 1 july 2011 "Supercapacitors: Principles and Characterization using Autolab", Autolab Application Note, SC01

[23] V. F. Lvovich, "IMPEDANCE SPECTROSCOPY Applications to Electrochemical and Dielectric Phenomena", A JOHN WILEY & SONS, INC., PUBLICATION, ISBN 978-0-470-62778-5

[24] M. Mellincovsky, A. Kuperman, C. Lerman, I. Aharon , N. Reichbach, G. Geula, R. Nakash, "Performance assessment of a power loaded supercapacitor based on manufacturer data", Energy Conversion and Management 76 (2013) 137–144

[25] M. Pucci, G. Vitale, G. Cirrincione, M. Cirrincione, IEEE 2013, "Parameter Identification of a Double-Layer-Capacitor 2-Branch Model by a Least-Squares Method", 978-1-4799-0224-8/13

[26] J. M. Miller, 2011, "Ultracapacitor Applications", IET Power and Energy Series 59, the Institution of Engineering and Technology, London, United Kingdom, ISBN 978-1-84919-071-8

[27] N. Devillers, S. Jemei, M. Péra, D. Bienaimé, F. Gustin, 2014, "Review of characterization methods for supercapacitor modeling" Institut FEMTO-ST, France , Journal of Power Sources 246 (2014) 596e608, Journal of Power Sources

[28] M. S. Islam, M. B. Hossain, M. N. Hossain, S. B. Alam and M. H. Chowdhury, "Modeling of a Double-Layer Capacitor with Individual Branch Response", Engineering and Computer Science 2010 Vol II, October 20-22, 2010, San Francisco, USA

[29] N. Kularatna, and J. Fernando, "Energy Storage Devices for Electronic Systems: Rechargeable Batteries and Supercapacitors",

[30] [2] Lei Zhang, zhenpo wang, Xiaosong Hu, Fengchun Sun, David. G. Dorrell, 2015 “A comparative study of equivalent circuit models of ultracapacitors for electric vehicles”, for Journal of Power Sources 274, 899-906

[31] M. S. Halper, J. C. Ellenbogen, March 2006, “Supercapacitors: A Brief Overview”, for the MITRE Corporation, McLean, Virginia, USA.

[32] V Sedlakova, J Sikula, J Majzner, P Sedlak, T Kuparowitz, B Buergler, and P Vasina, 19 March 2015 “Supercapacitor equivalent electrical circuit model based on charges redistribution by diffusion”, Journal of Power Sources 286 (2015) 58e65

[33] S. Buller, E. Karden, D. Kok, and R.W. De Doncker, 2001, “Modeling the Dynamic Behavior of Supercapacitors Using Impedance Spectroscopy”, 0-7803-7116-X/01/$10.00 (C) 2001 IEEE

[34] Pawan Sharma and T.S. Bhatti, 2 July 2010, “A review on electrochemical double-layer capacitors”, Energy Conversion and Management 51 (2010) 2901–2912

[35] Stephen Fletcher, Victoria Jane Black and Iain Kirkpatrick, “A universal equivalent circuit for carbon-based supercapacitors”, J Solid State Electrochem (2014) 18:1377–1387

[36] EIS Spectrum Analyser online help from “http://www.abc.chemistry.bsu.by” website.

[37] Zulkarnain A. Noorden and Satoshi Matsumoto, 4 March 2014, “A New Circuitry Model for Electric Double Layer Capacitor”, The Proceeding of 8th SEATUC Symposium.

[38] Electronic and Communication technology website at http://www.dataweek.co.za/

[39] TDK Techno Magazine, Electronic ABC on “Capacitors”, at http://www.global.tdk.com/techmag/electronics_primer/vol6.htm