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Research article

Range-extending Zinc-air battery for electric vehicle

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Abstract: A vehicle model is used to evaluate a novel powertrain that is comprised of a dual energy storage system (Dual ESS). The system includes two battery packs with different chemistries and the necessary electronic controls to facilitate their coordination and optimization. Here, a lithium-ion battery pack is used as the primary pack and a Zinc-air battery as the secondary or range-extending pack. Zinc-air batteries are usually considered unsuitable for use in vehicles due to their poor cycle life, but the model demonstrates the feasibility of this technology with an appropriate control strategy, with limited cycling of the range extender pack. The battery pack sizes and the battery control strategy are configured to optimize range, cost and longevity. In simulation the vehicle performance compares favourably to a similar vehicle with a single energy storage system (Single ESS) powertrain, travelling up to 75 km further under test conditions. The simulation demonstrates that the Zinc-air battery pack need only cycle 100 times to enjoy a ten-year lifespan. The Zinc-air battery model is based on leading Zinc-air battery research from literature, with some assumptions regarding achievable improvements. Having such a model clarifies the performance requirements of Zinc-air cells and improves the research community's ability to set performance targets for Zinc-air cells.

Keywords: range extender; Zinc-air battery; dual energy storage system; vehicle model; metal-air battery; single energy storage system; driving profile; vehicle use pattern

Abbreviations: BEV: battery electric vehicle; DOE: Department of Energy; EA: electrical accessory; ESS: energy storage system; EV: electric vehicle; FD: final drive; GHG: greenhouse gas; GM: general motors; HEV: hybrid electric vehicle; HWFET: highway fuel economy test; ICE: internal combustion engine; Li-Ion: lithium-ion; MSRP: manufacturer’s suggested retail price; PC: power converter; PC2: power converter 2; PHEV: plug-in hybrid electric vehicle; SOC: state of charge;

TC: torque coupling; UDDS: urban dynamometer driving schedule; UWAFT: University of Waterloo Alternative Fuels Team; VPA: vehicle propulsion architecture; VPC: vehicle propulsion controller; Zn-Air: Zinc-air

1. Introduction

With global greenhouse gas (GHG) emissions rising and the harmful effects of anthropogenic climate change becoming more apparent, there is a need to reduce the use of CO_2-emitting fuels such as coal, oil and natural gas. GHG emissions from the transportation sector are substantial and growing, accounting for 14% of global emissions [1], 26% of US emissions [2] and 23% of Canada's emissions [3]. The market for electric vehicles (EVs) is developing rapidly and EVs have the potential to substantially reduce emissions from this sector. However, EVs have thus far failed to gain widespread commercial market penetration, accounting for only 1.1% of global car stock and even less of a share in Canada, at 0.59% [4]. The main technological barriers to EV market penetration are their limited driving range, long recharging times and high cost compared to conventional vehicles powered by internal combustion engines (ICE) [5]. These concerns arise due to the limitations of the lithium-ion battery technology used in most EVs. While a significant improvement in nickel-metal hydride batteries has been made, and they are used in a limited number of hybrid vehicles, lithium-ion (Li-Ion) batteries dominate for plug-in hybrid (PHEV) and battery electric vehicle applications (BEV). However, Li-Ion packs are still expensive and provide insufficient energy density to make EVs competitive in the passenger vehicle mass market at this time.

One highly anticipated battery technology for electric vehicles are metal-air batteries, particularly Zinc-air batteries. Zinc-air batteries have a zinc anode and an air cathode; consequentially the battery has a very high theoretical energy density, several times higher than that of commercial lithium-ion batteries. Goldstein and coworkers and Toussaint and coworkers estimate Zinc-air batteries to be significantly cheaper than lithium-ion batteries [6,7], because they are easier to manufacture and are made from more common and less costly materials; the low price of the commercially available rechargeable Zinc-air battery from Eos Energy Storage validates these estimates [8]. They are also safer due to Zinc's lower reactivity compared to lithium, which allows the use of non-flammable electrolytes. However, Zinc-air batteries have not been used in commercial EVs because of their low power density and limited cycle life [9], which are key requirements for EV batteries.

Some have proposed novel vehicle architectures in order to overcome the limitations of current EVs. Bockstette and coworkers [10] modelled a two-battery vehicle architecture with a high energy, low power battery charging a high power, low energy battery, which in turn matches the power demand from the vehicle. They showed how this configuration reduced the combined cost and weight of the battery packs while meeting power and energy performance targets. Tesla Inc. has patented a control strategy for a similar architecture [11]. The patent describes a secondary metal-air battery which works in tandem with a primary battery to power the vehicle while avoiding lifetime limiting discharges on the metal-air battery. Catton and coworkers [12] modelled several vehicles with range extenders, including one with a Zinc-air battery pack range extender. The vehicle outperformed a regular battery electric vehicle (BEV) on range, cost and efficiency.

In this work the efficacy of a dual energy storage system (Dual ESS) is evaluated using a full vehicle model. The Dual ESS vehicle employs a small lithium-ion battery pack as the vehicle's primary power source and a large Zinc-air battery pack as a reserve energy source or range extender. Since rechargeable Zinc-air cells for vehicles are not yet commercially available, the Zinc-air battery pack is modelled based on leading literature on Zinc-air batteries with conservative assumptions regarding future improvements to the technology. The vehicle model provides a means to study both the Dual ESS structure and the performance of Zinc-air batteries in an automotive application.

2. Zinc-air batteries

Metal-air batteries have attracted widespread interest for their use in electric vehicles, mainly because of their high energy density but also because they are expected to be lower cost per unit energy than existing lithium-ion battery technology. However, metal-air batteries suffer from some drawbacks, the foremost of which is their limited cycle life. Metal-air anodes have generally not been reported to cycle more than 50–100 times at deep discharge before failure (though a few have demonstrated longer life under highly favourable circumstances), and some anodes such as aluminum have demonstrated even lower cycle life [13,14]. Metal-air batteries also suffer from low power densities due to their low voltages and low current densities, have high self-discharge rates and suffer from unwanted side reactions [13]. Also, because metal-air batteries are expected to take in oxygen from the air, CO_2 and water contamination are issues in some metal air batteries [13].

Of the available anode materials lithium, aluminum and zinc have been the most thoroughly investigated. Lithium-air batteries have the highest energy density of any metal-air battery [13], and as such have undergone extensive investigation. However, the lithium-air chemistry faces numerous challenges including moisture sensitivity, poor rate capability and irreversible side reactions, resulting in low cycle life, safety hazards and low power density [13]. Due to the current challenges with lithium-air batteries, the commercial focus has shifted to other materials. Aluminum-air batteries have gained widespread interest in academia and in industry. The Israeli battery company Phinergy is marketing an aluminum-air battery for electric vehicles and has attracted interest from global auto manufacturers [15]. However, aluminum-air batteries are not electrically rechargeable [13]. In order to reuse or recharge them, they must be recycled at a processing plant [13]. Consequentially, a battery swapping scheme would be necessary to facilitate the use of these batteries in electric vehicles. Such schemes have been proposed, for example by Nixon [16].

Zinc-air battery technology has been the subject of considerable research. Primary Zinc-air batteries are already used in hearing aids and other mature commercial applications [17], and have also been proposed for metal-air powertrains by Goldstein and coworkers and by Catton and coworkers [8,12]. Zinc-air batteries are not as energy dense as lithium-air or aluminum-air batteries, nor as powerful. However, they are electrically rechargeable to a limited number of cycles and do not suffer from side reactions to the same extent as lithium-air batteries [13]. Water does not harm Zinc-air batteries, which typically have aqueous electrolytes (though the cell can dry or flood if the humidity of the incoming air is not controlled) [14]. Consequentially, Zinc-air batteries are good candidates for electric cars, particularly as range extenders.

Zinc-air batteries have a zinc anode, an inert cathode where oxygen reduction and evolution take place, a separator and an electrolyte, which is usually aqueous. During discharge, the zinc undergoes a two-step reaction to form zinc oxide, while oxygen is reduced at the cathode [9].

