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Low temperature performance evaluation of electrochemical energy storage technologies.

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Abstract

The performance of electrochemical energy storage technologies such as batteries and supercapacitors are strongly affected by operating temperature. At low temperatures ($<0\text{ }^{\circ}\text{C}$), decrease in energy storage capacity and power can have a significant impact on applications such as electric vehicles, unmanned aircraft, spacecraft and stationary power storage. In this work, the discharge behaviour of nine different commercial electrochemical cells are evaluated, representing a variety of lithium-ion, nickel metal hydride, lead acid and supercapacitor technologies. Discharge capacity, energy, maximum power and impedance spectra with equivalent circuit analysis are compared at temperatures ranging from $+20\text{ }^{\circ}\text{C}$ to $-70\text{ }^{\circ}\text{C}$.

Results demonstrate that despite exhibiting the greatest loss in performance with temperature reduction, the lithium-ion batteries tested provide the highest energy and power densities down to $-30\text{ }^{\circ}\text{C}$ due to higher capacity and operating voltage. At lower temperatures, the lead-acid cell gives the highest energy density and supercapacitor the highest power density. A new simplified empirical method is introduced for lithium-ion cells to determine the optimum pre-heating temperature for maximum net energy output including heating efficiency. This new method can be used to assess the benefits of different cold-start thermal management strategies for electric vehicles. It is also demonstrated that the temperature of the lithium-ion cells tested can be accurately predicted from impedance phase change at low temperatures across a range of electrode materials.

1. Introduction

The use of electrochemical energy storage, such as batteries and supercapacitors, is widespread throughout many industries and is set to increase as the world transitions to a low-carbon energy system. As the performance and variety of potential usages for electrochemical energy storage increases, so does the variety of climates into which the technology is deployed. At low temperature ($<0\text{ }^{\circ}\text{C}$) reduced electrolyte conductivity and poor ion diffusivity can lead to a significant reduction in the capacity and performance of batteries [1].

Reduced low temperature battery capacity is problematic for battery electric vehicles, remote stationary power supplies, telephone masts and weather stations operating in cold climates, where temperatures can fall to $-40\text{ }^{\circ}\text{C}$. Furthermore, high altitude aerospace applications can be subject to even lower temperatures, especially in unmanned aerial vehicles (UAVs), where passenger cabin heating is not available and battery heating systems present a significant weight and energy penalty. This area is of increasing interest given the potential of high-altitude, low earth orbit, solar powered UAVs as a low-cost alternative to satellites, and the accompanying need to store energy for night-time use.

Of the competing electrochemical energy storage technologies, the lithium-ion (li-ion) battery is regarded as the current leader in terms of volumetric (Whl^{-1}) and gravimetric (Whkg^{-1}) energy density at standard temperature conditions ($20\text{ }^{\circ}\text{C}$) [2]. It is well documented in the literature that accessible battery capacity decreases significantly at low temperatures [3]–[7] [8]. Smart, et al. [3] documented a 33% reduction in capacity (Ah) and 43% reduction in energy (Wh) when the temperature of a $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ /carbon cell was reduced from $20\text{ }^{\circ}\text{C}$ to $-30\text{ }^{\circ}\text{C}$ with a 1.0C discharge. Likewise, Jaguemont *et al.* [4] recorded a 39% reduction in energy of a 100 Ah LiFeMnPO_4

commercial cell under 0.5C discharge at -20 °C compared to 25 °C. Recently, Sarmiento-Carnevali *et al.* [8] demonstrated a 30.9% reduction in electric vehicle range when reducing from 20 °C to -10 °C.

Several studies have focused on the mechanisms contributing to reduced performance at low temperatures [5] [6] [7] [9]. Zhang *et al.* [5] used electrochemical impedance spectroscopy (EIS) and equivalent circuit fitting to demonstrate that the primary reason for reduced performance in low temperature lithium-ion cells is an increase in the charge transfer resistance, due to slow reaction kinetics. Likewise, Nagasubramanian [6] conducted tests on commercial cells adapted to include a lithium reference electrode, concluding that the major contribution to increased impedance at low temperatures was the cathode electrolyte interface. Other studies, such as Ji *et al.* [7], have demonstrated that reduced Li^+ diffusivity in the electrolyte is a significant contributor to reduced performance, particularly at low state of charge.

In addition to reduced discharge performance, lithium-ion cells utilising graphite negative electrodes cannot receive reasonable rates of charge at low temperature as the risk of lithium plating and dendrite formation increases [10]. This is due higher polarisation causing the electrode potential to approach that of metallic lithium plating (<0 V vs. Li/Li^+), creating dendrites or mossy deposits on the anode interface [11]. This has a significant effect on the ability of electric vehicles to utilise regenerative braking in cold environments. Anode intercalation materials with higher potentials, such as lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$), reduce the probability of lithium plating at low temperatures. However, the theoretical lithium storage capacity of lithium titanate (175 mAhg^{-1}) is less than carbon (372 mAhg^{-1}), and the higher negative electrode voltage reduces the cell voltage, lowering the energy output [12].

