SCHOOL OF ENGINEERING AND INFORMATION TECHNOLOGY

Eggshell as a Renewable and Sustainable Resource for Energy Storage in Supercapacitors

ENG470 Electrical Engineering Honours Thesis

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Declaration

I declare that this thesis paper titled “Eggshell as a Renewable and Sustainable Resource for Energy Storage in Supercapacitors” is submitted to the Department of Engineering of Murdoch University in partial fulfillment of the Bachelor of Engineering Honours (Electrical Power and Renewable Energy Engineering).

I, Stephen Vaugh Higley confirm that the material contained in this thesis is the result of my research work, and the research achievements of others used in this thesis are referenced and cited in accordance with the university plagiarism rules. This thesis is the original copy of the thesis and has not previously been submitted to any level or higher degree.
Abstract

It is thought that eggshell biowaste from the cosmetic and pharmaceutical industry could be used as a precursor for energy storage as a suitable waste management plan and increase the sustainability of said industry rather than ending up in landfill. When comparing the morphology of synthetic calcium carbonate with eggshell it can be theorised that eggshell or one or more of the calcium carbonate polymorphs namely calcite, aragonite and vaterite could be used as an electrode for supercapacitors. By applying the morphological knowledge obtained through the literature survey and by physically and electrochemically characterising eggshell in three distinctive crystalline states of the calcite, will allow this thesis to confirm eggshell as a sustainable and renewable resource for electrode material for energy storage in supercapacitors.
Acknowledgement

The finalising of this thesis chapter will bring closure to my time at Murdoch University. The experience has helped me to focus on what is important to me and hone my skills for the future and for that reason I thank all my lecturers who have helped shape my understanding and assist in my professional development. I know I will have fond memories thanks to all the effort Murdoch has put into developing and taking the campus forward. I am sure my memories of Murdoch will be met with nostalgia and pride. Thank you.

I want to especially thank my wife for her understanding, patience and support throughout my studies. I have been crushed, mended and crushed again, yet she stood by me to support me and pick me up every time. I sense, in a way her deep gratitude for life that I can only reason is given to her by her Father in Heaven.

Lastly, I thank our Father in Heaven for his promises and His secure gift made possible through Jesus Christ, my security in all things past, present and evermore.
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1. Background

1.1. Introduction

In recent years, the focus on renewable and sustainable resources has been important on shaping our views regarding waste management and climate change. One metric that the World Energy Council (WEC) uses is the Trilemma Index tool that ranks 125 countries. “The World Energy Council’s Energy Trilemma Index tool, produced in partnership with Oliver Wyman, ranks countries on their ability to provide sustainable energy through 3 dimensions: Energy security, Energy equity (accessibility and affordability), Environmental sustainability.” [1]. Currently, Australia sits with an index rank of ‘33’ and a Balance score of ‘BBC’. The best case being ‘AAA’ rather than worst case, ‘DDD’. See Appendix G for a comparison of America and Zimbabwe. The trilemma prism is an inferred volume calculation based on (3) score results from the apex point (zero). The WEC was formed in 1923 and is accredited as the (emphasis added) UN-accredited global energy body, “ ... representing the entire energy spectrum, with over 3,000 member organisations in over 90 countries, drawn from governments, private and state corporations, academia, NGOs and energy stakeholders” [2]. The renewable energy sector has challenges when considering current economic trends and stability. With America and Australia rising from the 2008 Global Financial Crisis, fossil fuel has the advantage of base load applications because of its ability to sustain continuous energy output as well as respond to varying demands in residential, commercial and industrial energy consumption.

The renewable energy sector has raised much interest in hybrid models for generation. In diesel or petrol power generation management the main parameter of concern is efficiency and is achieved through gathering the information (data) that characterises energy demand in order to allocate and match the size of generator. This is also known as economic dispatch.

![Efficiency Curve](image-url)
The combustion engine is most efficient when operating on high-torque loads. The HOMER® software has a range of systems including diesel hybrid systems as well as two kinetic battery models. They provide some insight with diesel engine modelling efficiencies on their website [3].

For this reason, Toyota designed the *Prius* and exploited the energy output vs energy input more commonly known as the efficiency curve. Toyota’s engineering team achieved this by installing energy storage into the car. Although the capacity of the battery was small, this was enough to integrate the electric motor to offset low efficiency periods of operation during high ±acceleration.

Regarding the fact of entropy expressed in the laws of thermodynamics, the need to innovate sustainable and conservative waste management initiatives means extra costs can be offset by reducing synthetically manufactured products. This would further reduce pollutants and increase the health of the environment benefitting local fauna and flora while committing to ethical steps towards dutiful waste management.

Our knowledge of the physical laws of thermodynamics has not only increased our understanding in the physical sciences for economic reasons but also the socio-economics of sustainability. The need to innovate bio-waste for repurposing waste is not only beneficial for waste management but for adding value to products in the market, “Waste production is a perpetuating problem; its management has been a high priority for any countries across the globe. Repurposing waste materials into valuable products will not only improve sustainable development, but promote effective waste management.” [4].

The aim of this thesis is to show eggshell as a sustainable resource for electrodes in supercapacitors by physical and electrochemical characterisation of eggshell’s transitional phases through solid state in situ thermal decomposition and oxidation. The findings presented in this thesis will hopefully highlight eggshell as a valuable sustainable resource for future developers of renewable and sustainable technologies.
1.2. Safety & Training

The requirement to work in the electrochemical lab was to abide by the chemical laboratory rules and regulations as stipulated by Murdoch University as the prerequisite training requirement for this experimental-based honours thesis. It was the legal requirement of Murdoch’s ‘duty of care’ to ensuring students behave responsibly and act in accordance with their safety guidelines. Such safety guidelines covered risks, hazards, risk management and incident mitigation. Operational guidelines covered potential hazards, storage, security, decanting, GHS labelling & waste management through waste minimisation [5].

Handling and storage were maintained to ensure that safety was maintained by using appropriate gloves, approved safety glasses and lab-coat. A non-vacuum glass jar desiccator was used to reduce the hygroscopic effect which would reduce, specifically the calcium oxide sample. Oxides react with water molecules (hydrogen) to form hydroxides.

![Figure 2: Air tight desiccator](image-url)
1.3. Aims and Objective

The aim is to characterise eggshell physically and electrochemically from its natural state to other thermal states in the determination of eggshell as a sustainable resource for electrodes for use in supercapacitors.

1.3.1. Physical Characterisation

The objective of the physical characterisation is by taking cracked and discarded eggshell, and investigate noteworthy features during the processing and analysis of eggshell. The main reason broken eggshell was used, is because it pre-empted being boiled, where household tap water may ionise, react with or be absorbed into the eggshell as contaminants. The main concern was to preserve the naturally porous membranes and its chemical properties.

- Select a candidate eggshell sample based on socioeconomic availability.
- Clean the eggshell in preparation for experiments.
- Base the method and analysis on three eggshell samples (states) indicative of the thermogravimetric analysis (TGA) of ~41°C, 600°C and 950°C as samples for further analysis.
- Keep a logbook to ensure samples are kept separate.
- Determine useful temperature points during thermal decomposition states.
- Use the uncontrolled variable heating rate (maximum) for eggshell synthesis.
- Study the morphology of eggshell using various specialised instruments.
- Extend the analysis of caged eggs (ES#1) to pasture (ES#2) and farm roaming eggs (ES#3) through BET and SEM, presenting those results in BET only.
- Use academic resources to make predictions.
- Make improvements on failures.
1.3.2. Chemical Characterisation

Characterisation of eggshell will be achieved by cycling the activated electrodes using the Bio-Logic analyser in both the positive (cathode) and negative (anode) voltage regions of the three samples of ES 1.1, 1.2 and 1.3 (all three phase states of calcite).

- Test the electrochemical properties of eggshell to determine from their power and energy storage capacity if they are suitable for supercapacitors. Conduct two cycle test methods namely,
  - Cyclic Voltammetry to find the voltage region signature (VRS).
  - Galvanostatic Cycling to determine capacity and cycle stability.

The former will establish the characteristic voltage region signature (VRS) to determine each sample’s activity in each region, and the latter will determine capacity and cycle stability.

- To cycle test the active material for predictions on its possible life-cycle (span), chemical stability and any other notable characteristics as either an anode or cathode. A full sweep across both positive and negative regions.
- Determine which eggshell thermal phase state shows suitability for energy storage, furthermore if eggshell can be used for both anode and cathode electrodes.
- Determine capacitance per gram (specific capacitance) that each activated electrode can store by exposing a 1cm\(^2\) area to the electrolyte of a recorded mass (mg).
- Determine the power and energy density for determination of energy storage technology suitability and compare this analysis to the Ragone Plot (Figure 6).
- Finally, if there exists among the samples, a pair match that has similar cycling properties in cycle time and current, to be used as a complete electrode pair set.
1.4. Theory

To continue with this analysis, a few terms and concepts need to be discussed. Actions/reactions are described as:

In (inside) and Ex (outside) for,

- Situ – Location
- Vitro – Glass
- Vivo – Living.

1.4.1. Chemical Thermodynamics

Described as that aspect of thermodynamics which is concerned with the relationship of heat, work and other forms of energy which in chemical reactions, come to equilibrium and experience a change of state [6].

Thermodynamics is based upon the three laws of thermodynamics namely, (1) conservation of energy, (2) entropy of any isolated systems always decreases, and (3) entropy of a system approached a constant value as the temperature approaches absolute zero.

For most systems, we need only consider the first law:

\[ \Delta E = Q + W, \]

where \( E \) is internal energy, \( Q \) is heat and \( W \) is work. Each having magnitude and corresponding sign to indicate loss or gain [7].