Negative electrode:

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^- \quad (1a)$$

$$Zn(OH)_4^{2-} \rightarrow H_2O + 2OH^- + ZnO \quad (1b)$$

Positive electrode:

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (2)$$

Overall reaction:

$$2Zn + O_2 \rightarrow 2ZnO \quad (3)$$

Parasitic reaction:

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \quad (4)$$

Zinc-air batteries have a number of limitations which have thus far prevented their commercial use in electric vehicles. Their greatest limitation has been their poor cycle life—particularly at the anode, which can suffer from dendrite formation, shape change and passivation [14]. When Zinc-air batteries are electrically recharged, the zinc forms dendrites on the anode surface due to non-uniform local current densities. These high-current areas attract the highly soluble Zinc-oxide reaction products from along the anode surface and cause them to plate on the anode as dendrites [9]. These dendrites frequently break off from the anode, resulting in a loss of battery capacity. The dendrites can also cause cells to short circuit if they form a contact between the two electrodes [9], leading to cell failure and creating safety hazards. Researchers have tried to alleviate dendrite formation using different methods. Vatasalarni and coworkers coated their porous zinc electrode with polyaniline; the electrode exhibited a uniform morphology after 100 cycles and improved capacity over an uncoated electrode [18]. Lee CW and coworkers alloyed zinc with nickel and indium; their anode also showed reversibility after 100 cycles [19]. Parker and coworkers designed a porous anode which would trap the zinc oxide, with the result that during recharge operation the zinc would plate inside the pores [20]. They successfully demonstrated 45 charge-discharge cycles with no morphology change.

Deficiencies at the air electrode have also contributed to short cycle life and have limited specific power and roundtrip energy efficiency. Oxygen reduction requires a triple phase boundary, where the electrode is in contact with both the gas phase and the electrolyte. The inability of air electrodes to maintain a large triple phase boundary is a major impediment to high current density operation [9]. Researchers have investigated a wide range of catalysts, hoping they will prove more effective, more durable and cheaper than precious-metal catalysts. While some researchers have focused on unifunctional catalysts, a Zinc-air battery with unifunctional catalysts generally requires two air electrodes, one for charging and one for discharging. In order to preserve Zinc-air's specific energy and energy density advantages, researchers have increasingly investigated bifunctional catalysts. Jung and coworkers [21] showed that La_2NiO_4 layered perovskites significantly reduced voltage polarization, achieving a discharge voltage of 1.0 V even at 75 mA cm^{-2}. Lee D and coworkers have developed a novel bifunctional catalyst by growing Co_3O_4 nanowires directly onto a steel mesh [22]. A Zinc-air cell using this catalyst maintained a discharge voltage of 0.9 V at

17.6 mA cm^{-2}. The cell successfully demonstrated 1500 pulse cycles (5 minutes for each charge and each discharge) and 100 deep discharge cycles of 3 hours each.

In addition to limited cycle life and low power density, Zinc-air batteries suffer from other, less severe deficiencies. The introduction of air to the cell poses challenges, both because CO_2 can change the pH of the cell electrolyte and affect electrolyte conductivity, and because the cell can dry out or flood if the incoming air is not at the right humidification level [14]. These issues can be managed with an onboard air-management system, including a small CO_2 scrubber. The use of near-neutral electrolytes in Zinc-air cells has attracted interest as these electrolytes do not carbonize. Clark and coworkers developed a model for an aqueous $ZnCl_2$-NH_4Cl electrolyte [23], and Goh and coworkers demonstrated the satisfactory performance of a Zinc-air cell with a near-neutral electrolyte [24]. Eos Energy Storage uses a neutral electrolyte in their commercially available Zinc-air battery as well [25,26]. Gelling the electrolyte has been found to reduce water loss, and Mohamad found that using a 6 M KOH/gel electrolyte improved specific capacity to 657.5 mAh/g compared to a 2.8 M KOH/gel electrolyte [27]. Zinc-air batteries also have the potential for corrosion which results in the production of hydrogen gas. Several strategies have been undertaken in order to reduce zinc corrosion, including alloying with other metals (particularly indium and bismuth), surface coating with aluminum oxide or lithium boron oxide, and the use of chemical additives [9]. In spite of the potential for formation of hydrogen gas, Zinc-air batteries are considered safer than lithium-ion batteries due to the inherent reactivity of lithium, and the potential for lithium-ion batteries to suffer thermal runaway [28].

3. Vehicle powertrains

Commercially available electric vehicles fall into three categories: hybrid, plug-in hybrid and battery electric vehicles. Hybrid electric vehicles (HEV) are primarily powered by traditional internal combustion engines (ICE) but have small batteries able to power the vehicle at low speeds where engines are least efficient, and the battery pack also allows for regenerative braking to increase overall vehicle efficiency. The battery is charged by the engine rather than from an external source. Battery electric vehicles (BEV) have no ICE but rather a single large battery which powers the vehicle, and the batteries are recharged by plugging into a recharging station. At this time commercially available BEVs use lithium-ion batteries, which although better than any other commercially available battery technology are still costly and insufficiently energy dense to meet consumer demand for range and rapid recharging. Consequentially BEVs suffer from short driving ranges and high costs. Plug-in hybrid electric vehicles (PHEV) have powerful, moderately sized batteries as well as small ICEs. They differ from HEVs in that their batteries are powerful enough and large enough to power the vehicle independently for short to medium distances, even at high speeds, and can be charged by plugging the battery into an external outlet. Thus PHEVs have some charge depletion range. Compared to BEVs they are less costly due to the smaller battery and have greater driving range and the ability to quickly refuel due to the presence of the ICE. The ICE effectively acts as a backup power source or 'range extender' energy storage system (ESS) for the vehicle.

Hybrid powertrains employ variations on a few main architecture types, known as series, parallel and series-parallel split. PHEVs typically employ a series architecture (Figure 1a) due to its simplicity and because it allows the primary energy source to operate independently of the backup energy source. BEV architectures are simpler due to their having only one energy source (Figure 1b).

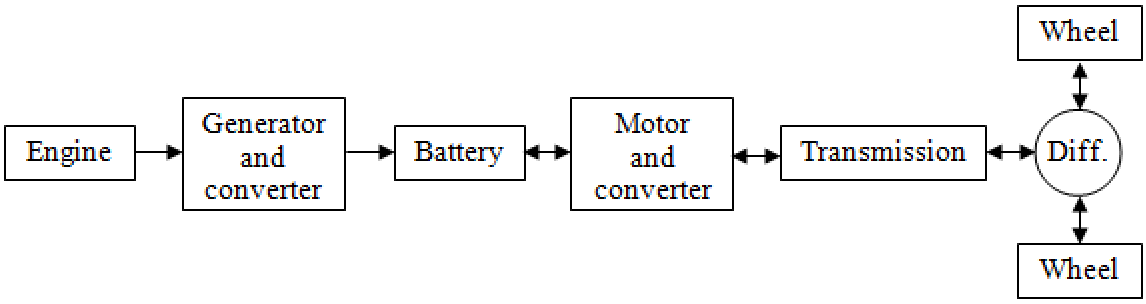

Figure 1a. A series hybrid vehicle architecture commonly employed by PHEVs.

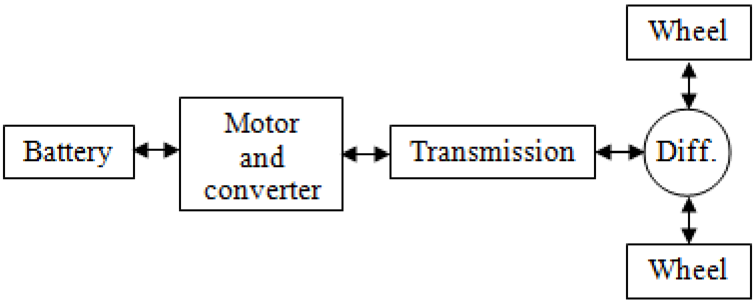

Figure 1b. The architecture of a traditional BEV.

Two vehicle architectures are modelled in this work. The vehicle of interest is the Dual ESS vehicle, which utilizes the PHEV series powertrain configuration except that the engine is replaced with a Zinc-air battery and the generator is replaced with a power converter. The other vehicle is the Single ESS vehicle, which utilizes the BEV powertrain with a large lithium-ion battery. The Single ESS vehicle is used to benchmark the performance of the Dual ESS vehicle. There is a recognition that the Dual ESS can achieve a power boost from a parallel configuration, and this will be explored in future works.

4. Model summary

4.1. Autonomie vehicle models

In order to study the Dual ESS architecture, two vehicle models were created in Autonomie, a vehicle modelling program developed by Argonne National Labs [29]. Autonomie functions by modelling the performance of individual vehicle components in response to the demands placed on the vehicle by the driver. The software feeds the speed and acceleration targets to the model, and the model calculates the performance of the individual components in response to those demands. Figure 2 shows the graphical user interface for the Dual ESS vehicle model.