Many studies have looked at different methods of improving battery performance in cold climates, either through changing cell materials, such as electrolyte additives for improved Li^+ diffusivity [13] or by raising cell temperature [7], [14], [15]. Increasing the battery temperature from a cold start is an effective method to improve performance. However, this requires either consumption of the batteries state of charge (SoC) or an external energy source such as an electricity supply, phase change material or another battery [14]. Heat can be applied either externally to the cell surface through the thermal management system or internally through the electrochemical reaction. An alternative method for self-heating cells proposed by Wang *et al.* [15] consisted of integrating a nickel foil heating element into the battery structure to facilitate fast self-heating from sub-zero temperatures. Ji *et al.* [7] also demonstrated the importance of pack design and thermal management by varying the heat transfer coefficient (h) of the cell surface in a numerical model, observing an increase in accessible capacity from 140 to 2250 mAh when changing from an isothermal ($h=\infty$) to adiabatic ($h=0$) boundary conditions at -20 °C.

Temperature measurement and estimation is also important in cold climates, especially in multicell systems such as electric vehicles where it may not be feasible instrument individual cells. It has been well documented that EIS spectra can be used to estimate internal cell temperature down to -20 °C [16]–[19] [20] [21], however temperatures lower than this have not been widely studied. Srinivasan *et al.* [16] used the phase shift at a single frequency to estimate the internal temperature of three different lithium-ion batteries between -20 °C and 66 °C. The relationship was also shown to be independent of SoC in the 40-100 Hz region because this frequency range can be attributed to the solid electrolyte interphase (SEI) layer at the negative electrode/electrolyte interface, which does not vary with SoC. Spinner *et al.* [17] used a 300 Hz single point perturbation to monitor online temperature in a LiCO_2 18650 cell for an expanded high temperature range from -10 °C to 95 °C. Zhu *et al.* [18] used a 10 Hz perturbation to correlate phase change and temperature on a LiFePO_4 pouch

cell, also considering the influence of temperature gradients on the cell and relaxation times before tests.

At low temperatures, such as those experienced during high altitude flight, electrochemical energy storage methods other than lithium-ion may be more favourable. Lead-acid batteries still have widespread use as starter motors in vehicles due to their reliability and high current capability at low temperature, despite poor gravimetric energy density [22]. Supercapacitors, although having high power density, typically possess lower energy densities than lithium-ion cells at room temperature. Their performance is less effected by low temperatures since energy is stored via electrochemical double layer capacitance (EDLC) as opposed lithium intercalation. The electrolyte however, can solidify at temperatures below -45°C depending on the choice of material [23]. Nickel-metal hydride (NiMH) batteries possess similar capacities to lithium-ion cells at a reduced cell voltage, but with the added capability to charge at temperatures down to -10°C [24]. A wide operating range and ability to trickle overcharge makes NiMH suitable for low power remote applications.

Whilst there have been several studies documenting performance of individual battery chemistries at low temperature; there is yet to be a direct comparative study of different electrochemical energy storage methods that addresses energy, power and transient response at different temperatures. Furthermore, there is also a lack of information in the available literature on performance at temperatures below -30°C , which is of particular interest to unmanned aerospace applications.

In this work nine different electrochemical energy storage technologies are directly compared in terms of capacity, volumetric and gravimetric energy density, maximum power output and transient response (through EIS) as a function of temperature from $+20^{\circ}\text{C}$ to -70°C . Cell chemistries have been selected with a focus on lithium-ion technologies with nickel hydride (NiMh), lead-acid and supercapacitor cells included for comparison. It is anticipated that the findings of this work will be of interest to a wide range of applications which require energy storage at low temperature and help to inform thermal management strategies to maximise system net energy density. This work has particular relevance to electric vehicles, remote energy storage and unmanned aerial vehicles.

2. Experimental setup

2.1. Material selection

The nine different energy storage methods used in this work consisted of six lithium-ion batteries of varying negative and positive electrode composition, a nickel hydride (NiMh) battery, a lead-acid battery and a supercapacitor. For a representative comparison, cells were sourced in 18650 format (18 mm diameter x 65 mm length) with the exception of the lead-acid battery and supercapacitor which were not available in this format. The lead-acid battery used had a 33.80 mm diameter x 60.85 mm length and the supercapacitor a 35.04 mm diameter x 60.88 mm length. Available manufacturers specification of the cells tested is shown in Table 1. Each cell is taken to be a representative example of the technology it represents, although definitive conclusions cannot be applied across all cells with common electrode materials due to variations in cell construction and electrolyte properties. The exact specification of the electrode and electrolyte material compositions for each cell are not available in the public domain with the exception of cells 1, 3 and 6 which were subjected to post-mortem studies in [25].