In electrochemical reactions, change in energy (\( \Delta E \)) happen during charge and discharge owing to work done and a certain amount of heat loss (\( Q \)). These cycles are completely governed by the 1st law in so far as there is a change in energy, there is either a change in work and/or heat. The biggest enemy in electrochemical reactions is the change in heat since heat in an open system means loss and a decrease in efficiency. The purpose of most sustainable studies is to attenuate heat loss or at least reintroduce certain heat loss into certain parts of the process to offset this loss. In electrochemical applications, we can substitute these heat losses (\( Q \)) for resistance (\( R \)). While most batteries are symbolically presented as a capacitor, there are resistive properties that constitute inevitable loss of energy to surroundings.
1.4.2. Sintering

“The agglomeration of metal or earthy powders at temperatures below melting point. Occurs in both powder metallurgy and ceramic firing. While heat and pressure are essential, decrease in surface area is the critical factor. Sintering increases conductivity, and density” [6]. While sintering is an option to be considered in manufacturing the active material for the electrodes, a binder will be used that electrochemically bonds the electrode to the active material.

1.4.3. Activation energy

Is the amount of energy (E_a) in joules (J) to convert one mole (mol) of reactant to a transition state from a ground state [6]. Reactions speed up due to collisions (kinetic) due to increases in temperature and pressure as well as chemical concentrations that increase collisions (frequency). Otherwise stated, it is a minimum energy required for a reaction to occur [7]. Activation energy is an important part of the thermal decomposition of eggshell as this energy will be required when placed into a furnace (in situ) transitioning eggshell from its ground state into one or more transitional states and then further explored for morphological precursor changes.

1.4.4. Free Energy (Gibbs)

For the Chemistry to be explained in the 2nd law of thermodynamics context, the Gibbs Free Energy Law will be used: \( \Delta G = \Delta H - T\Delta S \) where,

- G – System free energy (Gibbs)
- H – Enthalpy (heat) energy (J), where [+] means taken from environment/endothermic
- T – Temperature (K)
- S – Entropy (J/K)

In the Hawley’s condensed chemical dictionary 16th edition, Gibbs free energy is described as: “An exact thermodynamic quantity used to predict the maximum work obtainable from spontaneous transformation of a system. It also provides a criterion for the spontaneity of a transformation or reaction and predicts the greatest extent to which the reaction can occur, i.e. its maximum yield. Transformation of a system can be brought about by either heat or mechanical work. Free energy is derived from the internal energy and entropy of a system in accordance with the laws of thermodynamics” [6].
1.4.5. Calcination

This involves the heating of a solid to below melting point to the state of thermal decomposition or phase change (transition) other than melting point. This includes thermal dissociation, polymorphic phase transitions and recrystallisation [6]. Calcite (CaCO3) when calcined (thermally decomposed) will release carbon dioxide (CO₂) and produce evolved calcium oxide (CaO).

1.4.6. Electronegativity

Beside the Helium atom, all atoms that have fewer than eight electrons in their highest principle quantum level, are capable of accommodating electrons from outside the atom. This is because of low energy orbital vacancies. The evidence of the existence of such vacancies within these regions means that the nuclear charge can exert a significant attraction for electrons even though the atom is electrically neutral. The word electronegativity also means the tendency to be negatively charged. This makes such electron vacancies in their outer shells possible to form covalent and ionic bonds which are fundamental in forming chemical bonds. Highly attractive electronegative elements are halogens, sulphur and oxygen [6]. The inclusion of oxides means that this may be an advantage in the selection of active material for electrodes in electrochemical energy storage devices.

1.4.7. Oxidation and Reduction

Oxidation and reduction take place naturally and one example of that is when iron is in the presence of water, it rusts. The iron oxidises by losing electrons Fe(s) => Fe^{2+} (aq) +2e^- when in the presence of oxygen (O2) and moisture (H2O) combined. It is also understood that this process of rusting is seen as an electrochemical process that occurs in the same way as a battery on the iron surface. Because most iron is impure, iron acts as the anode while impurities act like the cathode and so many voltaic cells are formed. The reduction occurs at the cathode (impurities) where water reacts with air to form hydroxide ion H₂O + O₂ + 2e^- => 2OH⁻, such that the anode (Fe+) loses the electron and the cathode gains the electron thereby completing one cycle of the voltaic battery.
Hydrogen cations will return to water in the presence of oxygen anions, or otherwise will form to produce hydrogen gas (H₂). Simply put, oxidation (OIL) is the ‘loss of electrons’ and reduction (RIG) is the ‘gaining of electrons’, represented in the acronym OIL RIG.

**Simple battery operation**

Figure 3 shows the layout of a simple voltaic cell/battery while Figure 4 illustrates the voltage range during the electrochemical operation of both electrodes. The negative electrode is the reducing agent (electron donor) while the positive electrode is an electron acceptor such as lithium cobalt oxide, manganese dioxide, or lead oxide and calcium oxide. The chosen electrolyte is purely an ionic conductor which physically separates the cathode from the anode [8]. These differences in voltages will can be seen in the cyclic voltammetry testing in the chemical characterisation part of this thesis.

The voltage of a battery is comprised of the whole systems which include the cathode and the anode voltages and is known as the ‘working voltage’ as well as known as the open circuit voltage \( V_{oc} \) [9].
Electrochemical capacitors are also known as supercapacitors. Supercapacitor operation relies on electrostatic forces rather than voltaic chemical interactions of oxidation and reduction. In Figure 3 for example, the electrode is negatively charged placing an external voltage source into the circuit. The electrons are forced via charging into the electrode as stored energy. At the same time the electrolyte cations are attracted to the negatively charged electrode. This allows for more electrons to be charged onto the electrode with the addition of the capacitive effect in Figure 5. Cations accumulate and adsorb on the surface of the electrode, which is called the inner Helmholtz plane (IHP). The van der Waals forces (electrostatic forces) also allow for the attraction between cation atoms which orient themselves according to their size and polarity (dipole in the case of polyatomic ion). Capacity would be determined by the active material’s ability to donate or accept electrons while the pH (or concentration of electrolyte) can control the amount of ionic activity available as electrostatic capacity.

Electrochemical batteries are also batteries in their ability to also oxidise and reduce as part of their charge discharge cycle. These extra currents are summed with the capacitive currents from charging when discharged, so when charged or discharged, the electrochemical reaction occurs simultaneously with the capacitive electrostatic forces available and subject to Gibbs free energy range (energy gap).

The working voltage has a limitation described as a ‘electrochemical window’ of the electrolyte, determined by the energy gap from the lowest unoccupied molecular orbital (LUMO) to the Highest occupied molecular orbital (HOMO) of the

![Figure 5: Electrochemical Capacitor](image)
reactants. The anode and cathode must be selected so that the voltage \((uA)\) of the anode lies below the LUMO and the cathode voltage \((uC)\) is above the HOMO otherwise the electrolyte will oxidise on the cathode and reduced on the anode to form a passivating solid electrolyte interphase (SEI) film. One advantage of SEI is that while it does prevent the aggregation of electrochemically active particles, it also allows for uniform deposition across the electrodes [9].

1.4.9. Electrochemical Power Density

In order to standardise and relate the energy storage capacity of the eggshell with other such storage devices, a useful metric used by industry to place various energy storage technologies onto one graph, is the Ragone plot. The Ragone plot [8] in Figure 6 compares the specific energy versus the specific power of the storage device and quickly reveals the effectiveness of the technology.

![Ragone Plot](image.png)

The aim is to have values as high as possible within each block as well as keep production costs as low as possible. The drive in competition, is to develop the product into higher energy and power density production. More advanced technologies make themselves suitable for new markets such as FEVs (full electric vehicles). The higher specific energy has more capacity for mobile applications while mid to low would have more static roles.
1.4.10. Capacitance

Simply put, capacitance is a measure of the ability that a storage device must store charge and energy in electric fields:

\[ C = \frac{Q}{V} \]

Where \( C \) is capacitance (farads [F]), \( Q \) is charge (coulomb), and \( V = \text{voltage/potential (volt [V])} \).

Capacitance is also the physical property of a capacitor and independent of the charge or voltage (farads is a ratio of charge and potential) seen above. Important to note is that capacitance is always positive, this is because capacitance will increase when the charge enters the material (electrode) and decrease when the charge exits the electrode. The storage capacity (in farads) of eggshell electrodes will be tested and represented as both anode and cathode.

In most capacitors, the charge is located only at the electrode plates whereas electrolytic and electrochemical capacitors, the behaviour changes due to the physical differences of the dielectric used.
1.5. Morphology

![Eggshell diagram](image)

**FIGURE 7: ARTIST’S CROSS-SECTIONAL AREA RENDITION OF EGGSHELL [11]**

Eggshell is a sophisticated structure used by the avian specie for reproduction. The function of the membranes is to protect the crucial inner functions from the microbial and physical environment (damage), control hydration and gases through pores, and store calcium needed for embryonic development when calcium enriched yolk is depleted.

1.5.1. Crystalline Structure

Characterising observations made in vivo as well as in vitro of the eggshell crystal ultrastructure, are scarce about the key physiological processes and the eggshell matrix constituents responsible for these distinctive structures. Furthermore, microstructural crystal size and orientation can vary significantly from one eggshell to another and from one to another within the same species.

![SEM of eggshell](image)

**FIGURE 8: SEM OF EGGSHELL [11]**
The mechanical properties of eggshell are strongly influenced by the preferential orientation of crystals within its microstructure since calcite is cut (cleaved) easily along certain crystallographic directions, specifically the c-direction (same as y-direction in mathematics). Thus, eggshell is composed of calcite crystals which are smaller, less aligned, and stronger than larger highly formed and oriented crystals [11].

1.5.2. Ceramic qualities

The average commercial hen’s eggshell is light brown in colour and has a semi-gloss (sheen) amorphous surface finish that is low to moderately reflective. The material is brittle, fine and therefore cumbersome to handle. “Hen’s[sic] eggshell typically consists of ceramic materials constituted by a three-layered structure, namely the cuticle on the outer surface, a spongy (calcereous) layer and an inner lamellar (or mammillary) layer “ [10].

