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Temperature Effect on “Ragone Plots” of Lithium-Ion Batteries

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Temperature is a major factor affecting lithium-ion batteries (LIB) performances including power, energy and life. Energy density vs. power density ($E(P)$) charts known as “Ragone plots” are convenient charts for comparing the performance of energy storage systems (ESS) such as batteries, supercapacitors, fuel cells, flywheels, hydrogen and gasoline. Basically, Ragone plots allow one to determine the amount of energy E (Wh kg^{-1} and Wh l^{-1}) an ESS may deliver under a constant power load P (W kg^{-1} and W l^{-1}). In this study Ragone charts are achieved on commercial LIB cells at temperatures ranging from -20°C to $+55^\circ\text{C}$. Cells are first charged using CCCV protocol at C/10 up to 4.2 V at the ambient temperatures ($\sim 25^\circ\text{C}$). Then cells are discharged isothermally at constant rates ranging from C/5 to 10 C. To account for varying power and temperature Ragone isotherms are integrated over the power range yielding a functional Integrated Energy-Power ($\sqrt[2]{\int_P E(P)dP|_T}$). The ratio of integrated areas at T and at 25°C gives the “Energy-Power Index” (EPI) (%). The EPI vs. T profile shows a linear increase between -10°C and 25°C then it makes a semi-plateau between 25°C and 55°C .

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The major factors controlling the nominal energy a battery based ESS delivers are: i) state of health (SOH), ii) temperature and, iii) the drain power. SOH accounts for the ageing of the cell components including electrochemically active materials (anode, cathode, and electrolyte)¹ and inactive materials (separator, metal sheet substrates, electrode binder, additives, gasket, seals etc.).² Ageing adversely affects the lithium storage capability of electrode materials owing to crystal structure degradation³ and to inter-particles electrical disconnection.² Ageing also decreases the electrolyte conductivity leading to increased overall cell ohmic resistance.⁴⁻⁷

SOH is usually determined from the cell’ discharge profile at a well-defined temperature and discharge rate. The integration of the discharge curve (voltage vs. time or vs. capacity) gives the energy provided by the cell. Energy of an aged cell is related to that of a fresh under the same discharge rate to yield the SOH (usually given in %).

Temperature plays a major role in the cell energy density and power density.⁸ LIB discharge reaction is exothermic in nature (enthalpy variation $\Delta H < 0$).⁹ Therefore, the amount of energy should decrease as temperature increases. On the other hand, the lithium ions diffusion in anode and cathode materials and their mobility in the electrolyte are thermally activated processes. This implies that within the range of the cell’ thermal stability the rate of charge and discharge should increase with temperature.^{10,11} In general, the temperature dependence of energy has a bell shape starting with an increase up to a maximum then energy decreases with temperature.¹²

Charge and discharge rates also play a major role in the cell’ performance.^{13,14} In fact, by increasing the rate one increases the anode and cathode polarization together with the ohmic effect. Accordingly, with higher current rates the charge and discharge voltage limits are reached faster resulting in cell not being fully charged and fully discharged. This reduces the energy density and the charge-discharge cycle coulombic and energy efficiency. There also a Joule effect which increases with the charge and discharge rate leading to cell heating.¹⁵

Energy vs. power “Ragone plots” are convenient charts for comparing the energy and power densities of various energy storage devices and predicting the energy output under a well-defined power drain.¹⁶⁻²¹ Ragone plots are usually achieved by discharging a fully charged cell (or battery pack) under a constant power and by integrating the voltage over the discharge capacity (Ah) to get energy. Power and energy are related to the total mass or volume of the battery system (W/kg or W/l and Wh/kg or Wh/l , respectively), which makes it

possible to compare different battery systems as E vs. P or P vs. E charts.