Cell no.	Name	Technology	Positive electrode	Negative electrode	Nominal voltage / V	Rated capacity / mAh
1	Samsung 25R	Li-ion	LiNiCoAlO ₂ + LiNiMnCoO ₂	Carbon + Si	3.6	2500
2	Sony VTC6	Li-ion	LiNiCoAlO ₂	Carbon + Si	3.6	3000
3	Panasonic NCR18650b	Li-ion	LiNiCoAlO ₂	Carbon	3.6	3200
4	Samsung 22P	Li-ion	LiCoO ₂	Carbon	3.6	2150
5	GWL Power LTO18650	Li-ion	-	Li ₄ Ti ₅ O ₁₂	2.4	1300
6	A123 APR18650m1A	Li-ion	LiFePO ₄	Carbon	3.3	1100
7	GP410LAH	NiMH	NiOOH	Metal hydride	1.2	4100
8	Energys RSACP3702	Lead-acid	Pb	PbO ₂	2.0	2500
9	Green-Cap EDLC	Capacitor	Carbon	Carbon	2.7	500 F

Table 1 - Electrochemical energy storage technologies used

2.2. Test equipment

All cells were placed in a Weiss Technik C1500 environmental chamber and cycled using a Solartron 1280C potentiostat with four-wire remote sensing and 2 Hz sample rate. Cell surface temperature and environmental chamber temperature were recorded using type-K thermocouple probes and a National Instruments PXI datalogger. Before starting any tests, each new cell was cycled twice according to the manufacturer specification at 500 mA charge/discharge current and 20 °C.

Power tests were conducted using an Electro-Automatik EA-EL 3080-60b DC load bank. Voltage and current were recorded at 10 Hz throughout the power test using a LabVIEW interface.

Prior to testing, all cells were weighed and measured to enable gravimetric and volumetric analysis. An A&D HR250AZ balance ± 0.1 mg was used to measure the battery mass, insulated callipers ± 0.01 mm and micrometer ± 0.001 mm were used to measure battery length and diameter respectively.

2.3. Test procedure

Prior to each discharge test, cells were charged at 20 °C to avoid the potential of lithium plating on the negative electrode of the lithium-ions cells which occurs during low temperature charging [10]. The lithium-ion (cells 1-6) were charged using a constant current – constant voltage (CCCV) procedure with 500 mA current until either 4.20 V (cells 1-4), 3.65 V (cell 6) or 2.80 V (cell 5) and a 100 mA cut-off threshold. The lead acid (cell 8) also used the same CCCV procedure except with a 2.35 V constant voltage section. The NiMH (cell 7) was charged at 410 mA (0.1C) for 14 hours as per the manufacturer's specification, and the EDLC (cell 9) was charged under CCCV protocol at 500 mA until 2.7 V with a 100 mA cut off.

After charging, cells were soaked at the desired temperature for at least 12 hours then discharged at 500 mA constant current until the manufacture specified lower voltage limit. 500 mA was selected to reduce the effects of internal joule heating in the battery, whilst maintaining a representative discharge time. EIS was performed before and after discharge between 20 kHz and 5 mHz with a 20 mV perturbation. Cells were rested at open circuit potential for 30 minutes before impedance tests.

To investigate the influence of temperature on maximum power, each cell was charged to 100% SoC at 20 °C and underwent a 12-hour temperature soak. Each cell was then discharged at either maximum rated current (CC) or the current required to give the lower voltage limit (CV), whichever was lower. The maximum power was determined as the power delivered by the cell five seconds after initial current application. An exception to this rule is the supercapacitor which, due to the high rate of voltage leakage during the 12-hour temperature soak, was charged according the process described above at the test temperature after the soak, then left to rest for only 30 minutes before the discharge test.

All tests were repeated at 10 °C reduction intervals, starting from 20 °C and reducing until either the cell could produce less than 1% of its original capacity at 500 mA load, or -70 °C was reached. After testing was completed each cell underwent an additional two cycles at 20 °C to ensure that no significant (>1%) irreversible capacity reduction had occurred.

The test procedure was designed to minimise differences between the cells and provide comparable thermal performance results. However, the larger diameter of the lead-acid and supercapacitor cells means larger thermal gradients inside the cell and increased deviations from the measured surface temperature are possible. The potential influence of cell dimensions is mitigated by having a low constant discharge current (500 mA) and only applying the maximum power test for a short duration of five seconds, before any large thermal gradients are able to establish.

