Development of Electrochemical Characterization Methods and Advanced Capacitor Materials

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STATEMENT OF ORIGINALITY

I hereby certify that the work embodied in the thesis is my own work, conducted under normal supervision. The thesis contains no material which has been accepted, or is being examined, for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made. I give consent to the final version of my thesis being made available worldwide when deposited in the University's Digital Repository, subject to the provisions of the Copyright Act 1968 and any approved embargo.

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I hereby certify that this thesis is in the form of a series of papers. I have included as part of the thesis a written declaration from each co-author, endorsed in writing by the Faculty Assistant Dean (Research Training), attesting to my contribution to any jointly authored papers.

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By signing below I confirm that the Research Higher Degree candidate, Marveh Forghani contributed towards data generation/analysis and manuscript preparation for all the publications included in this thesis for which I am a co-author (Reference details in page iv of this thesis).

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LIST OF PUBLICATIONS

Publications Included in Thesis

1. **Forghani, M.**, & Donne, S. W., (2018). *"Duty Cycle Effects on the Step Potential Electrochemical Spectroscopy (SPECS) Analysis of the Aqueous Manganese Dioxide Electrode."* Journal of The Electrochemical Society, 165(3), A593-A602.

2. **Forghani, M.**, & Donne, S. W., (2018). *"Method comparison for deconvoluting capacitive and pseudo-capacitive contributions to electrochemical capacitor electrode behavior."* Journal of The Electrochemical Society, 165(3), A664-A673.

3. **Forghani, M.**, & Donne, S. W. (2019). *"Complications When Differentiating Charge Transfer Processes in Electrochemical Capacitor Materials: Assessment of Cyclic Voltammetry Data."* Journal of The Electrochemical Society, 166(8), A1370-A1379.

4. **Forghani, M.**, & Donne, S. W. (2019). *"Modification of the Step Potential Electrochemical Spectroscopy Analysis Protocol to Improve Outcomes."* Journal of The Electrochemical Society, 166(13), A2727-A2735.

Additional Publications

1. Dupont, M. F., **Forghani, M.**, Cameron, A. P., & Donne, S. W. (2018). *"Effect of electrolyte cation on the charge storage mechanism of manganese dioxide for electrochemical capacitors."* Electrochimica Acta, 271, 337-350.

2. Fellows, H. M., **Forghani, M.**, Crosnier, O., & Donne, S. W. (2019). *"Modelling voltametric data from electrochemical capacitors."* Journal of Power Sources, 417, 193-206.

3. Abbas, S. A., **Forghani, M.**, Anh, S., Donne, S. W., & Jung, K. D. (2019). *"Carbon Hollow Spheres as Electrochemical Capacitors: Mechanistic Insights."* Energy Storage Materials, Available online on the 28th June 2019.

4. **Forghani. M.**, McCarthy. J., Mavroudis. H. & Donne. S. W. *"Electroanalytical Characterization of Electrochemical Capacitor Systems."* Electrochimica Acta, Available online on the 7th October 2019.

5. **Forghani. M.**, McCarthy. J. & Donne. S. W. *"Oscillatory Current Behaviour in Energy Storage Electrode Materials."* Submitted on Journal of The Electrochemical Society on the 28th of August 2019.

Conference Presentations

1. **<u>Forghani, M.</u>**, & Donne, S. W., *"Effects of Different Duty Cycle on the Step Potential Electrochemical Spectroscopy (SPECS) Analysis."* PRiME 2016 meeting 2-7 of October 2016, Honolulu, USA.

2. **<u>Forghani, M.</u>**, & Donne, S. W., *"Effect of Temperature the Step Potential Electrochemical Spectroscopy (SPECS) Analysis of Manganese Oxides for Electrochemical Capacitors."* ISEE CAP 2017, 10-14 July 2017, Jena, Germany.

3. **<u>Forghani, M.</u>**, & Donne, S. W., *"Study of Ageing Mechanisms of Electrochemical Capacitor Materials Using Step Potential Electrochemical Spectroscopy (SPECS) Analysis."* ISEE CAP 2017, 10-14 July 2017, Jena, Germany.