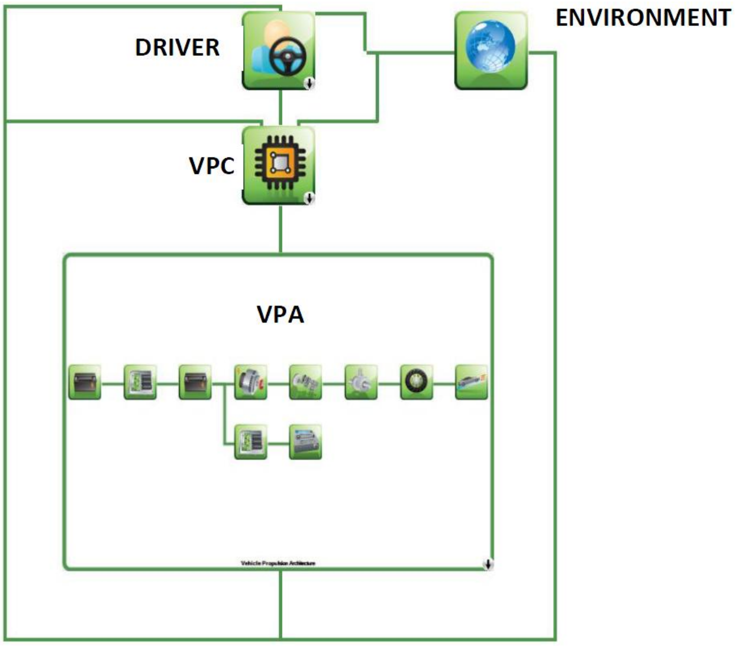

Figure 2. The graphic user interface of autonomie shows how the different components of the Dual ESS vehicle model are connected.

Each model contains four main blocks: the driver, the environment, the vehicle propulsion controller (VPC) and the vehicle propulsion architecture (VPA). The VPA and the VPC receive acceleration-related inputs from the driver block (e.g., target speed, road gradient), while the environment block specifies such inputs as wind speed and temperature. Based on those inputs, the VPC will set the vehicle's mode of operation, which changes the way certain components of the VPA are controlled. Based on all these inputs, Autonomie will calculate the performance required of each component in order to meet target speed and acceleration.

The VPAs of the Dual ESS vehicle and the Single ESS vehicle are shown in Figures 3a and 3b, respectively. Each block models a particular vehicle component. The far-right block contains the vehicle chassis model; the next blocks from right to left represent the wheels, the final drive (FD), the torque coupling (TC) and the motor. To the left of the motor is the block containing the lithium-ion battery model, which provides power to the motor and also to the electrical accessories (EA) through a power converter (PC2). In the Dual ESS VPA, the lithium-ion battery can in turn be charged by the Zinc-air battery (far left block) through a power converter (PC).

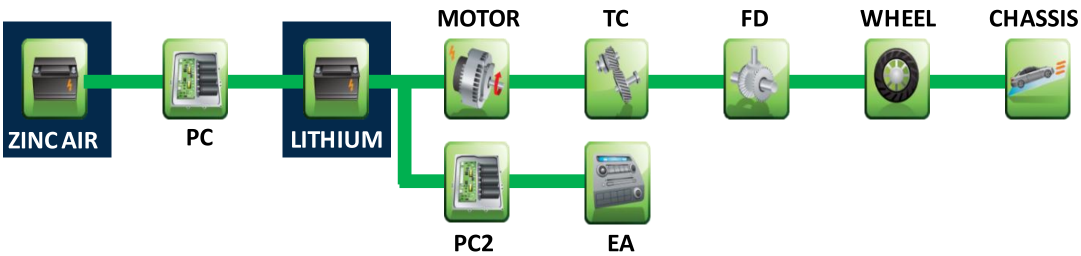

Figure 3a. Dual ESS vehicle propulsion architecture.

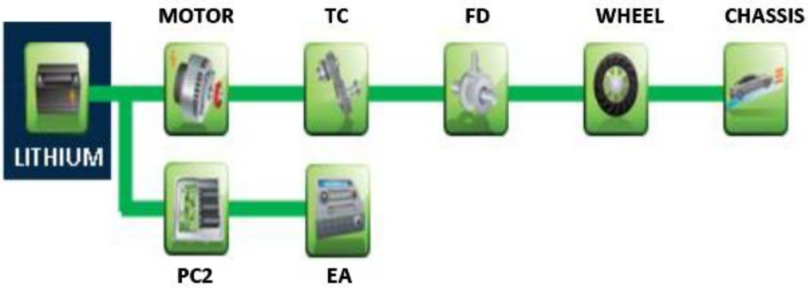

Figure 3b. Single ESS vehicle propulsion architecture.

4.1.1. EcoCAR 3 competition

Both vehicle models are based on the designs of the University of Waterloo Alternative Fuels Team (UWAFT) for the EcoCAR 3 Competition. Sponsored by the U.S. Department of Energy (DOE) and General Motors (GM), the EcoCAR 3 Competition is a green-vehicle design competition with student teams from universities accross North America [30]. For their design UWAFT retrofited a 2016 Chevrolet Camaro to make it a PHEV, installing a battery and a motor but maintaining a backup ICE ethanol engine for extended range. Both powertrains considered in this work use a similar VPA except that the range extender is not an ICE, but a Zn-air battery. Shared components include the chassis which is based on the 2016 Chevrolet Camaro chassis; the 62 kW motor model from the UWAFT design vehicle and the power converters which are 92% efficient as in the UWAFT design vehicle. The lithium-ion battery model also uses the same A123 Li-Ion cells as in the UWAFT design, although the pack configuration is not the same. The only component that is not based on the UWAFT design is the Zinc-air range extender.

4.2. The lithium-ion battery model

The lithium-ion cell model is based on the 20 Ah prismatic cell manufactured by A123. A123 cells have graphite anodes and lithium iron phosphate (LFP) cathodes [31]. This makes them a safer and potentially lower cost chemistry than other lithium-ion cells, but also less energy dense and power dense [28]. This chemistry was selected because the cells were available for the actual vehicle prototyping, and UWAFT was already using them in their vehicle. The cell performance parameters are given in Table 1 below.

Table 1. Lithium-ion cell specifications used in the model [31,32].

Parameter	Unit	Value
Cell Weight	g	496
Cell Capacity	Ah	19.5
Nominal Voltage	V	3.3
Nominal Energy	Wh	65
Specific Energy	Wh/kg	131
Energy Density	Wh/L	247
Cycle Life (1C, 100% DOD)		7000

In order to model the cell's polarization curve a simple equivalent circuit model was used. An equivalent circuit model treats the cell as a series of resistors and capacitors. Such models are less computationally intensive than electrochemical models which attempt to model the internal dynamics of the cell. A modified version of the Rint model, which treats the cell as a simple resistor [33], is used as the basis of the lithium-ion cell model. The Rint model is modified to use two different resistors for charge and discharge. Figure 4 depicts the modified Rint model. The modified Rint model is used because A123 provided UWAFT with detailed resitance values for charge and discharge, indexed by state of charge and temperature. Resistance increases with decreasing SOC and with decreasing temperature for both charging and discharging. A more advanced equivalent circuit model might adequately model the cell as well, but the data for such a model was unavailable. Figure 5 depicts the discharge curves of the A123 cells [34].

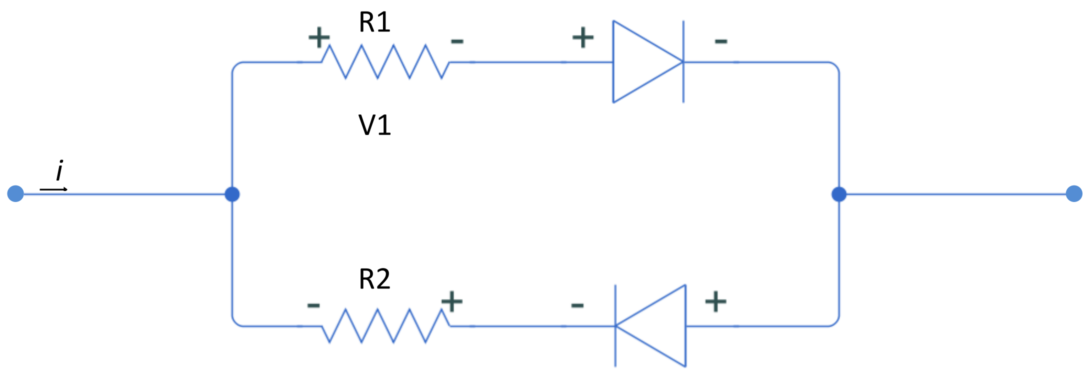

Figure 4. The modified Rint model.