2.4 Equivalent circuit

An electrochemical equivalent circuit was fitted to the impedance spectra to associate the dynamic response to physical components in the cell. The circuit, shown in Figure 1(a), consists of a Randles circuit with an inline inductor, where the semi-infinite Warburg element (W) is modelled using a constant phase element (CPE) at 0.5 fixed exponent. At low temperatures, an additional resistor CPE parallel circuit is added to reflect the evolution in behaviour, shown in Figure 1(b) and discussed in section 3.4. The circuits were fitted using ZView software and the Calc-Modulus solver method [26]. A two-step fitting process was used to reduce overfitting, first the circuit was fitted without the Warburg element from the high frequency intercept up to the inflection point (local minima) between the impedance arc and diffusion tail. Next the complete circuit was fitted across the entire impedance spectra using the values from the previous step as initial estimates.

Figure 1 - Equivalent circuits used for EIS analysis (a) High temperature circuit and (b) low temperature circuit

3. Results

3.1. Capacity

Figure 2(a) shows the voltage capacity relationship for cell 2 (Sony VTC6, $\text{LiNiCoAlO}_2/\text{Carbon+Si}$) from which accessible cell capacity and energy are determined. The discharge voltage plots from each of the 9 cells are not shown here for brevity, however the full data set from all cells used in this study is available. In this work, the term accessible capacity and accessible energy are used to describe the capacity and energy measured from the 500 mA constant current tests until the lower voltage limit of the cell is reached. Unless otherwise specified, all references to capacity and energy in the remainder of this work refer to the accessible values from constant current discharge tests.

The relationship between temperature and capacity for all the cells tested is shown in Figure 2(b). At 20 °C all cells operated very close to, or in excess, of their rated capacity and the capacity is seen to reduce with temperature. For most of the cells a linear reduction in accessible capacity with temperature is seen from +20 °C to -20 °C, followed by a sharp drop in the -20 °C to -40 °C range. For example, cell 2 accessible capacity reduces 11% from +20 °C to -20 °C but 82% from -20 °C to -40 °C. In the lithium-ion cells (1-6), the sharp reduction in capacity below -20 °C is likely due to ethylene carbonate (EC) component of the electrolyte precipitating, reducing the conductivity of the electrolyte [22], the remaining components dimethyl carbonate (DMC) and/or Propylene carbonate (PC) having a much lower dielectric constant [27]. Conversely, the lead-acid cell and the supercapacitor do not exhibit a significant reduction in capacity and can be discharged down to -60 °C at 500 mA. In a lead-acid cell the freezing point of the electrolyte is dependent on its specific gravity (SG), reducing to -70 °C at 1.28 SG [28]. The EDLC supercapacitor used in this work is believed to have a butyltrimethylammonium *bis*(trifluorosulfonyl)imide electrolyte [29], the supercapacitor also benefits from having a 0 V low voltage cut-off limit, meaning a higher voltage drop is permissible under discharge. None of the cells tested were capable of 500 mA discharge at -70 °C. This highlights the need for either thermal management systems or unique cell designs in extreme low temperature applications such as high-altitude flight or satellites.

(a)

(b)

(c)

(d)

Figure 2 - Discharge tests: (a) Discharge voltage of Sony VTC6 at different temperatures, (b) Capacity, (c) Energy and (d) Volumetric energy density of tested cells at different temperatures

3.2. Energy

The energy output from each cell, calculated as the product of current and voltage ($I \times V$) integrated over the discharge, is shown in Figure 2(c) and displays a similar temperature relationship to the capacity. The benefits of utilising higher voltage lithium-ion electrode materials such as LiNiCoAlO_2 , LiNiMnCoO_2 and LiCoO_2 can be clearly seen from the superior performance of cells 1-4 in the $+20^\circ$ to -20°C range.

The reduction in energy with temperature follows an Arrhenius type relationship, described in equation 1 where E_T is the measured energy output (Wh) at temperature T (K), E_{20} the measured energy at 20°C , R the universal gas constant and a and b are fitted constants. Table 2 shows the fitted parameters for the different cells tested in the -40°C to $+20^\circ\text{C}$ range along with the r^2 of the fit. With the exception of the EDLC and lead-acid cells which did not follow an exponential energy loss with temperature, a reasonable fit is seen on all the li-ion and NiMH cells. Cell 3 is seen to give the poorest fit, due to the rapid performance drop between -10°C and -30°C , likely due to the electrolyte precipitating at a higher temperature.

$$E_T = E_{20} - a \cdot \exp\left(\frac{b}{RT}\right)$$

1

Cell No.	Name	E_{20} / Wh	a	b / J·mol ⁻¹	r^2 value
1	Samsung 25R	9.22	5.51×10^{-7}	32204	0.996
2	Sony VTC6	11.00	3.31×10^{-9}	42212	0.995
3	Panasonic NCR18650b	11.74	1.33×10^{-4}	22324	0.862
4	Samsung 22P	7.79	4.62×10^{-7}	32223	0.988
5	GWL Power LTO18650	2.97	3.50×10^{-5}	22178	0.927
6	A123 APR18650m1A	3.06	3.50×10^{-8}	35493	0.987
7	GP410LAH	4.80	6.27×10^{-9}	39668	0.996

Table 2 - Fitted parameters for energy dependency on temperature using equation 1

3.3. Power

As with the accessible energy, the accessible power of the cells is seen to reduce with temperature due to a reduction in cell voltage under load. Figure 3(a) shows the power time history of Cell 2 at different temperatures, where 0 s corresponds to the point the step load is applied and 5 s the time at which the power was measured. At -20 °C and below, cell 2 was seen to transition from constant current to constant voltage mode under discharge to avoid dropping below the lower voltage limit. The gradual increase in power after this initial reduction can be attributed to Joule heating increasing the internal temperature of the cell, reducing the resistance.