4. **<u>Forghani, M.</u>**, & Donne, S. W., *"Deconvoluting Capacitive and Pseudo-Capacitive Contributions to Electrochemical Capacitor Electrode Behaviour."* 232^{nd} ECS MEETING, 1-5 October 2017, National Harbor, MD (greater Washington, DC area), USA.

5. **<u>Forghani, M.</u>**, & Donne, S. W., *"Modelling of Voltammetric Data from Electrochemical Capacitor Electrodes."* AiMES Conference, September 30-October 4, 2018 Cancun Mexico.

6. **<u>Forghani, M.</u>**, & Donne, S. W., *"Temperature Effects on the Performance of Activated Carbon Electrochemical Cell in Aqueous and Non-Aqueous Electrolytes."* AiMES Conference, September 30-October 4, 2018 Cancun Mexico.

7. **Forghani, M.**, & Donne, S. W., *"Effect of Electrolyte Cation on the Electrochemical Performance of AC Electrochemical Capacitor."* AiMES Conference, September 30-October 4, 2018 Cancun Mexico.

8. **Forghani, M.**, & Donne, S. W., *"Electrolyte Concentration Effects for Activated Carbon Electrodes Using Electroanalytical Methods."* ISEECap 2019, 6-10 May, Nantes, France.

9. **Forghani, M.**, & Donne, S. W., *"Electrolyte Ion Effects for Activated Carbon Electrodes Using Electroanalytical Methods."* ISEECap 2019, 6-10 May, Nantes, France.

ABSTRACT

This thesis focuses on developing the most common electrochemical methods; cyclic voltammetry (CV) and step potential electrochemical spectroscopy (SPECS). Although CV and SPECS techniques have previously been used for characterising the performance of various energy storage devices, this study shows that there is always a room for improving the present electrochemical techniques and just repeating the conventional electrochemical methods is not the best approach to study the modern electrochemical storage devices with novel and more complex electrode materials.

This thesis includes nine chapters. Chapter 1 is the introduction to the thesis. Chapters 2 to 4 focus on the literature reviews on the energy storage devices, electrochemical capacitor materials and electrochemical methods. Chapters 5 to 8 present four experimental studies on the electrochemical capacitors and Chapter 9 is the conclusion to this thesis.

Herewith, the various experimental parameters involved in these two techniques have been further explored, and the performance of these methods for characterising the behaviour of electrochemical cells was compared experimentally. This thesis presents the application of CV and SPECS methods on testing electrochemical capacitors with various electrode materials such as activated carbon and manganese dioxide with aqueous and organic electrolytes.

The SPECS method is based on applying a series of equal magnitude potential steps on a working electrode, with sufficient rest time to allow for quasi-equilibrium to be established for each step throughout an applied potential window. This slow sweep rate enables an electrode to approach its maximum charge storage capability. More importantly, it allows separation of charge storage mechanisms, such as electrical double layer charge storage and diffusion-limited processes. The effect of the two main experimental variables in SPECS; namely, the

potential step size and the electrode rest time, on the behaviour of the electrochemical capacitor is described in Chapter 5.

The contribution of the capacitive and diffusion-limited processes can be obtained via the voltammetric current-sweep rate dependence, voltammetric charge-sweep rate dependence and SPECS methods. These three methods were compared experimentally and also their limitations, and their advantages for interpreting the current data and their abilities to distinguish between the different charge storage mechanisms is presented in Chapter 6.

Some of the complications associated with using a common approach; namely voltammetric current-sweep rate dependence, to deconvoluting double layer and diffusion-limited contributions to the performance of an electrochemical capacitor electrode, have been explored and presented in Chapter 7.

Finally, Chapter 8 presents an improved methodology for the interpretation of SPECS data. The revised methodology provides an analysis method that produces performance data much closer to CV data, thus enabling both relative and absolute characterisation of electrochemical capacitor electrodes, as well as increasing the versatility of the SPECS analysis method.

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