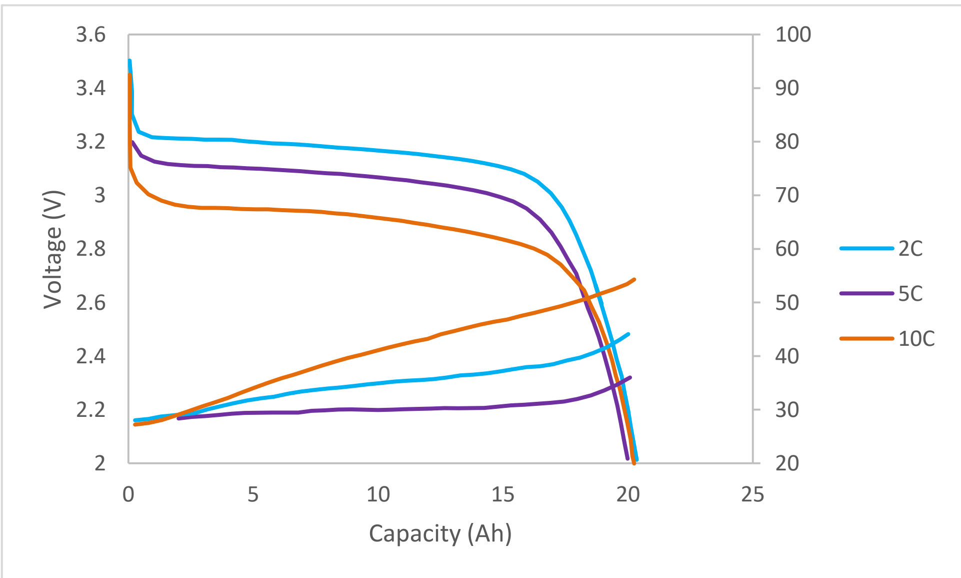

Figure 5a. A123 20 Ah cell discharge curve at various C-rates (data from [34]).

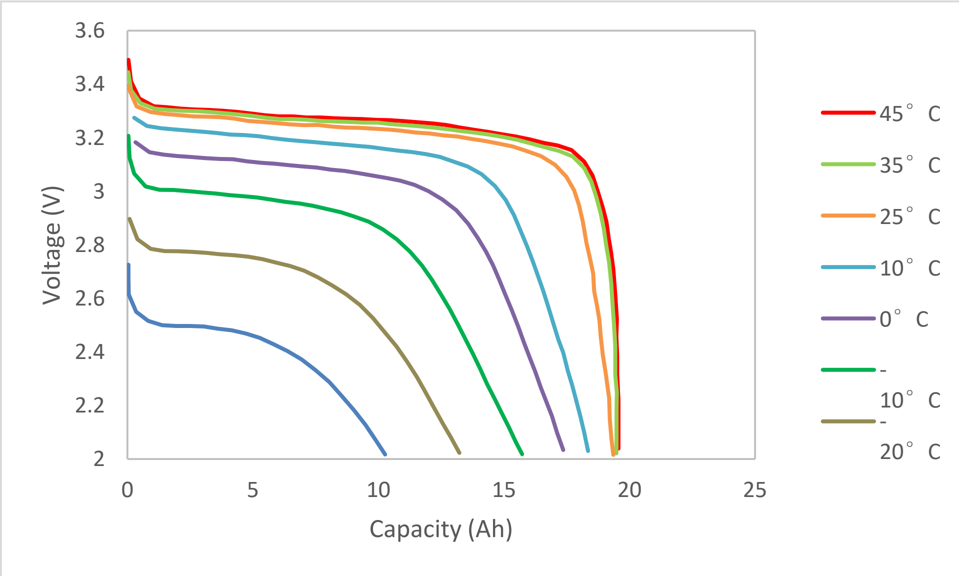

Figure 5b. A123 20 Ah cell discharge curve at 1C at various temperatures (data from [34]).

For both vehicles, the lithium-ion battery pack is comprised of modules each containing 15 individual cells connected in series. These modules are connected in series to form arrays, and the arrays are connected in parallel to form the pack. In the configuration of the current battery pack in the UWAFT EcoCar3 vehicle (of similar size and configuration) the pack is found to be 25% heavier than the combined weight of the cells due to the additional component, packaging and vehicle mount weights. This is factored into the model as a packaging factor. Because A123 cells have extremely good cycle life and because they operate better than other cells at high and low states of charge (SOC) [31] the cells have been set to operate between 100%–5% SOC in the simulation. The battery pack is estimated to cost $230/kWh, based on an average of the market-leading lithium-ion battery pack costs [35]. The effect of capacity fade on vehicle range is ignored for simplicity, but this effect should be incorporated into future work.

4.3. The Zinc-air battery model

Autonomie currently has no model for a Zinc-air battery pack; the potential to incoporate this technology into a vehicle is too recent an innovation. Three different studies were drawn upon in order to create the Zinc-air cell model in Autonomie. Eckl and coworkers [36] describe a mechanically rechargeable Zinc-air cell weighing 349 g, and having a volume of 167 cm^3, with a single zinc electrode sandwiched between two air electrodes. Both air electrodes are used for discharging and charging, rather than one being used for discharging and the other for charging. Because the cell was designed for practical use the cell volume and the mass of the non-active components were taken to be representative of that of a commercial Zinc-air cell. However, because the cell was not demonstrated to be electrically rechargeable other literature data were used to model the cell's electrochemical performance.

Parker and coworkers [20] tested a sponge-like Zinc-air anode, designed to increase cycle life and zinc utilization. Because the anode is specifically designed to be recharged, performs reasonably well under exacting conditions and has a practical thickness and mechanical strength, Parker's anode is used in the Zinc-air battery model. Parker's anode has a specific capacity of 694 mAh/g_{Zn}, a mass density of 1.29 g cm^{-3} and a thickness of 1–4 mm. The model assumes a thickness of 4 mm. Because Eckl's paper breaks down the cell mass by component, the mass of zinc in the cell is changed to reflect the new anode structure. In this work a cycle life of 150–200 cycles to 85% depth of discharge is assumed, which is a modest assumed improvement over the performance demonstrated by Parker. As with the lithium-ion battery, capacity fade is not modelled for the Zinc-air battery. Future work would be well served by modelling this effect.

The air electrode and catalyst described by Lee D and coworkers forms the basis of the air cathode. In the referenced work the electrode is made by growing Co_3O_4 nanowires directly onto a stainless steel mesh, which is placed against a commercial gas diffusion layer [22]. The polarization curve generated in Lee's study forms the basis of the model's polarization curve. However, the polarization curve reported in Lee's study is based on a much larger inter-electrode distance than in the model. Consequentially the polarization curve is adjusted to match the inter-electrode distance modelled in this study. The model's electrolyte is also based on the electrolyte used in Lee's study—6 M KOH—but is also saturated with ZnO so that ZnO formed during anode discharge would have reduced solubility and improved reversability [37].

The discharge polarization curve reported by Lee D and coworkers [22] was modelled per Equation 5; voltage losses were modelled as a combination of activation polarization (using Butler-Volmer kinetics) and Ohmic (solution and interfacial) resistance loss. The original solution resistance was reported by Lee D and coworkers as 1.76 **Ω** (obtained via equivalent circuit modelling of impedance measurements), and was multiplied by their electrode area (2.835 cm^2) to obtain the original R_s value of 4.99 **Ω** cm^2 used in this model. After obtaining values for the V_{OC}, α, i_o and R_{int} parameters through least squares fitting, a new discharge curve was modelled using a modified R_s value. $R_{s,mod}$ was calculated according to Eq 6, which reflected the cell geometry used in the present investigation. Parameter definitions and values are listed in Table 2. The new discharge polarization curve is shown in Figure 6. Due to the relative voltage stability of Zinc-air cells within the prescribed SOC range (15–100%), the effect of SOC on the model has been ignored.

$$V_{operating} = V_{OC} - \frac{RT}{\alpha F}\ln\left(\frac{i}{i_o}\right) - i(R_s + R_{int}) \quad (5)$$

$$R_{s,mod} = \frac{\frac{t_{Zn,avg}}{\varphi_{Zn}} + \frac{t_s}{\varphi_s}}{\sigma} \quad \mathbf{(6)}$$

The accuracy and sophistication of the Zinc-air cell model leaves room for improvement. A physics-based model of Zinc-air chemistry or an experiment-based model derrived directly from cell testing would serve equally well or better in some respects as the described model. The described model has the advantage of drawing on leading Zinc-air battery technology, however, whereas an experiment-based model derrives only from the best Zinc-air technology from a particular lab. A physics-based model would be acceptable but not necessarily appropriate as the purpose of analyzing Zinc-air performance within a vehicle model is to understand the potential of the technology rather than its internal mechanisms. A physics-based model might also be too computationally intensive for the vehicle model.