Figure 3(b) compares the gravimetric power density of each cell. As with the accessible energy, lithium-ion cells provide the best performance in the +20 °C to -20 °C region, typically associated with electric vehicles. Unlike the energy temperature relationship, an Arrhenius type relationship is not seen across all cells, this is particularly evident in cells 5 and 6 which are optimised for high power over high energy. At -40 °C cell 9 (supercapacitor) provided the highest gravimetric power density by a factor of 4.7. It is also worth noting that cells 8 (lead-acid) and 9 utilise protruding wire terminals at the top of the cell for electrical connection. The increased contact resistance between the terminals and load bank connections, along with increased distance between cell and remote voltage sensing wires may underestimate the actual power that can be delivered from these cells.

(a)

(b)

Figure 3 - Power test: (a) Sony VTC6 time history and (b) Maximum gravimetric power density from tested cells at different temperatures

3.4. Energy vs. Power

The relationship between energy and power of the cells at different temperatures is shown in the Ragone plots of Figure 4(a-c). For the limited number of cells tested it can be seen that the lithium-ion cells (cell 1-6) provide the best power and energy density at 20 °C but as temperature reduces, the performance of the lithium-ion cells reduce relative to the other cell types tested and the performance spread across the different lithium-ion cells increases. At -30 °C the supercapacitor is seen to provide specific power density comparable to the best lithium ion cells, although cells 1, 2 and 4 still provide the best energy density by a factor of two. It is not possible to draw definitive trends due to the small sample size, with only one NiMH, lead-acid and supercapacitor tested, but this does demonstrate the diminishing advantages of lithium-ion cells below -20 °C.

Figure 4 - Ragone plot (specific energy vs. specific power) of cells at (a) 20 °C (b) -20 °C and (c) -30 °C

3.5. Transient behaviour

Electrochemical Impedance Spectroscopy (EIS) was performed at the start and end of every capacity test to quantify the influence of temperature on transient behaviour across a wide bandwidth and to better understand the mechanisms leading to capacity loss at low temperatures. Nyquist plots for cell 2 are shown in Figure 5, experimental data from all the cells is available in the underlying data. As a general trend across all cells, the high frequency intercept (HFI) increased with reducing temperature, indicating an increase in cell resistance. The impedance arc was also widened with reducing temperatures, blending into the low frequency diffusion tail, typically associated with Warburg impedance, indicating a slowing of reaction kinetics and increase in charge transfer resistance with reducing temperature. This also led to impedance features transitioning towards lower frequencies as temperature reduced. For some of the cells tested, the diffusion tail could not be observed before the 5 mHz lower frequency limit was reached. As with the capacity and power tests, a significant reduction in performance was seen in the -20 to -40 °C region in the lithium-ion cells.

At low temperatures ($< 0\text{ }^{\circ}\text{C}$) the impedance response shape transitions from a typical Randles single arc and diffusion tail (Figure 5(c)), to a double arc and diffusion tail, with the additional arc being smaller and occurring at higher frequencies close to the HFI (Figure 5(d)). The smaller secondary arc is indicative of solid electrolyte interphase (SEI) layer effects [30][31]. The increased impedance is reversible once the cell returns to higher temperatures, indicating that the observed changes are due to reduced ionic conductivity and increased charge transfer resistance through the SEI layer rather than SEI layer growth.

Figure 5 - Temperature dependency of EIS spectra from Sony VTC6 cell at 100% SoC (a) Nyquist plot, (b) Zoomed Nyquist plot, (c) Fitted circuit above $0\text{ }^{\circ}\text{C}$ (d) Fitted circuit at $0\text{ }^{\circ}\text{C}$ and below

The evolution of impedance response shape and separation of time constants with reducing temperature means a single equivalent circuit model is not representative across the entire temperature range studied. To reflect this, the Randles circuit (Figure 1(a)) was used for EIS analysis at temperatures above $0\text{ }^{\circ}\text{C}$ and the additional R/CPE (Figure 1(b)) was used for EIS analysis at $0\text{ }^{\circ}\text{C}$ and below. Fitted equivalent circuit parameters at 100% SoC are shown in the supplementary information. Accurate equivalent circuit fitting was not possible for cells 2, 3, 5 and 6 at $-40\text{ }^{\circ}\text{C}$ due to changes in the impedance response shape and shifting of the diffusion tail to below 5 mHz. These points have therefore been excluded from the analysis.