Figure 7 displays two renditions from an article which shows the distinctive differences in structure noting that the eggshell is shared among other species (lizards, snakes, crocodiles, turtles and dinosaurs) besides the avian specie [11]. In Figure 9, there are two shards in the top left and right quarters that resemble the ceramic nature of broken cutlery.

Figure 9: Eggshell 1.1 Ceramic Chards
1.5.3. Porosity

In order to preserve and protect the function of embryonic growth of the avian chick, the ceramic structure of the eggshell has a multitude of pores seen in Figure 8, and also the FESEM results in Figure 32.

“The existence of these pores was first demonstrated in 1863 by John Davy, a member of the Royal Society from Edinburgh, without the aid of a microscope. He placed an egg in a jar of water and evacuated the air above the surface of the water with a vacuum pump. He noted that small bubbles of gas formed on the surface of the egg, and he deduced that there are minute openings in the shell.” [12]

Interesting to note is that the eggshell porosity depends on the pores that the eggshell has, “This value is the maximal amount of oxygen that can be obtained by passive diffusion through the fixed pores of the shell. Six hundred millilitres of oxygen per day may not seem very impressive to the reader (who will consume that amount in two minutes) but the molecular traffic through the 10,000 pores in the eggshell is remarkably intense.” [12].

Mesoporous material is defined as structures with pore diameters between 2nm and 50nm. Porosity in eggshell could have an influence on its electrochemical properties and other areas, and so will be further explored in the characterisation of eggshell.

1.6. Analysis Tools

Training was achieved for TGA, XRD, IR, IR-Raman, BET and SEM by the Murdoch laboratory technicians: Stewart Kelly, Ken Seymour, and Marc Hammond which ensured the samples could be analysed and the results presented for further discussion in this thesis.
1.6.1. TGA

The PerkinElmer STA 6000 (Simultaneous Thermal Analyzer) or Thermogravimetric analysis (TGA) instrument is an efficient quantitative method for comparing mass loss fractions and thermal energy (heat) curve. A tiny sample of a few milligram can be used to determine decomposition and qualitatively useful in detection of structural phase changes occurring during synthesis. Furthermore, TGA analysis (Figure 24) is useful in confirming expected synthesis reactions that have been previously undertaken and shown in existing literature. “The Thermogravimetric Analyzer (TGA) is an essential laboratory tool used for material characterization. TGA is used as a technique to characterize materials used in various environmental, food, pharmaceutical, and petrochemical applications” [13]. TGA is useful for confirming manual calculations with actual mass losses during thermal decomposition experiments. For this thesis, TGA forms the starting point for all other analysis and experimentation by forming a hypothesis where predictions are made, calculations performed, and results confirmed. Such decomposition calculations will be reviewed in the results section.

TGA is also useful for calculating the Activation energy for various samples which is useful for calculations that would predict the time interval with a given sample mass and input energy [14]. Eggshell has an activation energy of 47.83kcal/mol [15].

Figure 10: PERKINELMER STA 6000
The X-ray diffraction (XRD) instrument to be used at Murdoch is called Emma. Emma uses a Cu anode which will be explained in this section. XRD is also known as X-ray ‘powder’ diffraction since it has to be tested in non-aqueous solid form. The Chatani hemihydrate article [16] states that the testing of anhydrous and hydrous crystals is acceptable, since these structures are built (bonded) with the water molecule. Emma stands for enhanced multi-material analyser, and is available in theta-2theta or theta-theta geometry.

In X-ray crystallography, the XRD uses the Bragg diffraction condition:
\[ \theta = 2d\sin\theta = n\lambda \]
where \( \lambda \) is wavelength, \( n = \text{magnitude} \), \( d = \text{crystal plane spacing} \), \( \theta = \text{incident angle} \).

The most intense reflections of electromagnetic radiation are produced between the relation of the angles of incidence and the spacing of atomic planes in crystals. Maximum intensity of these waves occurs during constructive interference which happens when corresponding troughs and crests arrive at the same time at point (line). In the picture from the online Encyclopædia Britannica [17] as seen in Figure 11, lengths CB and BD together with the reflected angle \( \theta \) to determine \( d \) quantitatively by using the wavelength of the x-ray.
The diffractogram was used to obtain the diffraction pattern of eggshell and in this method the counts appear on the Y-axis while the angle $2\theta$ on the X-axis which can be seen in Figure 25 to 27. Particular attention regarding the diffractogram is that not all patterns are equal. The wavelength is a set wavelength during the entire X-ray emission process and is set either as cobalt (Co) or copper (Cu) anode which means that the $2\theta$ values will be different while the d-space value will be the same. So pictorially, the pattern may have some shift for the same crystal specie meaning that the peaks may appear on different integer values. The overall appearance would still have the same peak angle difference from peak to peak, just with a shift. The reason two anodes are used, is because in the case of Cu, samples rich in Mn, Cr, and Fe will certainly fluoresce Cu K-alpha radiation. Most diffractometers use a monochromator and filters to reduce these interferences. ‘Emma’ uses the Bragg-Brentano focussing geometry, using a Xe detector with a graphite monochromator, or in some models, a solid-state detector. Where a solid-state detector is used, it is best to determine if Cu or Co was used for the qualitative analysis. XRD plays a major part in the identification of and characterisation of eggshell in relating its behaviour to known species already used in the industry.

The aim is to show eggshell as a viable sustainable resource in comparison to other synthesised species (synthetics). Furthermore, by identifying the phases of eggshell during its thermal decomposition and subsequent crystal phase changes, it is then possible to test each phase to determine if those morphological changes have electrochemical or electrostatic advantages for use in supercapacitors.
1.6.3. SEM and EDS

Scanning Electron Microscope (SEM) imaging for morphology (qualitative) and topography (quantitative) regarding chemical composition and particle sizes.

For EDS, the compositional report of the sample is a rough estimation based on the area and depth of the electromagnetic X-ray on the surface of the sample. It is for this reason that these amounts are considered qualitatively and not quantitatively. The same applies to FESEM.

The principle of operation is that when a condensed electron beam is focused onto the surface of the sample, the electrons interact with the sample to produce five to six different types of secondary electrons. They are auger, secondary, backscattering electrons as well as fluorescent, continuum and characteristic X-rays. The most used operation of SEM is SEI (secondary electron imaging) where the secondary electrons are detected. There are options like backscattering, but these tend to naturally attenuate the electrons from structures and favour the flatter surfaces. The type of material also affects image by increasing electron scatter, so in the case of oxides which are generally white, adjustments need to be made to reduce the effects of luminescence and ‘charging’. It helps to reduce the charge voltage of the electron gun from 15kV to about 10kV or 5kV.

Unfortunately this product has been discontinued by the manufacturer [18], yet was valuable in learning the skills to use this technology for the characterisation of eggshell. While many hours can be used on such electron imaging, the analysis for this thesis was conducted on FESEM which will be explained further in this chapter.
Carbon and Gold Sputterer

To increase the scanning capability and the quality of the image, there are two methods available at Murdoch used to coat the samples, namely ‘carbon’ and ‘gold sputter’. A conductive stub (aluminium) is used to place the sample upon. This is done by first placing a carbon ‘sticker’ (conductive and adhesive carbon layer) onto the substrate, called a stub (Appendix E), thereafter approximately 5mg of sample is placed onto the sticky carbon surface. The idea is to spread this sample across the carbon substrate homogenously such that most particles are interacting with the carbon adhesive. A blower is used to remove the samples that won’t stick while also making sure to not touch the top surface of the stub to avoid contamination.

If there is carbon present in the sample, it is best to gold or platinum coat (Curtin University) the sample stub, as this is used to determine the amounts of carbon in the sample without there being the carbon coating on the surface adding a false representation of carbon in the sample. The stub is placed into the adjustable coating platform at about 45mm from the base of the glass tube. This will mean the sample is within the ‘even plasma distribution’ zone thereby creating a homogenous layer on all sides of the sample particles.

The coating size is determined by how much time the stub is placed under the plasma condition. If the sample were placed for 60 seconds, this means a depth in coating of 60s * 3 = 180 Å (angstrom). Later samples were coated at 90s = 270 Å. So, for the 90s, the SI (metric) unit amount from the Swiss unit is:

\[(270 \text{ Å} / 1 \times 10^{10} \text{ Å}) = 1000 \text{mm/x}\]

\[x = 2.7E-8 \text{ or } 27 \text{nm}.\]
Brunauer-Emmett-Teller (BET) analysis is used to determine the surface area of the sample relating to the morphological aspects of the sample surface such as porosity and crystal structure. Irving Langmuir depicted a relationship between the number of active sites on the surface of a solid undergoing adsorption and pressure which explains variation of adsorption with pressure. His theory is based on a few assumptions that relate to the physical and kinetic properties of atoms, (1) that a fixed number of adsorption sites are available on the surface of any solid, (2) all sites are of equal size and shape at the surface of the adsorbent, (3) each site can hold a maximum of one gaseous molecule while a constant amount of energy release occurs during this process, and (4) a dynamic equilibrium exists between free gaseous molecules and adsorbed gaseous molecules [19]:

\[
A (g) + B (s) \rightleftharpoons AB
\]

Where \( A (g) \) is unadsorbed gas molecule, \( B (s) \) unoccupied/vacant site on surface and \( AB \) the adsorbed gaseous molecule.

This is further explained in the reaction rate constants of \( K_a \) and \( K_d \) where \( K_a = [A] [B] \) and \( K_d = [AB] \) and represented in an equilibrium as \( K_a = K_d \) or \( [A] [B] = [AB] \).

Or

\[
K_a = \frac{[AB]}{[A] [B]}
\]

The equilibrium constant is represented in the above equation for the distribution between the gas and surface phase.