Table 2. Parameters for zinc air polarization curve model.

Parameter	Symbol	Unit	Modelled Value
Open circuit voltage	V_{OC}	V	1.4
Universal gas constant	R	J mol^{-1} K^{-1}	8.314
Temperature	T	K	298.15
Charge transfer coefficient	α	-	0.3209
Faraday constant	F	C mol^{-1}	96585
Exchange current density	i_o	A cm^{-2}	0.0002298
Solution resistance (original)	R_s	Ω cm^2	4.99
Interfacial resistance	R_{int}	Ω cm^2	0.604
Average zinc electrode thickness	$t_{Zn,avg}$	cm	0.2
Zinc electrode porosity	$φ_{Zn}$	-	78.5%
Separator thickness	t_s	cm	0.02
Separator porosity	$φ_s$	-	0.55
Electrolyte conductivity	σ	S cm^{-1}	0.6
Solution resistance (modified)	$R_{s,mod}$	Ω cm^2	0.458

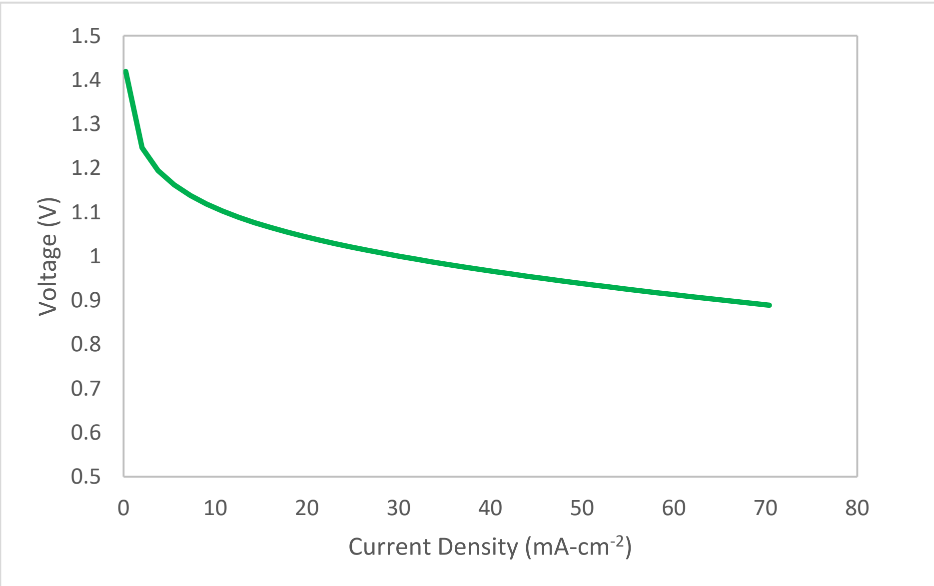

Figure 6. Discharge polarization curve of modelled Zinc-air cell.

By combining the results of the three studies and making reasonable adjustments, the Zinc-air battery model reflects the best anode and cathode performance with a realistic estimate of the total mass and volume of the Zinc-air battery pack. The cell parameters are listed in Table 3. A packaging factor of 25% has been assumed to account for the weight of additional components. There are currently few reliable estimates of what a commercial rechargeable Zinc-air battery might cost. Eos Energy Storage has commercialized a Zinc-air battery which they have been selling for $160/kWh; they have recently dropped their price to $95/kWh for orders fulfilled in 2022 [8]. One paper estimated the cost of producing an iron-air battery at $59/kWh [38] and Electric Fuels Ltd (EFL) published a paper claiming a mechanically rechargeable Zinc-air battery would cost $60/kWh for a low-power pack (and $80/kWh for a high-power pack) [6]. Starting from the EFL price of $80/kWh and adjusting for inflation and different nominal voltage the Zinc-air battery pack cost is estimated to be around $121/kWh. Toussaint and coworkers estimate the cost of a mass-produced, rechargeable Zinc-air battery at €50–100/kWh, corresponding to $61–122/kWh [7]. Thus, the price range of the Zinc-air battery pack is likely between $61/kWh and $160/kWh. In this paper the Zinc-air battery price is taken to be $150/kWh, near the higher cost estimate.

Table 3. The Zinc-air cell specifications.

Parameter	Unit	Value
Cell Weight	g	218
Cell Capacity	Ah	39.4
Nominal Voltage	V	1.0
Nominal Energy	Wh	39
Specific Energy	Wh/kg	181
Energy Density	Wh/L	236

4.4. Dual ESS control logic

Figure 7 illustrates the control logic pertaining to when each battery in the Dual ESS vehicle is activated. When both batteries are fully charged, the Zinc-air battery is disconnected and the lithium-ion battery powers the vehicle independently. When the lithium-ion SOC reaches 20%, the Zinc-air battery is activated and starts charging the lithium-ion battery. If at any point the lithium-ion battery SOC increases to 25% the Zinc-air battery is deactivated until the lithium-ion SOC drops to 20% again. Maintaining the lithium-ion battery SOC between 20–25% ensures that the Zinc-air battery only activates if the lithium-ion battery is in danger of running out of charge, thus minimizing Zinc-air battery use and preserving its longevity. If the Zinc-air battery ever drops below its minimum SOC of 15% it shuts off and is unavailable until the car is plugged in and recharged. The car continues to run on the lithium-ion battery until the lithium-ion battery reaches its minimum SOC of 5%, at which point the car has completely charge depleted.

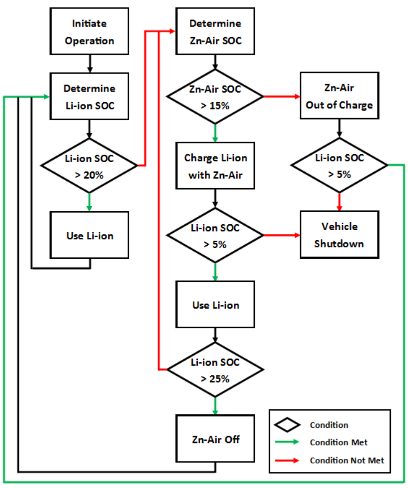

Figure 7. Dual ESS battery pack control logic.

4.5. Drive cycles

In order to test vehicle performance under typical conditions, the US Environmental Protection Agency tests vehicles using specific drive cycles which are representative of typical driving patterns. In this paper, only the two main drive cycles are used. The Urban Dynamometer Driving Schedule (UDDS) is typical of city driving patterns, while the Highway Fuel Economy Test (HWFET) is typical of highway driving patterns. For the purpose of calculating range, fuel economy, cycle life and other vehicle parameters, it is assumed that 55% of driving can be represented with the UDDS and the balance with the HWFET. This is in line with older EPA standard fuel economies, which took a weighted average (55%/45%) of the fuel economies under the two drive cycles [39].

4.6. Zinc-air battery longevity model

A key design consideration is the useful life of the Zinc-air battery pack. Zinc-air cells have a cycle life of only 150–200 cycles, yet must last many years of operation. In order to maximize the Zinc-air battery pack life the pack should be used only sparingly, and thus the basic novelty of this simulation. In this simulation the potential for a Zn-air pack to be used as a range extender over the life of a vehicle is demonstrated, as it can be employed in a limited charge-discharge mode. Data from the 2009 US National Household Transportation Survey (Figure 8) indicates that most US drivers drive only short- to medium-length distances each day. Consequentially a well-designed Dual ESS vehicle will have a lithium-ion battery pack large enough to power the car independently of the Zinc-air battery pack on most days. Taking the US NHTS results to be representative of a typical user's driving patterns, the Zinc-air battery pack's useful life can be estimated based on the frequency of the driver's long-distance trips.