In general, fitted resistance values increased across all cells as temperature reduced. The HFI resistance (R_1) increase is primarily caused by a decrease in electrolyte ionic conductivity, shown in Figure 6(a). This is evident by the large increase below -20 °C where the EC component of the electrolyte is likely to precipitating [22]. The increased ionic resistance leads to larger polarisation effects, reducing power density and accessible capacity, however the polarisation effects of this parameter alone are not sufficient to account for the capacity and power loss seen at low temperatures. An increase in charge transfer resistance (R_3) with reducing temperature represents a reduction in reaction kinetics at the electrode/electrolyte interface [32]. This behaviour has been observed separately for LiFePO₄ positive electrodes [33] and carbon negative electrodes [34], demonstrating the process can be attributed to both electrodes in lithium-ion cells. The increase in charge transfer resistance has been linked to an associated decrease in the exchange current density at low temperatures [35], requiring increased overpotentials for the same current density through the Butler-Volmer kinetics.

R_2 in the equivalent circuit of Figure 1(b) can be attributed to the resistance of the SEI layer [5]. Figure 6(d) shows a general exponential increase in SEI resistance with reducing temperature across the lithium-ion cells. This behaviour, indicative of an Arrhenius type relationship, supports the previous findings of [35] but extends the observation lower limit from -10 °C to the lower operating limit of the cells tested. The increase in SEI resistance with reducing temperature can be attributed to the lower kinetic energy of the lithium-ions leading to slower diffusion through the interface layer [9].

Cell 5 also exhibited an increase in R_2 with reducing temperature despite having a Lithium Titanate negative electrode, which due to its higher half-cell potential is not subjected to the same level of SEI growth of graphite. The increase may be due to smaller SEI layers on the positive electrode and Lithium Titanate negative electrode, evidenced by the fitted R_2 being consistently lower than most of the other lithium-ion cells with the exception of the -10 °C fitted circuit. This demonstrates the increasing R_2 resistance cannot be solely attributed to the graphite SEI layer.

Solid state diffusion in the active material is represented by the Warburg diffusion element [31]. Fitting results show a reduction in the Warburg coefficient (σ) with reducing temperature, shown in Figure 6(b). The Warburg coefficient can be correlated to the effective diffusion coefficient (D) through equation 2, where R is the universal gas constant, n the number of electrons transferred, F the Faraday constant, c^* the bulk concentration and subscript O and R the reactant and product respectively [36].

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \left[\frac{1}{c_R^* \sqrt{D_R}} + \frac{1}{c_O^* \sqrt{D_O}} \right] \quad 2$$

Assuming that bulk concentration does not change significantly with temperature, the relative change in effective diffusion coefficient with temperature is proportional to the square of temperature divided by Warburg coefficient ($D \propto (T/\sigma)^2$), shown in Figure 6(c). This demonstrates a relative increase in solid state diffusion coefficient with reducing temperature, which contradicts expectations. To ensure this was not a result of overfitting the equivalent circuit, the process was repeated using the gradient of $\omega^{-1/2}$ vs. impedance at low frequencies to estimate the Warburg coefficient σ [31], this showed a similar trend to the equivalent circuit fitting (Figure S2). A similar unexpected increase in diffusivity with reducing temperature was observed by [37] for Nickel Manganese Cobalt (NMC) positive electrode material through galvanic intermittent titration (GITT) analysis, compared to a decreasing diffusion coefficient for graphite. Further post-mortem analysis

would be required to investigate the observed phenomena in more detail, which are beyond the scope of the present work. However, the observed behaviour does indicate that solid state diffusion in the active material does not strongly contribute to the reduced capacity and power seen at low temperatures.

EIS analysis demonstrates that a reduction in electrolyte conductivity and diffusivity combined with increased charge transfer resistance across the electrode/electrolyte interface are the main causes of capacity and power loss at low temperatures across the range of different chemistries tested. SEI layer effects in the lithium-ion cells were more prominent at lower temperatures, indicating the potential of low temperature characterisation tests for improved diagnostics in cell degradation studies. The remainder of this paper will focus on how cell response at low temperature can be used for online temperature estimation and analysis of lithium-ion cell thermal management and heating strategies.

Figure 6 – The influence of temperature on fitted equivalent circuit elements (a) R_1 (b) Warburg coefficient (c) $(T/\sigma)^2$ and (d) R_2 (0 $^{\circ}\text{C}$ and below).