In this study, lithium ion cells based on LiCoO_2 cathode and graphite anode initially fully charged at the ambient temperature ($\sim 25^\circ\text{C}$) are discharged isothermally between -20°C and 55°C at different C-rates (C/5 to 10 C). This enables Ragone plots to be achieved at different temperatures. To account for temperatures and rates variables we introduce a new metrics; the Energy-Power Index (EPI). EPI (in %) is defined as the ratio of the root squared integrated area under the Ragone profile achieved at temperature T vs. the same achieved at 25°C . The EPI vs. T profile shows a linear increase and semi-plateau. This feature is discussed in terms of tradeoff between temperature effects on the thermodynamics and the kinetics of LIB.

Experimental

Commercial cylindrical lithium-ion cells rated 700 mAh, 3.7 V are used in this study. Cells are 4.4 cm in length, 1.25 cm on diameter and 12.125 g in average weight. Firstly, cells are cycled three times between 2.5 V to 4.2 V at ambient temperature temperatures with an Arbin battery cycler using CCCV charging protocol (C/5 rate up to 4.2 V, then 4.2 V is applied till current dropped below C/25). This is followed by a discharge at C/5 rate to 2.5 V cutoff voltage. The achieved discharge capacity is $700 \text{ mAh} \pm 10 \text{ mAh}$. The last step of cycling is a full charge to 4.2 V.

Secondly, charged cells are placed in an environment chamber (Wötsch C4-340) and temperature T is set to -20°C , -10°C , 0°C , 10°C , 25°C , 35°C , 45°C and 55°C . At each T six discharge C-rates are applied C/5, C/2, 1C, 2C, 5C and 10C to 2.5 V cutoff voltage. Two cells are used for tests at each T and C-rate to check for reproducibility.

A fully discharged fresh cells is open in a glove box filled with dry argon. Anode and cathode materials were extracted and washed with DMC then dried in vacuum. Anode and cathode materials are analyzed by powder XRD with an X’Pert Pro diffractometer (reflection $\theta-\theta$ geometry, $\text{Cu K}\alpha$ radiation, receiving slit of 0.2 mm, scintillation counter, 30 mA, 40 KV). The diffraction data are collected at 0.02 step widths over a 2θ range from 10 to 70° . The surface morphologies of the composite powders are further measured by scanning electron microscope (JEOL-JEM-2011) and compositions of cathodes by energy dispersive analysis of X-rays (EDAX) systems from Oxford Instruments.

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Figure 1. (a) XRD patterns, (b) SEM image, (c) EDAX analysis of composite LiCoO_2 cathode; and (d) XRD patterns of graphite anode.

Results and Discussion

Electrode materials characterization.—Fig. 1a shows the XRD chart of the cathode material. The XRD chart is indexed in the hexagonal symmetry, space group $166, R\bar{3}m$. XRD results confirm no impurities are present in the cathode material. The SEM image presented in Figs. 1b–1c indicates cathode particles have multifaceted morphologies with particle in the $1\ \mu\text{m}$ range. Small particles are also present and belong to carbon black additive and polyvinylidene fluoride binder. Elemental analysis of cathode by EDAX (Fig. 1c) shows cobalt and oxygen elements in atomic ratio corresponding to LiCoO_2 . Therefore, the active cathode material consists of pure LiCoO_2 .

The XRD pattern on the anode material depicted in Fig. 1d shows peaks characteristic of highly graphitized carbon with strong peak at $2\theta = 26.6^\circ$ corresponding to the (002) diffraction line of graphite.