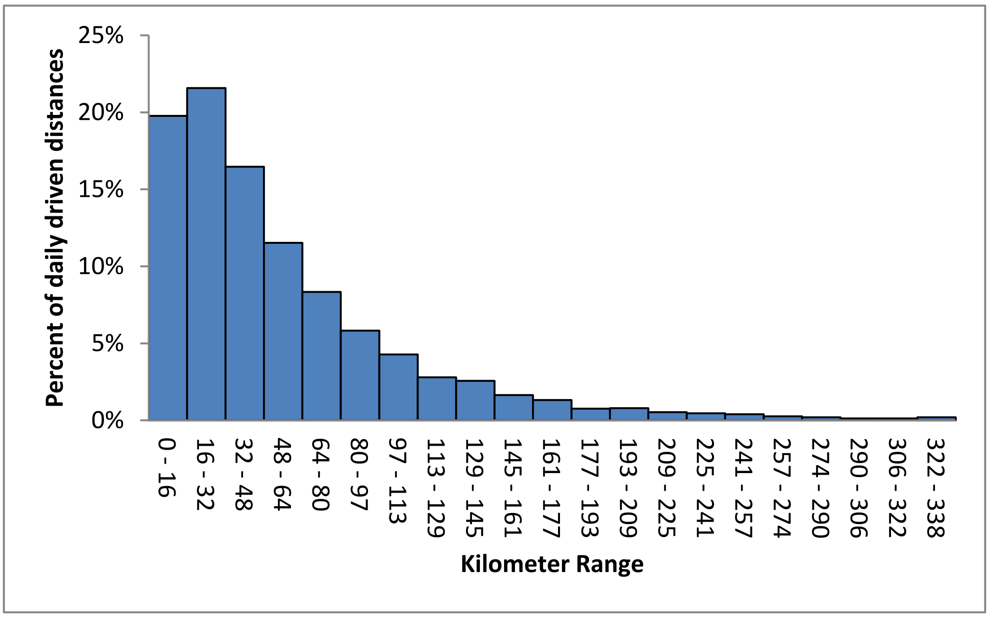

Figure 8. Summary of US driving patterns [40]. In this study, the typical US driver is assumed to have this driving pattern.

5. Results and discussion

5.1. Battery pack size optimization

Initially the Dual ESS vehicle was tested with 3, 5 and 7 lithium-ion module arrays and 6, 10 and 14 Zinc-air module arrays, for a total of nine battery pack configurations. These configurations were tested with UDDS and HWFET cycles and the results averaged, with a 55% weighting for UDDS results and a 45% weighting for HWFET results. Table 4 shows the key results.

Table 4. Dual ESS battery pack size first optimization.

ID[1]	Li-Ion Energy[2] [kWh]	Zn-air Energy[2] [kWh]	Total Energy[2] [kWh]	Range [km]	Battery Cost [USD]	Zn-air Battery Life[3] [yrs]	Li-Ion Fuel Economy[4] [km/kWh]	Zn-air Fuel Economy[5] [km/kWh]
Li3-Zn6	19	58	77	326	$14,921	7.2	3.83	2.27
Li5-Zn6	32	58	90	374	$18,060	15.9	3.75	2.20
Li7-Zn6	45	58	103	416	$21,198	33.3	3.62	2.11
Li3-Zn10	19	96	116	468	$21,731	10.3	3.46	2.28
Li5-Zn10	32	96	129	506	$24,869	21.4	3.43	2.21
Li7-Zn10	45	96	142	541	$28,007	42.0	3.41	2.13
Li3-Zn14	19	135	154	591	$28,540	12.4	3.22	2.21
Li5-Zn14	32	135	167	622	$31,678	25.1	2.95	2.14
Li7-Zn14	45	135	180	651	$34,817	47.5	2.87	2.08

[1] ID number denotes number of arrays in each pack e.g., Li3-Zn6 has 3 lithium-ion arrays and 6 Zinc-air arrays; [2] Usable energy i.e., based on minimum lithium-ion SOC of 5% and minimum Zinc-air SOC of 15%; [3] Based on 150 total cycles; [4] Vehicle fuel economy when powered by lithium-ion battery, Zinc-air battery off; [5] Vehicle fuel economy when powered by Zinc-air battery.

It should be noted here that the vehicle has lower fuel economy and higher overall battery pack costs as compared to commercial EVs. This is primarily because of the heavy Chevrolet Camaro vehicle base and the conservative battery pack design assumptions that have been made in this simulation for pack weight, as well as the high target range of 500 km which none but the most expensive vehicles are able to attain. The results are more meaningful in comparison to the Single ESS vehicle.

The preliminary results show that for each battery size combination except for Li3-Zn6 the Zinc-air battery lasts at least ten years. Interestingly, regardless of the Zinc-air battery pack size each successively larger lithium-ion battery pack roughly doubles the lifetime of the Zinc-air battery pack. This is the main value of vehicles with larger lithium-ion battery packs, which have shorter ranges compared to similarly-priced vehicles with larger Zinc-air batteries and smaller lithium-ion packs. For example, the Li7-Zn6 combination costs as much as the Li3-Zn10 combination, lasts 23 years longer but travels 50 km less on a single charge. Of course, such a long battery life adds relatively little value since most vehicles are not used for more than 15 years. The large lithium-ion battery simply increases the vehicle’s cost while failing to meet the vehicle’s range target of 500 km. Similarly, vehicles with 14 Zinc-air arrays have ranges greatly in excess of the target range but also extremely high battery pack costs. The Li3-Zn6 and Li5-Zn6 combinations are inexpensive but with comparatively low range, and in the Li3-Zn6 combination the Zinc-air battery pack lasts only 7.2 years. The most appropriate configurations are therefore the Li3-Zn10 and Li5-Zn10 combinations.

To determine more precisely the best battery pack combination, the Dual ESS vehicle was retested with 3, 4 and 5 lithium-ion arrays and 9, 10 and 11 Zinc-air arrays. Table 5 shows the key results.

Table 5. Dual ESS battery pack size second optimization.

ID[1]	Li-Ion Energy[2] [kWh]	Zn-air Energy[2] [kWh]	Total Energy[2] [kWh]	Range [km]	Battery Cost [USD]	Zn-air Battery Life[3] [yrs]	Li-Ion Fuel Economy[4] [km/kWh]	Zn-air Fuel Economy[5] [km/kWh]
Li3-Zn9	19	87	106	434	$20,028	9.6	3.59	2.29
Li4-Zn9	26	87	113	456	$21,598	14.1	3.53	2.26
Li5-Zn9	32	87	119	475	$23,167	20.5	3.51	2.22
Li3-Zn10	19	96	116	468	$21,731	10.3	3.46	2.28
Li4-Zn10	26	96	122	487	$23,300	15.0	3.47	2.25
Li5-Zn10	32	96	129	506	$24,869	21.4	3.43	2.21
Li3-Zn11	19	106	126	502	$23,433	10.8	3.41	2.28
Li4-Zn11	26	106	132	519	$25,002	15.8	3.42	2.24
Li5-Zn11	32	106	139	537	$26,571	22.5	3.38	2.20

[1] ID number denotes number of arrays in each pack e.g., Li3-Zn6 has 3 lithium-ion arrays and 6 Zinc-air arrays; [2] Usable energy i.e., based on minimum lithium-ion SOC of 5% and minimum Zinc-air SOC of 15%; [3] Based on 150 total cycles; [4] Vehicle fuel economy when powered by lithium-ion battery, Zinc-air battery off; [5] Vehicle fuel economy when powered by Zinc-air battery.

Several of these battery pack combinations offer good performance. In particular, the Li4-Zn9, Li3-Zn10, Li4-Zn10 and Li3-Zn11 configurations are similarly priced, offer good Zinc-air battery life and long range. Although all these configurations could be considered the most suitable, the Li4-Zn10 combination is selected because it essentially meets the target range of 500 km and because the excess Zinc-air battery life would make the vehicle more appealing to drivers worried about having to carefully manage the Zinc-air battery so as not to overuse it.

The CO_2 scrubber for the Zinc-air battery is sized to cover a year of use by the battery. The scrubber was sized per Eq 7, and the amount of water necessary for humidification per Eq 8. Table 6 details the parameter values. Humidification is necessary because the adsorbent, LiOH-Ca(OH)$_2$, performs vastly better at high humidification levels [41]. The adsorption coefficient of LiOH-Ca(OH)$_2$ is taken to be 313.5 mg CO_2/g$_{adsorbent}$ [41], based on an average of repeated tests. Based on ten cycles a year and a 30% buffer, the CO_2 scrubber should contain 3.7 kg of adsorbent and 49.6 kg of water. This weight is negligible compared to the weight of the vehicle.

$$m_{ads} = \left(\left[\frac{m_{Zn}\times(SOC_{max}-SOC_{min})}{mm_{zn}} \times \left(\frac{n_{O2}}{n_{zn}}\right) \times \left(\frac{n_{air}}{n_{O2}}\right) \times C_{CO2} \times mm_{CO2}\right] \div K_{100}\right) \times N \times (1+B) \quad (7)$$

$$m_{H2O} = \left[\frac{m_{Zn}\times(SOC_{max}-SOC_{min})}{mm_{zn}} \times \left(\frac{n_{O2}}{n_{zn}}\right) \times \frac{P_{vap}}{0.21P_{atm}} \times mm_{H2O}\right] \times N \times (1+B) \quad (8)$$

Table 6. Parameters and numerical data for CO_2 scrubber sizing.