BET is like the Langmuir adsorption theory, except it is more defined regarding more areas such as:

(1) homogenous surface (equal amounts of atoms throughout),

(2) limited molecular interactions. Excludes inter molecular interactions or lateral adsorption,
(3) local equilibrium. The upper most layer (liquid) is in equilibrium with the gas phase molecules such that the rate of adsorption is equal to the rate of desorption. Furthermore, no net change in the number of adsorbed molecules at any vapour pressure means that the system is saturated,

(4) kinetically limited process. For the reaction rate to change, energy must be provided in the form of heat. Two distinctions are made, one is that the for the surface adsorption layer, the energy amount required is equal to the heat of adsorption and secondly, subsequent adsorption layers are treated as equal to the energy required for condensed liquid (condensation), and

(5) infinite adsorption at saturation. When Po is reached, and adsorption is reached across all vacancies of the surface and thus surrounded by condensed liquid-phase, the rate of change of adsorption in theory tends to infinity. It is therefore expected that there be a sudden exponential increase in the adsorption rates after the first layer.

It is this curve (Appendix D) between the adsorption of the 1st and 2nd layers that are used to determine the surface area of that sample (solid). Nitrogen is used to control the energy over the test cycle as well as the gas that is used in situ for the rate of adsorption. The Dewar (centre, Figure 15) is filled with nitrogen and placed into the BET instrument at STP while at the same time the samples (in an evacuated glass tube) are slowly immersed into the ‘boiling’ liquid as sensors monitor pressure (ΔP) of the incoming nitrogen gas.

A general rule is that for d (diameter):

- < 2 nm = microporous,
- 2-50 nm = mesoporous,
- > 50 nm = macroporous.
1.6.5. **FESEM**

The FESEM instrument in Figure 16 used for the three states of Eggshell characterisation, was the Zeiss-Neon 40EsB instrument at Curtin. This instrument had greater resolution than the SEM instrument at Murdoch. The field emission microscope concept of operation consists of a high melting point metallic sharp tip (cathode) and a conducting fluorescent screen (anode) all enclosed within a vacuum. The sample is made highly negative to create the condition for field emission to take place.

The advantage of FESEM over SEM is improved graphical representation in sample morphology. Higher surface area is an indication of greater ionic activity which is suitable for supercapacitors and useful in predicting enhanced energy storage capacity in eggshell.

These advantages are because the technology and arrangement of that technology is different. SEM uses a minimal spot size (thermionic emitter) and high voltage, then rasters over the sample to demagnify the signal producing the image. Whereas the FESEM (electromagnetic) field emitter gun provides high focussed electron beams at lower than 5kV. The overall picture has better spatial resolution providing enhanced 3D depth.
The Field Emission Scanning Electron Microscope (FESEM) model Zeiss-Neon 40EsB at Curtin is a renowned brand of optical instrument developed by Carl Zeiss from Germany.

The FESEM instrument was operated to ensure that the samples were handled and processed for viewing and further analysis efficiently.

The stubs (See Appendix E) were arranged in order of Thermogravimetric decomposition of ground Eggshell (ES1.1), Calcium Carbonate (ES1.2) and Calcium Oxide (ES1.3). Each sample is represented at three magnification levels, namely x500, x3500 and x20 000. This can be seen in the results section in Figure 32 – 34.

1.6.6. Cyclic Voltammetry

This Electrochemical potentiostat/galvanostat instrument (Bio-Logic SP-150) is controlled by the EC-Lab® software [20]. The Bio-Logic instrument uses numerous methods to test energy storage technologies. Eggshell electrochemical analysis was predicated on two methods of testing namely Cyclic Voltammetry and Galvanostatic Cycling. The former will establish the characteristic VRS (voltage region signature), and useful determining eggshell’s energy capacity cycling in the latter.
2. Literature Review

2.1. Management

“Chicken eggs are commonly used in enormous quantities in the food processing and manufacturing industries, restaurants, households and even in the pharmaceutical industry, and their shells are disposed as solid waste. The eggshell represents ~11wt% of the total egg weight, and is composed of calcium carbonate (~94 wt.%), calcium phosphate (~1 wt.%), magnesium carbonate (~1 wt.%) and organic matter, as well as smaller quantities of strontium, sodium, iron, potassium and chlorine” [21].

Discarded chicken eggs increase in toxicity causing salmonella growth in landfills due to the protein membranes of the eggshell that remain. The odour from large quantities are also unpleasant for workers and surrounding communities. The handling of large scale eggshell biowaste is cumbersome and expensive for waste management as this biowaste attracts pests such as rodents and cockroaches.

“Most eggshell waste is discarded because further processing is too expensive and cumbersome, and unprocessed (i.e., still having the calcium carbonate (CaCO$_3$) eggshell and protein-rich membrane together) eggshells are considered useless. Sending unprocessed eggshell waste to landfill is associated with a cost of more than $40 a ton depending on the location of the landfill” [22].

Finding alternative solutions to this problem inevitably raises costs, and could be rewarding as there is much research into the repurposing of this product. So rather than see it go to waste, research has already shown that this is a valuable resource, if not a product on its own.
2.2. Sustainability

Sustainability means that the product can be used at a certain level or rate while causing little or no damage to the environment, thus such a product is deemed ‘sustainable’. The literature on waste eggshell use suggests that this biowaste can be prepared for a wide range of applications (Cambridge Dictionary 2018). “Promoting the sustainable development of such materials is important in order to ensure that these materials can be made affordable and accessible by all patients in an environmentally considerate manner.” [4]. A recent study on the harmful effects of the sun on products from ultraviolet light has been used to provide further ways to improve sustainability of bio-waste. “Photodegradation causes a steady loss of the useful physical, mechanical and optical properties of materials, necessitating their replacement over time. Because UV (Ultraviolet) light is most harmful in this regard, many materials now contain UV-protective additives. However, these additives are not always effective and durable, can be expensive, and their natural extraction or synthetic production can be harmful to the environment” [22]. Substitution of bio-waste into the production process broadens the resource network and alleviates burden on synthetic products which is healthy for competition. Other mentions are the removal of heavy metals [23] and using eggshell waste to substitute [24] for building lime (aka builder’s lime or quick lime).

2.3. Innovative Applications

HAp (hydroxyapatite) is an essential element used in biomedical applications such as orthopaedic and dental implants. The eggshell precursor together with a synthetic substitute for urine is used to produce the calcium phosphate ceramic material. “Strategies for producing sustainable materials and manufacturing process for various applications are vital for sustainable development. Biomaterials are an essential element of regenerative medicine and have a vast range of applications in the biomedical industry. Producing HAp entirely from waste materials containing calcium and phosphate will enhance its environmental sustainability”. The findings were, “This study demonstrated that HAp biomaterial powder can be potentially synthesised entirely (emphasis added) from biowastes in a simple batch reactor.” [4].
A similar study was also performed for non-medical industrial applications to synthesise HAp using chemical precipitation (ionic, covalent, polar & hydrogen bonds). The method used for calcination and analysis characterising the morphology of the eggshell bio-waste in this HAp article has been used to form part of the analysis in this thesis project as a means to apply the thermally induced crystal changes. “For example, it is used as a catalyst for chemical reactions, host materials for lasers, ion conductors and gas sensors. There are different phases, which usually appear as trace impurities during the synthesis of a specific calcium phosphate ceramics phase,”

One researcher used two tests, the first was to use unprocessed eggshell specimens washed and cleaned with ethanol and placed on top of various polystyrene samples under light to simulate the harmful UV effects of the sun. The second test used ground eggshell in a more practical form to test the transmittance of UV light. Transmittance is the ability of a surface to transmit radiant energy to its further side. “UV light has deleterious effects on many materials, including synthetic polymers and naturally-occurring biopolymers such as skin, hair, and wood. These materials absorb UV, triggering photolytic and photo-oxidative reactions, resulting in photodegradation and therefore a steady loss of useful physical, mechanical, and optical properties. Substantial efforts have gone into reduction of photodamage and improvement of durability of photodegradable materials upon exposure to UV light using both organic and inorganic additives” [22].

2.4. Renewability

Finding sustainable bio-waste products for electrode manufacture is evident in the amount of academic literature available. Since the recent advancement of storage capacity of the lithium ion battery which allowed for hybrid systems using the renewable technologies of wind and solar power generation, it makes sense to further develop and improve the existing energy storage technology. At the same time, research should be undertaken to investigate biologically produced material as sustainable resources such as eggshell. Eggshell used as a precursor for anode material for super-capacitors does not seem to exist in academic literature, articles nor published literature. However, there are a few published articles where eggshell is used for doping lithium titanium oxide (LTO) anode material with calcium abundant avian (chicken) eggshell. “The CaCO₃ is believed could be a good Ca
source for the dopant of LTO. The outer membrane of the eggshells can be taken and utilized for a natural CaCO3 which is also believed having finer structure than the commercial one.” [25]. The same team a year earlier (2017) also noticed the advantage of the eggshell CaCO$_3$ crystal structure over synthetic CaCO$_3$, “Furthermore, there is also possibility of improving discharge capacity by doping LTO with Ca. Eggshell is known as one of kitchen waste that contains amount of CaCO$_3$, especially in the outer membrane. It is believed that waste eggshell can be utilized as Ca-source for the dopant of LTO. Furthermore, nature-based CaCO$_3$ has finer structure than commercial-based CaCO$_3$. This fact can cause Ca atoms to substitute Li atoms become easier.” [26].

The incentive to integrate a sustainable resource like eggshell into the renewable energy market is self-evident in so far that both achieve the same environmental concern as well as the need to minimise process costs to be competitive in local and international markets.