Isothermal discharge profiles.—The voltage vs. discharge capacity profiles at different C-rates and at same temperatures between -20 and $+55^\circ\text{C}$ are shown in Figs. 2a–2h and discharge capacity values are presented in Table I. Figs. 2a–2h and capacity values presented in Table I clearly shown that similar capacities close to 700 mAh are obtained at low (C/5) to high C rates of 2C between 55 and -10°C (highlighted in Table I). However, the energy density is not same at all rates and temperatures. There are two observable kinetics effects on discharge profiles with temperature and rate. The first effect is a voltage decay with rate at each temperature. This effect is expected since it includes electrode polarization and ohmic contribution. The second effect is a voltage delay (i.e. a decrease followed by an increase) at the beginning of discharge. This effect is noticeable at 10C-rate at temperatures $\leq 10^\circ\text{C}$ together with 5C-rate at -10°C and -20°C and 2C at -20°C . The voltage delay together with a decreased average discharge voltage at lower temperatures and higher rates are due to slow Li ion diffusion in anode^{22,23} and cathode^{24,25} and to lower electrolyte conductivity.²⁶ The increase in capacities at moderate C-rates of 1C and 2C at -20°C in Fig. 2-e) could be due to a local heating owing to Joule effect. The sloping discharge profile at 0.5 C and 1 C at -20°C as compared to flatter profile at 2C (Fig. 2-e) most likely results from a tradeoff between two conflicting factors; the discharge

rate and the Joule effect. Lower discharge rates tend to generate less Joule effect, therefore higher cell polarization which is controlled by temperature. Finally, at high C rates of 5C and 10 C at -20°C the voltage quickly drops below cutoff voltage of 2.5 V.

Galvanostatic discharge profiles.—Discharge profiles at same rate (a) C/5, (b) C/2, (c) 1C, (d) 2C, (e) 5C, (f) 10C, and different temperatures between 55°C and -20°C are depicted in the Fig. 3 and corresponding discharge capacities in Table I. From Fig. 3 and Table I it is very clear again that the cell capacities are almost identical at same rate and different temperatures between 55 and -10°C , except for -20°C . Noteworthy is the energy density at C/5 rate is almost similar for all the cells at all discharge temperatures. The cells' performance starts declining slowly at C/2 rate depending on temperature and the decay in energy density is significant at higher rates (1C and higher) and is maximum at lower temperatures. Performance limitations at high-rates of $>1\text{C}$ during discharge is essentially due to the cell overpotential of anode and cathode polarization and to ohmic drops. Accordingly, the cutoff voltage of 2.5 V is reached before the cell is fully discharged, which translates to lower energy density. From the Figs. 2–3 and Table I, it can be concluded that the rate and temperature at which lithium ion cells are discharged show cumulative effects on the electrochemical performance. The discharge voltage of cells decreases with the decreasing of temperature and increasing discharge rate.

Ragone plots and energy-power index (EPI).—In order to analyze the change in energy with respect to temperature and C-rate, it is useful to have all the parameters in single Ragone plot. Ragone charts of lithium ion cells discharged at different C-rates and temperatures are shown in Fig. 4. It is clear from Ragone charts that the cells discharged at high C-rates have low energy density and cells discharged at lower temperatures show less efficiency in terms of energy compared to lithium ion cells discharged at high temperatures. As the temperature increases, there is an increase in efficiency of lithium ion cells.

The Ragone charts obtained at 25°C , 35°C , 45°C and 55°C are very close making it difficult to differentiate their efficiencies. In this temperature range the cells energy output is almost stable. This should

Figure 2. Discharge profiles of lithium ion cells at different C-rates at (a) 55°C, (b) 45°C, (c) 35°C, (d) 25°C, (e) 10°C, (f) 0°C, (g) -10°C, and (h) -20°C.

Table I. Discharge capacities for lithium ion cells discharged at different C rates at different temperatures.

Temperature (°C) → Rate ↓	55	45	35	25	10	0	−10	−20
	Discharge Capacity (Ah)							
C/5	0.704	0.705	0.706	0.714	0.706	0.705	0.704	0.257
C/2	0.709	0.709	0.7	0.6911	0.718	0.708	0.706	0.382
1C	0.684	0.709	0.709	0.708	0.709	0.682	0.706	0.570
2C	0.691	0.706	0.7	0.697	0.706	0.703	0.698	0.680
5C	0.673	0.695	0.689	0.688	0.695	0.687	0.681	-
10C	0.642	0.662	0.655	0.672	0.694	0.682	0.666	-

Figure 3. Discharge profiles of lithium ion cells at different temperatures under (a) C/5, (b) C/2, (c) 1 C, (d) 2 C, (e) 5 C, (f) 10 C.