Parameter	Symbol	Unit	Modelled Value
Mass of adsorbent	m_{ads}	kg	3.7
Mass of water	mH_2O	kg	49.6
Mass of zinc in battery pack	mz_n	kg	163.4
Maximum SOC of ZnAir pack	SOC_{max}	-	100%
Minimum SOC of ZnAir pack	SOC_{min}	-	15%
Molar mass of zinc	mmz_n	kg/kmol	65.4
Ratio of reacting oxygen to reacting zinc	(nO_2/nz_n)	-	0.5
Ratio of moles of air to moles of oxygen in the air	(n_{air}/nO_2)	-	4.76
Concentration of CO_2 in the air	CCO_2	ppm	400
Vapour pressure of water (at 30 ℃)	P_{vap}	kPa	4.25
Atmospheric pressure	P	kPa	101.325
Molar mass of CO_2	$mmCO_2$	kg/kmol	44
Molar mass of water	mmH_2O	kg/kmol	18
Adsorption capacity of adsorbent	K_{100}	$mgCO_2/g_{adsorbent}$	313.5
Number of Zinc-air cycles per year	N	-	10
Buffer	B	-	30%

The zinc air battery pack lifetime is worth analyzing in more detail, since it is highly dependent on the user's driving patterns and the cycle life of the Zinc-air battery. In Figure 9 the Zinc-air battery cycle needed to last ten years (based on the driver profile outlined in Figure 8) is plotted as a function of the number of lithium-ion arrays.

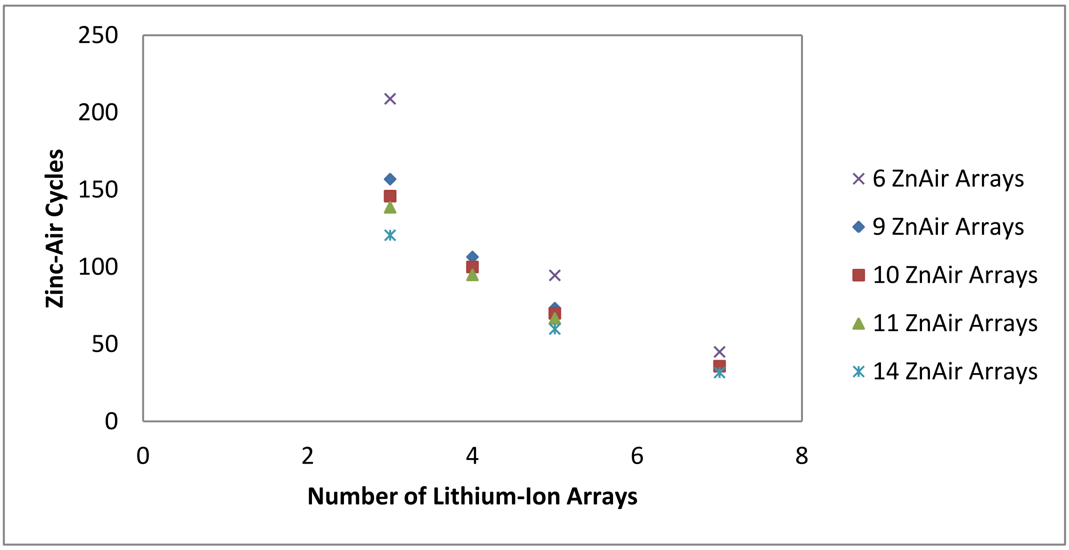

Figure 9. Number of Zinc-air cycles needed for ten years of operation.

The Zinc-air cycle life required to reach ten years of use reduces by roughly 30% for each additional lithium-ion array (6.5 kWh) included in the powertrain, and this remains true regardless of Zinc-air battery pack size. This reduction occurs because larger lithium-ion battery packs reduce the percentage of trips where the Zinc-air battery pack is required and because it reduces the use of the Zinc-air battery even on longer trips.

In this investigation a cycle life of 150 cycles has been assumed, but based on the results in Figure 9 clearly even 150 cycles are excessive with a large enough Li-Ion battery pack. Parker and coworkers have demonstrated 45 charge-discharge cycles [20] which would be enough to sustain the Zinc-air battery for ten years if the vehicle's lithium-ion battery pack comprises 7 arrays (48 kWh). Having a 4-array lithium-ion battery pack (27 kWh) means the Zinc-air battery can be sustained for ten years with a cycle life of only 100 cycles. This clearly demonstrates the viability of low-cycle life battery range extenders in vehicles when used as a secondary energy source (although only when the vehicle owner mainly drives short-to-moderate distances most of the year). Conversely, a greater Zinc-air cycle life reduces the size of the lithium-ion battery required. A Zinc-air battery with a cycle life of 300 cycles might last ten years even if the lithium-ion battery had only two arrays (14 kWh). A vehicle with such a configuration would have greater safety and lower cost due to the reduced lithium-ion battery size, which demonstrates the value of modest Zinc-air battery cycle life improvements. However, it is important to note that Zinc-air cells have not yet achieved the cycling performance assumed in this investigation. The Dual ESS battery pack was cycled at up to 40 mA cm^{-2} and the cycle life was taken to be 150 cycles, whereas Parker's anode achieved only 45 cycles at 24 mA cm^{-2} [20] and D. Lee's cathode was cycled at 18 mA cm^{-2}, though higher current densities were achieved [22].

5.2. Performance comparison between Dual ESS and Single ESS

The Single ESS vehicle was designed with no Zinc-air battery but instead with a large lithium-ion battery pack comprising 15 arrays and having a nominal energy of 102 kWh. Table 7 compares the battery packs of each vehicle. Table 8 compares the Single ESS and Dual ESS vehicles on performance-related measures.

Table 7. Battery pack specifications for the Dual ESS and Single ESS vehicles.

Parameter	Unit	Dual ESS-Lithium-Ion pack	Dual ESS-Zinc-air pack	Single ESS-Lithium-Ion pack
Cells per module	-	15	4	15
Modules in series	-	7	72	7
Arrays in parallel	-	4	10	15
Total cell weight	kg	208	627	781
Packaging factor	-	1.25	1.25	1.25
Pack weight	kg	260	784	977
Nominal pack voltage	V	347	288	347
Pack capacity	Ah	78	394	294
Pack energy	kWh	27	113	102
Maximum SOC	-	100%	100%	100%
Minimum SOC	-	5%	15%	5%
Pack cost	USD	$6,277	$17,023	$23,538

Table 8. Performance summary of the Dual ESS and Single ESS vehicles.

Properties	Unit	Dual ESS	Single ESS
Vehicle Weight	kg	2721	2651
Range-UDDS	km	459	383
Range-HWFET	km	521	449
Fuel Economy-UDDS	km/kWh	3.20[1]/2.13[2]	3.35
Fuel Economy-HWFET	km/kWh	3.80[1]/2.40[2]	3.93
Battery Pack Cost	USD	$23,300	$23,538

[1] Refers to the fuel economy when vehicle is powered by the Li-Ion battery, [2] Referes to the fuel economy when vehicle is powered by the Zn-Air battery.

There are several points of interest in the results. First, as previously indicated both vehicles achieve lower fuel economy and have higher battery pack costs as compared to commercial EVs due to the heavy vehicle base, conservative battery pack design and large battery packs. However, the vehicles also travel hundreds of kilometers further on a single charge than all but the most expensive EVs. The relevance of the results is in how the Dual ESS architecture compares to a similar vehicle with a Single ESS architecture. In that regard, the Dual ESS vehicle performs well, travelling 75 km further on a single charge compared to the Single ESS vehicle, which costs about the same. Although the vehicles have equal weight, the Dual ESS vehicle has more energy storage due to the Zinc-air battery's higher energy density. This higher energy content allows the Dual ESS vehicle to travel further than the Single ESS vehicle in spite of its low fuel economy. The Zinc-air fuel economy is lower than the lithium-ion fuel economies of both vehicles for a number of reasons. First, Zinc-air cells are much less efficient than lithium-ion cells due to their high levels of voltage polarization. The Zinc-air battery pack has a round-trip energy efficiency of 56–59% when charged with a Level 2 charger (6.6 kW), compared to an 85% round-trip energy efficiency for lithium-ion cells [28]. Second, the energy from the Zinc-air battery must pass through a power converter; 8% of the Zinc-air's energy is lost at this stage. Third, some of the energy from the Zinc-air battery is put towards charging the lithium-ion battery rather than directly powering the car. Lithium-ion batteries are highly efficient, but they still have efficiency loses due to their charge/discharge voltage separation. Thus, some energy is lost by having the Zinc-air battery power the vehicle through the lithium-ion battery. The Dual ESS vehicle is also less fuel efficient than the Single ESS vehicle when powered only by its lithium-ion battery. This is because the Dual ESS vehicle's lithium-ion battery is smaller than the Single ESS vehicle's and thus has to operate at a higher C-rate.