In a recent article, the following was stated: “To accomplish with the urge from the battery-manufacturing field, alternative materials are under investigation aiming at finding a good trade-off among availability, cost, performance and eco-friendliness, which is sustainability. Bio-waste derived materials are attracting much interest, since they are good candidates for the scaled-up production today’s battery market is calling for.” and further states “However, to the end of the overall sustainability of such bio-waste derived battery materials, even the manufacturing processes need to be low-energy demanding.” [27]

Furthermore, the renewable energy sector would benefit by removing the stigma of ‘fluctuating power’ which the public have generally interpreted as ‘intermittent power’. With prices of renewable generation products dropping, the need to seize and close the gap for reliable and sustained power, can be achieved especially in remote areas where micro grids are economically more viable.
3. Methodology

The methodology used in this thesis is drawn from various literature using solid-state thermal decomposition involving full or partial calcination by using a furnace to determine the evolved species. The in-situ synthesis of eggshell by furnace allows the moisture, volatiles, and oxidation state to be characterised. Moreover, these states can be tested later for its suitability as anode material. Most inorganic and organic materials can be broken down or manipulated into parts. As the process of decomposition occurs, careful note needs to be taken as these stages reveal the properties of these phase changes. For this reason, physical changes were monitored by careful weighing samples during testing of these phase changes. Eggshell and its transitional states have been hypothesised to influence its electrochemical characteristics. The three samples will be cycle tested over a shorter period than would be tested in industry because of time limitations for this thesis. The electrochemical characterisation will use an electrolyte with a high basic pH of 14.3 and a molarity of 2M/L for all three samples during all cyclic voltammetry tests. Two cycling techniques will be used while only the electrode and charge parameters will be changed over this duration.

3.1. Assumptions

All equipment used in this thesis will be used for quantitative analysis, and likewise that all equipment used in this thesis will be used for qualitative analysis. Assume STP was used in all literature specifically for the solid-state synthesis of eggshell. Hen’s eggshell is homogenous in chemical composition and crystal structure. Laboratory equipment available in Murdoch, will always be adequate and serviceable. Heating and cooling periods are done at a variable rate during furnace eggshell synthesis. The eggshell sample chosen is representative of all other caged hen’s eggs. The calculation for the energy storage (capacitance, energy and power) was based on the premise that samples put through cyclic voltammetry testing of up to 500 cycles would show increasing stability towards the end, and decreasing stability towards the beginning. It was for this reason that selecting points to be analysed were reversed from the end and halved and used for the next point, thus the points were chosen as follows: 500, 500/2, 250/2, 125/2 etc. This meant more points available for the plots where more critical areas needed representing.
3.2. Exclusions

This study will exclude pasture, free range and farm roaming samples. Pasture (P) and farm roaming (FR) samples (ES 2.1-3 and ES 3.1-3) will be calcined and analysed with BET and SEM to corroborate the findings with caged eggshell (ES 1.1-1.3). Further comments will be made in the BET and SEM results and discussion section regarding P and FR samples.

3.3. Physical Characterisation of Eggshell

3.3.1. Selection and Grinding

The sample chosen for this thesis was chicken eggshell (see Figure 19). The most abundant eggshell is the caged hen’s egg, and for this reason it was selected. The eggshell was cleaned with deionised water and then dried in the oven overnight at 70°C, removed and ground fine with an inert glass mortar and pestle (Figure 20).

Grinding the eggshell is a slow continuous force which is done by twist/rolling the wrist in order to shatter the natural curve of the eggshell across one imaginary line. This tactic was better than placing the pestle on one spot to shatter the ceramic eggshell because eggshell can face up or down. Eggshell facing up is harder to crack than facing down. So, by rolling the pestle across the sample with low force, the eggshell cracks regardless of their orientation. Once the larger fragments were reduced to 3-4 mm, more force was applied vertically with less movement in the lateral component. Much of the reduced fragments once particle size, were once again rolled with lateral forces while rolling the wrist. Higher frictional forces required to reduce particle size to fine powder meant that the glass pestle and mortar could break down the glass pestle, cause contamination and create heat. The grinding process took
approximately 30 minutes. Lastly, the ground eggshell was placed on a scale (sartorius) and measured at 13.1689g in mass. The ground eggshell sample formed the basis for all laboratory processing. During the physical characterisation and experimental stages of caged eggshell, pasture (P) and farm roaming (FR) eggshells were introduced as a secondary objective to add quantitative and qualitative insight and flavour to the thesis. This will be added to the results section under the BET heading.

3.3.2. Eggshell Calcination

3.3.2.1. The Furnace

The furnace was booked at the hydrometallurgy laboratory (240.2.057) for synthesis of calcium oxide (CaO) using solid state method (Figure 21) using a sample size of 995mg.

The first sample was calcined for 3 hours at 875°C to follow the full decomposition of eggshell to CaO as indicated in the physiochemical study of CaCO₃ from eggshells [15] with extensive thermogravimetric analysis conducted at various constant temperature rates as well as recent TGA results. The first sample (Figure 22) results when tested by XRD analysis showed (diffractogram) an incomplete crystal phase shift, so was repeated with a new sample at 950°C.

By using the furnace, it would produce two samples which will be referred to interchangeably as CaCO₃ (600°C) or 1.2, and then CaO (950°C) or 1.3.

The 1st numeral was to establish the eggshell source and the 2nd numeral for the crystal phase shift or oxidation state. Thus Eggshell ES 1.1 would represent caged eggshell and 1st phase of ground eggshell having undergone no thermal morphological change, ES 1.2 would
be the thermal half decomposition-state of eggshell while ES 1.3 would be the full thermal decomposition or oxidised state. The controller for this furnace was not set for constant temperature increase or decrease rates because this thesis chose more emphasis in laying the groundwork for eggshell analysis, while others can make further refinements. Optimal performance and improvements of the calcination process and its impact on the eggshell crystal structure are to be suggested for further future analysis based on this study.

3.3.2.2. Improvements

The first batch to enter confirmed unsuccessful by XRD analysis in Figure 22 which confirmed an incomplete crystal phase shift from CaCO$_3$ to CaO at 875°C. Radiant and transmittance energy rate was adjusted (Figure 25) by increasing sample surface area, raising the temperature to 950°C, while reducing the sample size from 995mg to 413.2mg.

![XRD Calcination Attempt 1 No Match](image.png)
The crucible (35mm x 30mm) can be seen in Figure 23 on the left with its replacement on the right. The experiment was repeated and will be presented in the results section. The problem with this crucible is that it is conical in shape tapering to a diameter almost half its top diameter. It was postulated by the Technical Manager Mr Ken Seymour that the top surface area in the crucible may be insufficient for the volume of sample used, moreover the conical shape meant that the sample gains height at initial low volumes and this tends to make the process take longer. With the decomposition of the sample on releasing gas, it would be analogous to boiling water. When the H₂O molecules desorb, they absorb energy and the result is a heat loss to the surrounding which is why the kettle will not venture to far beyond 100°C while there is water in the kettle. The results were indeed matching the same structure as synthetic CaO in Figure 27.

3.3.3. Agglomeration

Agglomeration is synonymous with flocculation and coagulation which is the process of contact and adhesion of particles dispersing to form larger clusters. This occurs during the heat energy added to a mass of bonded atoms where smaller atoms cluster together to aggregating larger ones (Figure 29 and 31).

In the article by Schnebelen et al it is said that “Experiments realized with a high concentration in sodium chloride (2M) showed that the modification of the electrostatic environment did not change the particle size distribution and the morphology of the agglomerates. This indicates that the electrostatic interactions are not responsible for the agglomeration, but the formation of crystalline bridges induced by the crystal growth” and concludes, “Finally, by varying the experimental conditions, it appears that the agglomeration constant increases with the temperature whereas there is an optimal value regarding the shear rate.” [28]. By choosing various thermal states for the eggshell samples, the changes in agglomerated particle sizes can be observed (SEM and FESEM) and linked to both temperature and surface area.
3.4. Electrochemical Characterisation

3.4.1. Electrolyte

Sodium Hydroxide (2 mol/L) was used for the experiment, while NaOH is also known as a strong base. Molar Mass = 39.997 g/mol.

Molarity: \[2\text{NaOH} = 2\text{Na}^+ + 2\text{OH}^-\]

Concentration of ions (pH):

\[
[H^+] \cdot [OH^-] = 1.0 \times 10^{-14} \text{M}
\]

\[
[H^+] = 1.0 \times 10^{-14} \text{M} / [OH^-] = 1.0 \times 10^{-14} \text{M} / [2\text{M}] = 5 \times 10^{-15} \text{ (unit less)}
\]

\[
\text{pH} = -\log(5 \times 10^{-15})
\]

\[
\therefore \text{pH} = 14.3 \text{ (Basic)}
\]

It is normal to calculate higher than a pH of 14 since this is a logarithmic calculation based on the proportion of total possible of H+ cations and OH- anions in a little of water which are equal in a glass of water.

Some compounds are soluble in higher concentrations than others. Most pH meters will default the reading to pH 14 since higher concentrations decrease exponentially approaching pH 14. Thus, it is true that 1M of OH- ions will have a pH of exactly 14.0, and 1M of H+ ions will have an exact pH of 0.0. See pH Scale review in Appendix C. From the calculation, it is seen that the NaOH solution with a molarity of 2, has a high basic pH. The high pH level will be tested in vitro with three active materials as electrodes. Testing the electrochemical and electrostatic reaction over many cycles will confirm the stability of eggshell.
3.4.2. Electrode Manufacture

3.4.2.1. Selection and Composition

The aim was to select a suitable electrode substrate that is chemically inert. Gold is known to be inert due to its noble-metal status (resists oxidation), yet it is very expensive. So, the graphite electrode was chosen due to its relative inertness and its availability. Some offcuts from previous electrode cuttings made ideal sizes to test the three active materials of eggshell. Graphite (carbon) was also chosen due to its resilience to heat and low resistivity of 0.3 to 6 µΩ/m. Graphite is also widely used to melt iron. The active materials are three transitional states of eggshell namely calcite, calcium carbonate and calcium oxide and their numerical equivalent is 1.1, 1.2, and 1.3.

The composition proportions for mixing and their target masses are as follows:

- Graphite electrode (substrate)
- Acetylene black (AB) improves conductivity, composition (15%)
- Binder - polytetrafluoroethylene (PTFE), composition (10%)
- Active material – all three states of eggshell, composition (75%)
- N-Methyl-2-Pyrrolidone. Added dropwise as needed (aq)

Acetylene black (AB) is a sub type of carbon black and considered a higher purity. There are various grades of purity available from 50% - 100% as well as high conductivity versions suitable for the battery manufacturing industry [28].