3.6. Temperature estimation

One area of interest that has been studied in the literature is the use of impedance spectra to estimate the internal temperature of the cell [16]–[19] [20] [21][38][39], however the lower

temperature limits of this methodology have not yet been evaluated meaning it cannot be reliably applied to extreme low temperature applications. In the current work, a linear relationship between phase angle and temperature was evaluated at different frequencies using data at both 100% and 0% SoC. Figure 7(a) and Figure 7(b) shows the relationship between phase change and temperature for the cells studied at 50 Hz and 200 Hz respectively. A linear regression analysis of the phase angle temperature relationship was performed at each tested frequency using the MATLAB curve fitting toolbox, the r^2 parameter is used to quantify the quality of fit. Both the NiMH and lead-acid cells showed a very poor agreement with phase change at any of the frequencies, indicating this diagnostic method is not compatible with these specific cells, and possibly chemistries in general. However, Hande [40] demonstrated resistance measurement through current interrupt as a potential temperature measurement method for these chemistries.

Figure 7 - Relationship between phase change and temperature at (a) 50 Hz and (b) 200 Hz for the lithium-ion based cells

Cell No.	Optimum Frequency / Hz	r^2 at optimum frequency	r^2 at 200 Hz
1	63.2	0.9383	0.8945
2	251.8	0.9565	0.9553
3	12.62	0.9638	0.8299
4	158.9	0.9655	0.9578
5	25.18	0.9546	0.8940
6	1002	0.9907	0.8439
7	2000	0.8536	0.0013
8	0.01	0.4022	0.0374

Table 3 - Temperature prediction ability of phase change using linear least squares regression fit

Table 3 shows the fitting results for each of the cells tested, both at the optimum frequency (corresponding to the smallest error) and at 200 Hz; fitting was performed jointly on impedance spectra taken at 100% and 0% SoC. All the lithium-ion cells (Cells 1-6) are able to deliver a strong linear correlation between phase angle and temperature at a specific frequency, but that the optimum frequency can change dramatically between cells. Cells with similar chemistry, such as cells 1,2 and 4 do display similar optimum frequencies for phase related temperature prediction around 200 Hz, but other cells such as cell 3 (LiFePO₄) (1002 Hz) and the highly energy optimised Cell 3 (20 Hz) differ by up to an order of magnitude. Figure 7(c) shows the temperature, phase change relationship for cell 2 at both 100% and 0% SoC. A good fit can be seen at both SoC values in the +20 °C to -20 °C, but at -30 °C and below the phase change is no longer independent of SoC, leading to potential errors in temperature estimation. In this specific case, the variation in temperature prediction between 100% and 0% SoC at -30 °C is 15.1 °C. Conversely, cell 6 (Figure 7(d)) phase change remains relatively independent of SoC at low temperatures. This is likely due to the higher optimal frequency of 1002 Hz compared to 251.8 Hz for cell 2 highlighting dynamics that do not undergo a significant transformation below -20 °C.

Overall, phase shift can provide a useful indication of cell temperature, even at very low temperatures, but the frequency at which it should be measured will vary between different cell types, and at very low temperatures (below -20 °C) SoC effects may need to be considered for some cells. Phase shift temperature estimation allows individual cell temperature estimation in a pack with only voltage measurement and a small current excitation. This information can be used in a battery management system (BMS) to determine allowable charge rates at low temperature to avoid lithium plating or can also be applied to estimate cell available energy as a function of phase angle if the SoC is known. Either through the relationships described in section 3.2 or direct relationship using exponential fitting. Additionally, this technique can be used to estimate cell-to-cell temperature distribution in electric vehicle battery and assist with the development of battery thermal management systems for electric vehicles.

3.7. Heating strategies

To investigate effectiveness of heating strategies and thermal management systems in energy storage applications, the energy required to raise the cell temperature from an initial temperature T_{init} to a new temperature T can be expressed using equation 2. Where m and C_p are the cell mass (kg) and specific heat (J·kg⁻¹K⁻¹) respectively and η the efficiency of heating the cell, (fraction of energy transferred to the cell thermal mass). The heating thermal energy could come from an external source such as an ancillary battery, mains supply or from the cell itself (neglecting the

additional Joule heating). Combining equations 1 and 2, the influence of raising cell temperature prior to discharge on overall net energy output can be investigated, shown in equation 3. The empirical fitting of equation 1 from 500 mA constant current discharge data means that errors will increase as the current deviates from this value. However, the results are representative of the challenges faced in cold-start thermal management systems in electric vehicles and presents a simple methodology to determine the optimal energy consumption of battery heating strategies. The empirical relationship in equation 1 can also be easily determined for additional cells or application specific duty cycles by measuring discharge energy at different temperatures.

$$E = \frac{1}{\eta} m C_p (T_{init} - T) \quad 3$$

$$E_{total} = E_{20} - a \cdot \exp\left(\frac{b}{RT}\right) - \frac{1}{\eta} m C_p (T_{init} - T) \quad 4$$