Figure 10 shows the energy of each battery of the Dual ESS vehicle during repeated HWFET cycles. The lithium-ion battery powers the vehicle independently until the lithium-ion SOC drops to 20%, at about the 98^{th} kilometer. At this point the Zinc-air battery starts charging the lithium-ion battery at a constant power rate, while the lithium-ion battery continues to power the vehicle. This results in the lithium-ion battery oscillating above and below 20% capacity depending on the demands of the driver. This continues until the Zinc-air battery is depleted (reaches 15% SOC) at about the 505^{th} kilometer. At this point the Zinc-air battery shuts off and the lithium-ion battery powers the vehicle independently again, draining until reaching 5% SOC at the 521^{st} kilometer.

One of the obstacles to electric vehicles is their long recharge time. While regular vehicles can be refilled in a matter of minutes from the gas pump, batteries take much longer to recharge under normal circumstances. And although it is possible to recharge lithium-ion batteries using rapid recharging stations, large power spikes can be difficult for electrical grids to manage. Having even a few vehicles undergo rapid recharging in a 22 MW/9 MVAR distribution grid decreases the grid's voltage stability by 25–45%, according to work by Dharmakeerthi and coworkers [42]. The same work also shows that rapid recharging during an unexpected generator shutdown decreases grid stability by 40–60%. Consequentially designing vehicles so as to not require rapid recharging would be highly beneficial to the electrical grid and the long-term prospects of electric vehicles. In this, the Dual ESS vehicle does not improve upon the Single ESS vehicle. Because of their high voltage polarization Zinc-air batteries take more energy to recharge than lithium-ion batteries, resulting in longer recharge times and wasting more energy. Furthermore, the Dual ESS vehicle's combined battery energy is larger than that of the Single ESS vehicle, further lengthening recharge times. And unlike lithium-ion batteries which can be rapid-charged provided the grid does not destabilize Zinc-air batteries are naturally low-current batteries, limiting their charge rate.

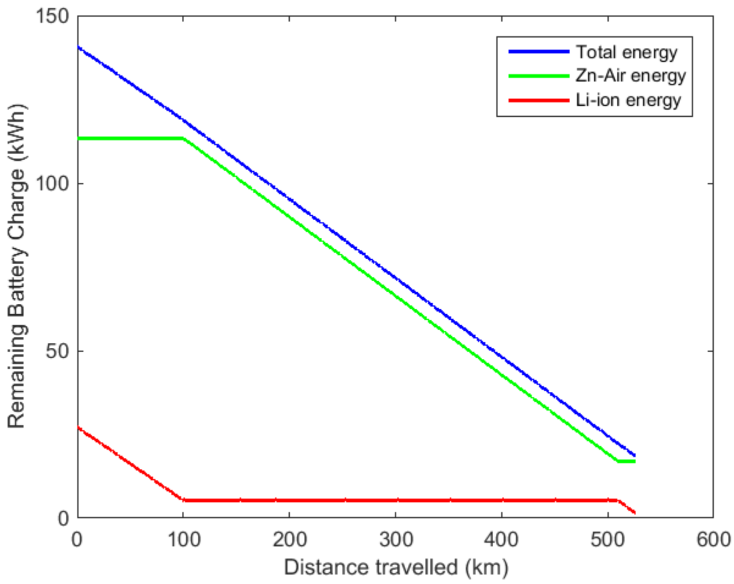

Figure 10. Dual ESS battery energy during continuous highway driving.

5.3. Economic and environmental analysis

In order to analyze the environmental impact and the economics of the Single ESS and the Dual ESS vehicles, these vehicles are compared to a 2016 Chevrolet Camaro and to a traditional PHEV, which has a small lithium-ion battery pack and an ICE as a secondary power source. The results are shown in Table 9. The official Camaro numbers are used in estimating the vehicle's fuel economy [43]. The PHEV Camaro has a lithium-ion battery pack identical to that of the Dual ESS vehicle as described in Table 7, and its fuel economy under charge-sustaining mode is taken to be the same as that of a 2014 Chevrolet Volt [44] (because PHEVs do not need powerful engines, the PHEV Camaro's engine will be more fuel efficient than the 2016 Camaro's engine).

Table 9. Economic and environmental factors.

Measure	Units	Dual ESS	Single ESS	PHEV Camaro	2016 Camaro
Estimated MSRP[1]	USD	$43,660	$43,900	$36,290	$26,700
Fuel Costs[2]	USD/yr	$680	$570	$770	$2,300
Maintenance Costs[3]	USD/yr	$1,540	$1,540	$1,610	$1,920
US CO_2 emissions[4]	kg/yr	2926	2560	2845	5370
CAN CO_2 emissions[4]	kg/yr	1120	980	1504	5370

[1] Based on 2016 Camaro's base price [45], adjusted for battery pack prices, engine costs [46] and cost of battery- and engine-related components, [2] Based on $1.2/L and $0.10/kWh, [3] Based on per-kilometer costs estimated by Propfe and coworkers [47], [4] Based on emissions factors for gasoline and power plants [48] and on the emissions intensity of the overall grid in the US [49] or Canada [50].

The manufacturer's suggested retail price (MSRP) of the Dual ESS and Single ESS vehicles are high, but not so much higher than some of the commercial vehicles on the market. The Chevrolet Bolt, for example, costs $37,500 USD before subsidies but travels over 100 km less on a single charge than the Dual ESS vehicle [51]. The Bolt also serves as an illustrative contrast with the Single ESS vehicle, travelling a similar distance but costing much less and having a much smaller battery pack (60 kWh to 100 kWh). This demonstrates the degree to which the model is constrained by the heavy vehicle base and conservative battery pack design with heavy battery chemistry.

It is particularly notable that the Dual ESS vehicle has higher fuel costs and emissions than the Single ESS vehicle. The reason for this is the Zinc-air battery's poor roundtrip energy efficiency. The individual Zinc-air cells of the Dual ESS battery pack charge at roughly 1.8V and discharge at 1.0 V in a level 1 or level 2 charger, for a 56% roundtrip efficiency. By comparison lithium-ion batteries are typically 85–95% efficient [28]. The Dual ESS vehicle has 20% more power-plant related emissions than the Single ESS vehicle, and in fact emits more GHG emissions than the PHEV if a high percentage of the electricity is generated from fossil fuels.

Maintenance costs are lower for the Dual ESS and Single ESS vehicles due to their not having engines, but not drastically lower as sometimes anticipated for fully electric vehicles. Propfe and coworkers [47] estimate that batteries and their electrical components have sufficiently high maintenance costs that electric vehicles have only a moderate advantage.

6. Conclusions

A Dual ESS vehicle powertrain with two complementary battery packs was modelled and optimized in order to demonstrate the potential of this type of vehicle architecture and of Zinc-air battery technology as a limited cycle range extending pack. The Dual ESS vehicle showed superior range relative to the Single ESS vehicle, going 75 km further on a single charge while costing the same as the Single ESS vehicle. In particular, the model demonstrated that a low cycle life, even as few as 150 cycles, does not preclude Zinc-air batteries from being used in electric vehicles. The Dual ESS vehicle's Zinc-air battery is projected to last 15 years even with only 150 cycles on the Zn-air pack. However, the results do show that improvements in Zinc-air battery cycle life would be highly desirable, and that Zinc-air cells need to be able to cycle well at higher current densities in order to be successful. Improvements in the depth of discharge of anodes and reductions in voltage polarization would also greatly enhance the technology's attractiveness. Further analysis showed that the Dual ESS vehicle produces substantially less emissions than a conventional Camaro and that vehicle owners will pay much less in fuel costs and modestly less in maintenance costs.

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Conflicts of interest

All authors declare no conflicts of interest in this paper.

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