The binder polytetrafluoroethylene (PTFE) was used due to its ability to improve cell performance of electrodes according to the 2002 article published in Japan by Manickam and Takata [29]. Comparing PVDF and PTFE mixed active material electrodes shows that after continuous cycling, it was still inert without the decomposition of fluorine atoms. The solvent used was the aprotic solvent N-Methyl-2-Pyrrolidone. Aprotic is the antonym of protic. Protic means it has H-N or H-O bonds. The ‘a’ means ‘without’, and ‘protic’ refers to protons or hydrogen atoms. With aprotic, no hydrogen atoms are present. A common example is acetone.
3.4.2.2. Manufacturing Process

The compositional mass percentages are relatively standard in the industry for testing active material and adding more of the binder or AB does not make any substantial improvements to the conductivity of the electrode. As a safety precaution, the three samples were to have two electrodes made such that a total of six electrodes were manufactured.

The target mass for the active material was decided to be 15mg per electrode. This meant 30mg for two, with 20mg (40%) waste during mixing. Thereby a total of 50mg for each eggshell thermal state (~41°C, 600°C and 950°C). After the process and technique is revised, the waste of 20mg should reduce slightly.

The electrode mass was measured so that the active material after drying could be determined. The mass amounts were measured and then placed into the mortar vessel and mixed together with an inert stainless-steel spatula. This was then made aqueous by adding the solvent dropwise into the mixture, then mixed until homogenous and dense.

A heated platform was used and set to 100 - 150°C to dry the solvent, thereby binding the active material to the electrode. The spatula was used to transfer this mixture to the 1cm² section of the two graphite electrodes, small amounts at a time, waiting also for the previous aqueous amounts to solidify (dry).
3.4.3. Calculations

The calculations below were applied to 10 selected points from the 500 cycles. Stability calculations were performed using two methods to confirm these amounts for capacitance (C) and power (P). The formulas used for calculations were,

Capacitance, \( C = \frac{Q}{V} \) [coulomb/volt]

From which we derive the instantaneous formula for current,

\[
\frac{dQ}{dt} = C \cdot \frac{dV}{dt} \] [farads]

\[
I \text{ (current)} = C \cdot \frac{dV}{dt} \] [amperes]

For the charge and discharge cyclic voltammetry, the mode of testing was constant current and cyclic voltage. This means that the instantaneous formula for current can be used to derive capacitance with some algebraic manipulation of the differential equation, thus

\[
C = \frac{(I \cdot t)}{V} \quad \ldots \quad (C1)
\]

2nd method: \( C = \text{integral (area under curve)} \left[ \frac{I \cdot dt}{dV} \right] \) in excel \( \ldots \quad (C2) \)

The change in time (dt) and the change in voltage (dV) which is based on \( dV = (V_{\text{final}} - V_{\text{initial}}) \) is applied to the data set columns from each cycle, and so for each cycle charge and discharge capacity can be determined using equation C2.

Energy, \( E = \frac{(C \cdot V^2)}{2} \) [W.s] \( \ldots \quad \ldots \quad (E1) \)

To derive power from the energy, we multiply energy [W.s] by inverse time t[s], thus

\[
\text{Power, } P_{\text{inst}} = \frac{dE}{dt} \quad \text{SI unit ‘s’ cancel.}
\]

But instead of instantaneous power, we are interested in the average power over the discharge period and not the whole charge/discharge period so,

\[
P_{\text{ave}} = \text{integral (area) of } \left[ \frac{dV \cdot I}{t} \right] \quad \ldots \quad (P1)
\]

2nd method: \( P = \frac{(C \cdot V^2)}{2} \) [W] \( \ldots \quad \ldots \quad (P2) \)

Both P1 and P2 were used for power calculation in excel with the answers very similar as shown in Appendix B from cells I16 and P36. Likewise, capacitance using formula C1 and C2 was used to determine the cells in N7 and N28 and match with precision.
4. Results

4.1. Eggshell Analysis

4.1.1. Furnace Calcination

From the TGA analysis we can conclude the final composition in mass (g) of the synthesised eggshell from ~calcite to calcium oxide. This calculation presumes that no other elements exist in the calcite sample ES1.1 other than CaCO$_3$ since already stated that ES is ~94% CaCO$_3$. Placed 413.2mg of eggshell in furnace at 950°C. After 3 hrs removed the sample once cooled, and measured sample to have 223.3mg mass.

Calculated theoretical compositional loss %:

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} \\
\text{MW: } 40.078 + 12.0107 + 15.999 \times 3 & = 100.1g \\
& = 56.01g \\
100\% \times \frac{56.01}{100.1} & = 55.95\%
\end{align*}
\]

Estimated mass composition:

Given original mass: 413.2mg

\[413.2\text{mg} \times \frac{56.01}{100.1} = 231.2\text{mg}\] \hspace{1cm} (1)

Actual mass composition: \[223.3\text{mg}\] \hspace{1cm} (2)

Composition loss %:

\[100\% \times \frac{223.3}{413.2} = 54.04\%\] \hspace{1cm} (2)

Therefore, the decomposed sample is +3.4% difference of actual.

Or ~94% CaCO$_3$ of eggshell:

\[0.94 \times 413.2\text{mg} \times \frac{56.01}{100.1} = 217.33\text{mg}\] (-2.7% difference of actual)

The volatile mass is therefore predicted to be CO$_2$ with some other elements present such as magnesium carbonate ~1% and calcium phosphate ~1% [10]. So that would drive the theoretical value higher, towards 220mg and above, since the masses of the other elements have been omitted.
4.1.2. TGA

A small sample of ~40 mg was placed into the TGA receptor where the thermal and heat energy effects are measured and represented on an excel spreadsheet graph in Figure 24, from the exported data. The right-hand side of this figure shows the volatile decomposition mass loss of eggshell from 39mg to 36 mg during the thermal phase transition of eggshell between the temperatures of 40°C to ~720°C.

A few important changes take place namely moisture loss, medium and high volatile loss and final decomposition state of the eggshell. The results were expected to follow the decomposition of calcite (CaCO₃) to calcium oxide (CaO) with the release of volatiles (gaseous) and carbon dioxide (CO₂): CaCO₃ (s) $\xrightarrow{\text{heat}}$ CO₂ (g) + CaO (s), however this decomposition is theoretically for ‘pure’ (synthetic) calcite and excludes moisture and other volatiles.

In Figure 24, the moisture in %wt. would completely desorbed by ~220°C with release of low to medium volatiles with the sample further decomposing from 220°C to 600°C. The last decomposition phase of high volatiles occurs from 600°C to 860°C to a final oxidised state of 860°C (CaO).

![TGA of Eggshell](image.png)

**FIGURE 24:** TGA OF EGGSHELL (LEFT) WITH EXPANDED VIEW (RIGHT)
4.1.3. XRD, diffractogram outputs

An XRD analysis was performed on the eggshell and the recorded data was presented graphically and compared with an extensive library confirming eggshell is a very close match to synthetic calcite, yet it is not considered calcite but eggshell. There are various synthetic calcite forms [30] and we can verify that eggshell has a high phase match to synthetic (industry manufactured) calcite as seen in Figure 25. The diffractogram shows thin blue lines indicating the synthetic product while the other represents the eggshell.

![XRD diffractogram of eggshell (~41°C) - Calcite](image)
**FIGURE 26:** XRD ES 1.2 DIFFRACTOGRAM OF CaCO3 (600°C) - CALCITE

**FIGURE 27:** XRD ES 1.3 DIFFRACTOGRAM OF CaO (950°C) - LIME
4.1.4. BET diagrams outputs

Adsorption and desorption curves can be seen in Appendix D. The surface is calculated by the software by determining the empirical point where the adsorption to the sample surface becomes condensation of the second layer of atoms transitioning from gas to liquid. This is between the Y asymptote and the X asymptote.

**Table 1: BET Surface Analysis Results**

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**Figure 28: BET Surface Area Analysis of Eggshell #1, #2 and #3**
4.1.5. SEM, Diagrams outputs etc

**Figure 29:** SEM ES 2.3 CAO (950°C)

**Figure 30:** SEM THERMAL COMPARISON OF ES 2.2 AT 450°C VS ES1.2 AT 600°C

**Figure 31:** SEM ES 3.1 GROUND EGGSHELL ~41°C
4.1.6. FESEM

Figure 32: Eggshell 1.1 at x500 x3500 x 20000 Magnification

EHT = 5.00 kV  Signal A = SE2  Aperture Size = 20.00 µm
WD = 4.8 mm  Sample 1.1 (Eggshell)
Figure 33: Calcium Carbonate 1.2 at x500 x3500 x 20000 Magnification
FIGURE 34: CALCIUM OXIDE 1.3 AT X500 X3500 X 20000 MAGNIFICATION
4.1.7. EDS, Diagrams outputs

**Figure 35: EDS Ground Eggshell**

**Figure 36: EDS CaO**

**Figure 37: EDS CaCO3**
4.2. Electrode Analysis

4.2.1. Cyclic Voltammetry

This 1st method of cyclic voltammetry is used to qualitatively identify the storage ability of all three samples by viewing the area inside each closed loop. The greater the area, the greater the presumed storage capacity. The voltage ranges can also be used for the second cyclic testing method of galvanostatic cycling.

**Figure 38:** CV (ES 1.1, 1.2, 1.3) Sample Comparison - Negative Region

**Figure 39:** CV (ES 1.1, 1.2, 1.3) Sample Comparison - Positive Region
4.2.2. Galvanostatic Cycling (Charge-Discharge)

This is where the extracted the raw data will be quantitatively used for the determination of specific capacity. The charge/discharge cycles are all going to be represented and analysed in excel since the cycles are continuous when extracted from the graphical Bio-Logic EC-Lab V11.16 software raw data. The regime used constant current and cyclic voltage throughout the galvanostatic cycling for all three samples of eggshell.