Figure 4. Ragone chart of lithium ion cells discharged at different temperatures.

be assigned to opposite effects as temperature increases; an increase in electrode kinetics and electrolyte conductivity on one hand and a decrease in electrode utilization rate due to the overall exothermic character of discharge reaction on the other hand. In order to account for the cell energy performance over the whole power range we introduce the integrated power energy function, IPE. IPE is achieved by integrating the Ragone charts. And individual integrated energy or integrated power are obtained by taking the square root of the obtained integrated values in Eq.

$$IPE(T) = \sqrt{\int_P E(P) dP|_T} \quad [1]$$

Note IPE is expressed in $Wh^{1/2} kg^{-1}$.

To normalize IPE data we use the energy power index (EPI), where the obtained square root integrated values are converted to percentages by considering the value obtained at 25°C as standard or 100% as shown in Eq. 2.

$$EPI(T) = 100 \sqrt{\frac{\int_P E(P) dP|_T}{\int_P E(P) dP|_{25^\circ C}}} \quad [2]$$

EPI or normalized electrochemical performance of lithium ion cells presented in Fig. 5 increases linearly from $-10^\circ C$ to $25^\circ C$ then EPI stabilizes between $25^\circ C$ and $55^\circ C$. Table II summarize the EPI and IPE data.

Figure 5. Energy-power index (EPI) profile of lithium ion cells.

Table II. IPE values of lithium-ion cells vs. temperatures and corresponding EPI values in percentages.

Temperature ($^\circ C$)	IPE ($Wh^{0.5} kg^{-1}$)	EPI (%)
-10	554.4	93.34
0	571.09	96.15
10	579.3	97.49
25	594.2	100
35	591.7	99.85
45	594.3	100.06
55	597.1	100.47

The low efficiency of the lithium ion cells at low temperatures is due to reduced electrolyte conductivity and lithium ion diffusivity. As temperature increases up to $25^\circ C$ the EPI increases linearly mostly due to improved lithium ion transport kinetics. Then the EPI increase becomes almost negligible above $25^\circ C$. If the specific cell chemistry based on graphite anode and $LiCoO_2$ cathode operating cells ambient temperature should yield the best in terms of power and energy together with cycle life. In fact it is established that as operating temperature increases the cycle life decreases due to enhanced electrode and electrolyte degradation. Noteworthy is the good performance of these cells over wide ranges of temperatures and discharge rates provided charging is performed at the ambient temperature and under relatively low rates. A study is currently underway in our group on the effect of charging at high temperatures under different rates on the energy and power performances of the graphite/LCO cells. We are also investigating on the role of the cell chemistry on the EPI, which may help selecting the best chemistry according to varying discharge temperatures and rates.

Conclusions

Discharge temperature and C-rate have great influence on the performance of graphite/LCO lithium ion battery. Using integrated energy vs. power function and normalizing data to a new Energy-Power Index 'EPI' we show that EPI increases linearly with temperature up to $25^\circ C$ and remain almost constant between $25^\circ C$ and $55^\circ C$. This suggests that operating these cells close to $25^\circ C$ should provide the best tradeoff between energy storage performances and cycle life. An increase in EPI with temperature is expected as at low temperatures the performance is controlled by the cell reaction kinetics and by the electrolyte conductivity. The fact that EPI stabilizes above $25^\circ C$ is less expected and denotes a tradeoff between the cell reaction kinetics and thermodynamics, which are respectively favorable and unfavorable to the overall energy output.

A decrease in energy density at low temperatures and high rates is mainly due to a decay in discharge voltage rather than discharge capacity. At low temperatures and high rates cells show a voltage delay perhaps due to local heat due to Joule effect.

More work is needed to understand the effect of the cell chemistry and the state of health on the EPI.

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