Using the parameters from Table 2 and a specific heat capacity of $896 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ for an 18650 cell from [41], the relationship between thermal energy required for preheating and total system energy output can be explored. Figure 8(a) shows the calculated total energy output for cell 2 when theoretically pre-heated from different initial cold-soak temperatures. It can be seen that whilst the drop in capacity with temperature reduction is non-linear (equation 1), the energy required to raise the cell temperature (equation 2) is linear, resulting in a linear shift between the total energy outputs from different initial temperatures. For example, the difference in total energy output from a cell pre-heated from -30°C to 0°C then discharged, and a cell pre-heated from -10°C to 0°C then discharged, is the energy required to heat the cell from -30°C to -10°C . One implication of maintaining the same energy profile with initial start temperature is that the optimum pre-heating cell temperature for maximum total energy output (equation 3) remains independent of initial temperature. This is seen in Figure 8(a), where the optimum temperature for cell 2 at 50% heating efficiency is 2.45°C . Below this temperature, the total discharge energy can be increased by heating to 2.45°C . Actively heating above 2.45°C will result in a loss in total discharge energy as the energy required to raise the cell temperature is not offset by the increase in energy output.

Figure 8(b) demonstrates how the efficiency of the cell heating influences the calculated total energy output at different initial temperatures for cell 2 when heated to its optimum temperature. At low temperatures (-20°C and below), pre-heating has a significant improvement on the total discharge energy output, even at heating efficiencies as low as 25%. At -10°C and above, the benefits of pre-heating are relatively small for the cell and discharge current that equation 3 are based upon. From a -10°C initial temperature, only a 3.6% improvement in discharge energy is achieved when heating up to its optimum temperature at 100 % efficiency compared to no pre-heating. This compares to a 11.3% and 31.4% improvement in available discharge energy from initial temperatures of -20°C and -30°C respectively. These values are only representative of cell 2, but a similar process can be performed for the other cells in Table 2.

As the heating efficiency increases, so does the optimum heating temperature, Figure 8(c) shows the calculated optimum heating temperature using equation 3 for the seven cells fitted in Table 2. For cells greater affected by temperature reductions, such as cell 1 (Samsung 25R), it is better to heat the cell up to higher temperatures. At heating efficiencies of 80% and higher the cell should be heated to 20°C , the maximum temperature considered in this low temperature study. The analysis shows that cell 3 (Panasonic NCRb) should be heated to 20°C at much lower efficiencies, although

this may be a result of the poor fit of equation 1 ($R^2 = 0.862$) due to the rapid energy reduction in the -10 to -30 °C region in this energy optimised cell.

The methodology presented in equation 3 demonstrates a simple but powerful methodology to compare energy outputs and evaluate high level heating strategies for different cells under a known duty cycle from simple testing prior to detailed thermal system design. This can be applied in applications ranging from the design of thermal management systems to the energy optimisation in electric vehicle battery management systems. The findings also suggest that in temperate climates where the temperature is unlikely to drop below -10 °C, the benefits of installing a battery pre-heating thermal management system in electric vehicles is small, even if the heating comes from an external source and is highly efficient, the maximum energy gain is typically less than 10%.

Conversely for electric vehicles which regularly encounter temperatures below -20 °C, a battery pre-heating thermal management system will have a significant benefit, even if it has a poor heating efficiency.

Figure 8 - Theoretical energy output from equation 3. (a) Cell 2 total energy output when heated from different initial temperatures $\eta=0.5$, (b) Cell 2 total energy output when heated to optimum temperature of 2.45 °C (c) Optimum temperature at different heating efficiencies.

Conclusions

The performance of nine commercial electrochemical energy storage cells of similar size and form factor have been evaluated at low temperatures. Despite having the largest reduction in accessible energy with temperature, lithium-ion cells still present the best discharge performance down to -20 °C due to higher initial capacity and operating voltages, making them the most suitable energy storage technology for electric vehicle applications from the various cells tested. From -40 °C to -60 °C, the lead-acid cell in the test was the best performing in terms of energy and power.

Electrochemical impedance analysis demonstrated that performance reductions at low temperatures can be attributed to reduced ionic conductivity, reduced ionic diffusivity and increased charge transfer resistance. Single frequency phase angle was seen to have a linear relationship with temperature, independent of state of charge down to -20 °C, across the range of lithium-ions cells tested. Thus, allowing sensor free cell temperature estimation in lithium-ions packs.

Finally, a novel method for simplified analysis of pre-heating thermal management strategies was introduced that only requires knowledge of the cell energy output with temperature, mass and heat capacity. It was shown that for the lithium-ion cells tested, pre-heating at temperatures above -10 °C does not have a significant influence on total cell energy for the 0.5 A discharge current tested. However, at lower temperatures pre-heating can be very effective, even with poor heating efficiencies less than 50%. It was also shown that the optimum pre-heating temperature for maximum net energy output is independent of initial temperature. This presents a simplified tool to assess the potential benefits of thermal management systems in a range of applications including electric vehicles, remote stationary energy storage and aerospace.

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