500 cycles were chosen to be the duration and at this point the programmable logic condition is met to stop the data logging and further cycling. Each cycle is recorded between (and including) two parameters working off conditions specified on the logic instruction board (interface). The amount of mA is entered as well as the start and end voltage. The current was chosen to ensure the voltage set points were reached. In the cases where voltages were not going to be reached for a certain sample, the previous cyclic voltammetry results for that same sample were reviewed to find the new suitable voltage that’s permissible and not outside its VRS. The cycling regime had two instruction pallets which reversed the current when the set point was reached, thus its continuous cycling would commence. A stop limit was provided if the number of cycles reached 500 as well as a condition for a minimum voltage change of 10mV for a set amount of time.

The pallet was previously setup as a template for these types of tests and each electrode just needed a few parameters changed specifically from their VRS and the current required to reach the set point voltage. In cases where the active material did not reach the required voltage, the current was just increased. The objective was to get the cycles to occur as slow as possible in order to have enough data points and charge recorded. The charge discharge stability of the graphs reveals trends which would be a factor in selecting the active material for electrodes which is why manufactured electrodes are tested over thousands of cycles.
Figure 40: Anode Cyclic Discharge of Eggshell

Figure 41: Cathode Cyclic Discharge Stability of Eggshell
4.2.3. Anode and Cathode Discharge Cycle Times

**Figure 42:** Eggshell Cycle Time as Cathode

**Figure 43:** Eggshell Cycle Time as Anode
4.2.4. Electrode Matching – cycle time

**Figure 44: Electrode Pair Match - 1**

**Figure 45: Electrode Pair Match - 2**
4.2.5. Ragone Plot of Anode and Cathode

**Figure 46: Eggshell as Anode on Ragone Plot**

**Figure 47: Eggshell as Cathode on Ragone Plot**
5. Discussion

5.1. Physical Characterisation of Eggshell

The calcination of eggshell using the predictions of volatile loss in the literature review, TGA together with calculations, confirm the major compositional loss % to be CO\(_2\) and to a lesser degree, moisture. The XRD analysis confirms the thermal states through the diffractograms as ~41°C calcite, 600°C as calcite, and 950°C as calcium oxide. Calcite is one of the polymorphs of Calcium Carbonate. The amplitudes, counts, and placement of the crystal angle (degrees) confirm the three samples as thermally synthesised states, except for ground eggshell, which is synthesised during egg production within the hen. The precursor eggshell at STP is ~calcite, one of the three polymorphs of calcium carbonate, as confirmed in the XRD results showing the typical peak at angle 29.4° in Figure 25.

BET Analysis shows in Table 1 and Figure 28 the surface areas of ES #1 as a decrease from ~41°C to the next higher thermal state of 600°C while then increasing largely to 950°C. The other samples of the BET analysis ES #2 and ES #3 show steady increases from ~41°C thermal state.

The SEM analysis equipment in Figure 30 shows that the morphology of calcite at 450°C and 600°C, are very different. The 450°C sample had not yet started its agglomeration process and maintained most of its precursor ceramic phase. The FESEM results in Figures 32 and 33 have shown the morphological changes that are helpful to understand the thermal effects on agglomeration sizes, particularly the transition from the precursor ceramic surface structure of calcite (~41°C) to calcite (600°C). From the eggshell analysis in the SEM and FESEM, it is evident that the pore sizes are close to 250nm (¼ of the 1µm), 50-500nm in CaCO\(_3\), and 100nm – 1µm which means it is not mesoporous but rather microporous.

The EDS shows the qualitative results in Figures 35 to 37 to have the chemical composition of C, Ca, O, K and Si. The gold peak is not flagged simply because this peak is due to the gold spluttering needed to ionise/coat the surface with an electrically conductive layer required for the operation of the microscope. Potassium is also known to have carbonate forms, so it is likely that this would also be contributing to CO\(_2\) losses.
5.2. Electrochemical Characterisation

The cyclic voltammetry test results in Figure 38 and 39 show the electrochemical and electrostatic activity in the form of current (mA) during voltage sweep ($E_{we}$). This was useful in determining the likely voltage range from the VRS used later in the cyclic capacity tests. Calcium oxide (CaO) in Figure 39 shows far greater activity in the negative region with extensive chemical activity displayed at $-0.65V$ (oxidation) and $-0.8V$ (reduction). Extended information of the cycling can be seen in Appendix F-1. The cyclic activity has shown that this process is reversible and stable. This reversibility seems to lend credibility to the idea that as CaO reacts with OH$, it leaves a hole and at the same time Na$ reacts with the oxide electrode. It may well be that this is reversible because the sodium ion is only slightly smaller than the calcium ion. The suggested reaction for CaO with the sodium hydroxide electrolyte: CaO + 2NaOH => Ca(OH)$_2$ + Na$_2$O (balanced)

The Galvanostatic results were most important for calculations to determine specific power, energy, capacitance and charge discharge stability. Rigorous tests will place the electrode under physical strain and test the active material as it would normally be used when produced for the market.

Samples were all tested and recorded at one voltage and one current value which is the voltage and current that provided reasonable charge to start cycling. Where currents are higher than others, this meant that the active material needed more charge to initialise the cycling process.

The samples that showed the best discharge capacity:

- Anode are CaCO$_3$ (Figure 40)
- Cathode are CaO (Figure 41)
- Both are CaCO$_3$ as their collective farad value after the 500$^{th}$ cycle is approximately $0.8 + 0.92 = 1.72$ F/g.

The Best discharge stability:

- Anode: CaCO$_3$ (Figure 40)
- Cathode: CaCO$_3$ (Figure 41)
The Least discharge stability:
- Cathode: CaO (Figure 41)

The Best cycle time stability:
- Anode: CaCO$_3$ (Figure 43)
- Cathode: CaCO$_3$ (Figure 42)

The Least cycle time stability:
- Anode: CaO (Figure 43)

The best cycle time electrode-pair is CaCO$_3$ (anode) and CaO (cathode) is seen in Figure 45.

The best Specific Power:
- Anode: CaCO$_3$ (Appendix B-3) of 450.37 W/kg
- Cathode: CaCO$_3$ (Appendix B-2) of 192.81 W/kg

The best Specific Energy:
- Anode: CaCO$_3$ (Appendix B-3) of 0.1251 Wh/kg
- Cathode: CaCO$_3$ (Appendix B-2) of 0.05356 Wh/kg
6. Summary

The furnace mass loss results were 3.4% difference of those calculated, and this was owing to the assumption of a homogenous calcite sample of CaCO₃.

TGA was useful in defining the decomposition of eggshell into components/phases such that further characterisation of the eggshell’s morphology is made possible. The %wt. in TGA of eggshell was not verified, yet this was calculated manually to determine by atomic weight losses if a successful percentage of decomposition was conducted as was confirmed in the furnace results.

The XRD analysis was instrumental in determining the desired phase shift from the precursor eggshell and served to identify each phase as synthetic calcite (41°C), calcite (600°C) and lime (950°C). The XRD diffractograms affirmed the experimental process qualitatively through graphical representations of the three samples by comparing them with similar digitally archived species.

The physical characterisation of eggshell shows it is naturally doped and eligible as a supercapacitor for energy storage in its crystalline state of calcite as shown in journals and from the EDS results in Figures 35 to 37. The EDS results also show significant amounts of other dopant metal species, where dopants are primarily added to increase efficiencies for optimisation purposes. The contribution of natural dopants in this thesis is therefore unknown and thus not conclusive. A simple method would be to use an ‘experiment control’ as a suitable reference for comparison. By using synthetic CaCO₃ and CaO as the ‘control’ it is possible to test these samples through cyclic voltammetry to qualitatively infer the usefulness of the naturally occurring dopants. One sustainable solution for eggshell could be the use of Ca to dope the existing Li active material in LTO [20].

A possible by-product of supercapacitors is hydrogen H₂ as this can be a valuable resource for fuel cells [8] especially if such a system is designed as a multi-stage process making viability and sustainability possible not to mention the low impact on the environment and move towards a carbon neutral position. For low-temperature fuel cells, Hydrogen gas is the preferred fuel source while hydrogen as an energy resource is not readily available [8]. Eggshell shows mechanical stability when overcharged and could point to more sustainable and renewable benefit in producing the by-product of H₂.
The galvanostatic cycling shows CaCO$_3$ as the most stable state, yet further cycling (1000s) is suggested to confirm the stability since after 500 cycles, since the samples are still transient. Two possible matches show some promise for the eggshell as supercapacitor.

In the additional ES#2-3, the external shell membrane was removed. This is a possible reason why the BET results from calcination were not as good as caged egg. That said, ES#1 results may have been largely influenced by the external membrane. These samples are not worthy of further consideration and cannot be compared with ES#1.

Figure 45 shows a possible match for the anode/cathode pair however, their cycling current was different. CaO (Figure 57, Appendix F-4) was charged at 1mA while CaCO$_3$ (Figure 55, Appendix F-3) was charged at 1.6mA. This means that CaO would charge quicker if a higher mA rate was used and thereby no longer a match for CaCO$_3$: 100%\((1-1nA/1.6mA) = 37.5\% \) loss. This loss can be matched by allowing the CaO cathode a 37.5% weight gain to match cycle time.

The most stable option would be to use CaCO$_3$ for both anode and cathode since CaCO$_3$ as cathode has 0.78F/g while CaCO$_3$ as Anode has 0.9F/g. CaCO$_3$ as cathode is still in transient stage and clearly shows a positive trend (Figure 56, Appendix F-3) towards 0.9F/g to match the CaCO$_3$ as anode. Specific Power and specific Energy is both the best results by CaCO$_3$ (600°C) as

- Cathode: 192.81 W/kg and 0.05356 Wh/kg
- Anode: 450.37 W/kg and 0.1251 Wh/kg

The Ragone plot in Figure 46 and 47 show CaCO$_3$ (600°C) as the eggshell sample that performs the best among all other thermally synthesised eggshell states. A possible reason for lower cathode values in the Ragone plot would be that power and energy are proportional to the voltage of 0.7V whereas for the anode plot, the voltage is -1V and gives a better energy performance value. Once the electrode-pair is tested together as a supercapacitor in the same electrolyte, the Ragone plot would have the best energy and power density representation.
7. Conclusion

Eggshell in its thermally synthesised state of CaO (950°C) has its best specific capacitance results of all other samples however, when considering the negative trend, the best option for stability is CaCO₃ (600°C) as the most suitable eggshell candidate for use as cathode in supercapacitors. CaCO₃ (600°C) furthermore produces the best power and energy density.

Not only does CaCO₃ show a positive trend as cathode, but its use as anode has shown an insignificant negative trend. The difference in farads means that CaCO₃ as cathode needs to improve its cycle time from 12s to 20s to match the cycle time of CaCO₃ as anode. This can be done by increasing the CaCO₃ active material mass by ~40% more than the anode.

The growing trend today is to find suitable complex nanostructures which increases the sample’s density and surface area which can prove to be expensive. The sustainable advantage of eggshell through this study shows that eggshell need not be synthesised at 950°C but would only require 600°C. The lower energy synthesis savings would lead to a reduction in activation energies and require much less energy required for oxidation states. In addition, eggshell could prove to have advantage of being naturally doped over other synthetic equivalents and throughout the tests as presented in the results, eggshell meets the requirement within its specific power and specific energy density as a supercapacitor.

This thesis has shown by physical and electrochemical characterisation through calcination of eggshell and thorough cyclic analysis, that eggshell is stable, sustainable and a renewable resource as electrode material for energy storage in supercapacitors. As a renewable resource, CaCO₃ maintains the sequestering of CO₂ the release of CO₂, as synthesised within the hen, which proves through eggshell analysis that CaCO₃ electrodes would support the renewable industry in energy storage capacity, lower the production of CO₂ and decrease the reliance on CO₂ producing fossil fuel.
Future Thesis Considerations

- Agglomeration characterisation through constant thermal energy rates could help define crystal phase shifts advantageous in pore sizes and optimised surface area.
- Extended electrochemical and physical characterisation using the same thermal decomposition methodology for the other two polymorphs of aragonite and vaterite.
- Explore different synthesis techniques without destruction of eggshell’s dopants.
- Doping of eggshell by mixing forms of lithium (Li) such as lithium carbonate produced from brines [31] could see a sustainable boost for both egg consumption and Li reserve depletion.
- The use of open source software OpenFOAM’s [32] and open source CFD toolbox [33] for modelling thermal decomposition would be advantageous to determine sample decomposition rates of various sample compositions and sizes.
- A complete analysis of the full composition and the molecular structure of eggshell, or at least the oxidised state of eggshell, calcium oxide.
- A comprehensive life cycle stability assessment of eggshell and its transitional forms that requires tens of thousands of cycles to test the active material and electrolyte pH for robustness and longevity.
- Feasibility study for domestic off-peak storage as well as a replacement for capacitor banks used by the electrical utilities for its reactive power component to assist in the stability of bus voltages.
- Eggshell as a suitable electrochemical battery for use in households for short term power storage to offset utility peaks with secondary function to produce hydrogen for fuel cells for either use in household energy production or fuel for a fuel cell electric vehicle (FCEV).
- Full electrochemical comparison between eggshell states and its matched synthetic equivalents.
8. References


# Appendix A: Specie Inventory

## Table 2: Specie Inventory

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*Note: Further details and explanations provided in the text.*
### Table 3: Calculation Methodology

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- **Active Material [g]**
  - V
  - A (constant)

- **Capacitance [F]**
  - Cycle
  - Discharge
  - Charge
  - 1: 0.01349444, 0.01670560

**Discharge-Charge of Voltage**

- **Voltage (V)**
  - 0

- **Time (s)**
  - 0 - 20

- **Energy (J)**
  - 0.007675

- **Energy (Ws)**
  - 0.454798

- **Specific Energy (Wh/kg)**
  - 0.128333

- **Specific Power (W/kg)**
  - 545.80

- **SUM check**
  - 949.76
### Table 4: Eggshell as Cathode (Power and Energy)

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<th>Discharge</th>
<th>% Difference</th>
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### Table 5: CAO as Cathode (Power and Energy)

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### Table 6: CaCO3 as Cathode (Power and Energy)

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### Appendix B-3: Anode Power and Energy Density Table

#### Eggshell as Anode (negative region)

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Specific Capacitance [F/kg]: 391.91
Energy [J/kg]: 0.00460
Energy (Ws/g): 0.19595
Specific Energy (Wh/kg): 0.05443
Specific Power (W/kg): 195.953

#### Calcium Carbonate as Anode (negative region)

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Specific Capacitance [F/kg]: 900.74
Energy [J/kg]: 0.00760
Energy (Ws/g): 0.45037
Specific Energy (Wh/kg): 0.12510
Specific Power (W/kg): 450.370

#### Calcium Oxide as Anode (negative region)

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Specific Capacitance [F/kg]: 679.94
Energy [J/kg]: 0.005941
Energy (Ws/g): 0.339971
Specific Energy (Wh/kg): 0.094436
Specific Power (W/kg): 339.971

---

**Table 7: Eggshell as Anode (Power and Energy)**

**Table 8: CaO as Anode (Power and Energy)**

**Table 9: CaO as Anode (Power and Energy)**
13. Appendix C: pH log and pH log-log plot Comparison

**Figure 48: Logarithmic pH Scale**

**Figure 49: pH log-log Plot (Basic)**
14. Appendix D: BET Adsorption-desorption 100 point Cycle
15. Appendix E: FESEM and SEM Sample Stubs
16. Appendix F-1: Cyclic Voltammetry Comprehensive Analysis

**Figure 51: CV Eggshell (~41°C) All Regions**

**Figure 50: CV CaCO3 (600°C) All Regions**

**Figure 49: CV CaO (950°C) All Regions**
17. Appendix F-2: Galvanostatic Cycling of Eggshell (\textasciitilde{41°C})

\textbf{Figure 53:} Eggshell CD Stability Positive Region (1.0mA, 0 to 0.7V)

\textbf{Figure 52:} Eggshell CD Stability Negative Region (1.6mA, 0 to -1V)
18. Appendix F-3: Galvanostatic Cycling of CaCO$_3$ (600°C)

**Figure 54:** CaCO$_3$ CD Stability Negative Region (1.6mA, 0 to -1V)

**Figure 55:** CaCO$_3$ CD Stability Positive Region (1.6mA, 0 to 0.7V)
19. **Appendix F-4: Galvanostatic Cycling of CaO (950°C)**

- **Figure 56**: CAO Cd Stability Positive Region (1mA, 0 to 0.6V)
- **Figure 57**: CAO Cd Stability Negative Region (2.6mA, 0 to -1V)
Appendix G: WEC Trilemma Index

UNITED STATES

TRILEMMA INDEX RANKINGS AND BALANCE SCORE

<table>
<thead>
<tr>
<th>RANK</th>
<th>Score</th>
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<th>2016</th>
<th>2017</th>
<th>Trend</th>
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| Energy performance | 11 | 4 | 8 | ▶ | A |
| Energy security    | 15 | 13 | 24 | ▶ | A |
| Environmental sustainability | 80 | 73 | 75 | ▶ | C |

TRENDS AND OUTLOOK

- The United States drops by 1 place this year to rank 15. Whilst exhibiting strong performances in both energy security, where it ranks 6th globally, and energy equity, this is offset by a relatively weak score in terms of environmental sustainability. This results in a balance score of AAG.
- Due to advances in horizontal drilling and hydraulic fracturing, shale gas production has become economically viable in recent years. The Energy Information Administration (EIA) estimates that the country has more than 2,784 trillion cubic feet (tcf) of technically recoverable natural gas, including 2,013 tcf of proved reserves (the discovered, economically recoverable fraction of the original gas-in-place). Production of shale gas is expected to increase from a 2007 US total of 1.4 tcf to 4.8 tcf in 2020. The significant increases in domestic oil and gas production will greatly reduce oil imports over the next 10 years, and lead to increased exports of refined products and possibly natural gas.
- The recent decision by the Trump administration to withdraw from the Paris Agreement has added uncertainty to the US energy sector. Nevertheless, commitment among Americans remains high in supporting renewables development, with some cities pledging to stick by earlier commitments to target emissions decreases and increase shares of renewables.

ZIMBABWE

TRILEMMA INDEX RANKINGS AND BALANCE SCORE

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<th>RANK</th>
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<th>Trend</th>
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</table>

| Energy performance | 50 | 27 | 60 | ▶ | B |
| Energy security    | 120 | 120 | 121 | ▶ | D |
| Environmental sustainability | 109 | 109 | 105 | ▶ | D |

TRENDS AND OUTLOOK

- Zimbabwe drops 7 places in this year’s index to rank 120. Whilst exhibiting a good performance in the energy security dimension, energy equity and environmental sustainability scores remain low, resulting in a balance score of BDD.
- Over the past few years, Zimbabwe has made continued efforts to improve its energy security, energy access and environmental footprint. The installation of a 100 MW project and increased energy imports have resulted in improved energy security and reliability, with tangible impacts for consumers. Since December 2015 there has been any load shedding in Zimbabwe. Energy equity is addressed through the rural energy master plan, which is being implemented. Moreover, after signing the Paris Agreement, the government has committed to reducing the country’s carbon footprint by 30% by 2020. This has already seen a marked shift of power projects to hydro and solar, which is expected to improve the country’s environmental sustainability in the future. In addition, the use of biofuels is further promoted, with an increase in the blending ratio from 15% today to 20% by 2018.
- Additional policy developments include: establishment of an independent energy regulator; amendment of the Electricity Act to promote energy efficiency in the public utility; promotion of public-private partnerships to spur development in the petroleum and power sector and the adoption of a long-term, government-driven renewable energy technologies programme.