

Electrochemical Prozac: Relieving Battery Anxiety through Life and Safety Research

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Abstract

The relatively recent application of lithium ion battery technology to automotive applications has led to a resurgence of plug-in electrified vehicles globally. A mass adoption of this evolving technology will be further enabled by achieving future cost reductions and performance improvements. As a result, methods to efficiently optimize the prediction and design of this technology for life and safety are a field of active research. Examples of the new analytical test tools and methods are described which seek to advance the understanding of life and safety response of lithium ion batteries. As these tools and methods mature, the ability of lithium ion technology to supplant liquid hydrocarbons fuels in the transportation sector will increase over time, thereby positively contributing to the global environment.

Introduction

Lithium ion batteries are enabling a new generation of electrified vehicles to be commercialized by a range of global automakers. A variety of governments including the United States, European Union, China and Japan have announced increasingly strict fuel economy regulations for their respective jurisdictions. The modern fossil fuel powered automobile has been the subject of continuous engineering improvement for over one hundred years [1]. Comparatively, modern electrified automobiles are a relatively new technology, yet their potential for petroleum displacement makes them a key component of virtually all automakers current and future product portfolios.

In this paper, the different performance requirements placed on batteries by the broad range of electrified vehicles will be examined. Additionally, new tools to improve the identification and prediction of failure mechanisms will be introduced. A discussion of existing safety testing and the results of recent research efforts in this area will be presented next. By addressing the sources of uncertainty in battery failure mechanisms, either performance or safety related, researchers will enable significant improvements in future generations of battery power vehicles.

Transportation Battery Needs

Electrified vehicles can be designed to have varying levels of their traditionally liquid fuel powered performance features electrified. It is possible to classify the various types of electrified vehicle designs by their increasing levels of electrification (Figure 1). In order of increasing power and energy demands, commonly electrified vehicle features include stop-start, regenerative braking, motor assist and electric vehicle (EV) drive. The ability of hybrid electric vehicles (HEVs) to perform these functions allows for differentiation between stop-start, mild, strong and plug in electric hybrids (PHEVs). HEVs are distinguished by the ability to convert their liquid fuel energy into either mechanical or electrical energy. Likewise, plug in vehicles can be subdivided into either PHEV or EV labels depending on whether they consume fossil fuels at all (PHEVs) or are purely electric (EVs).

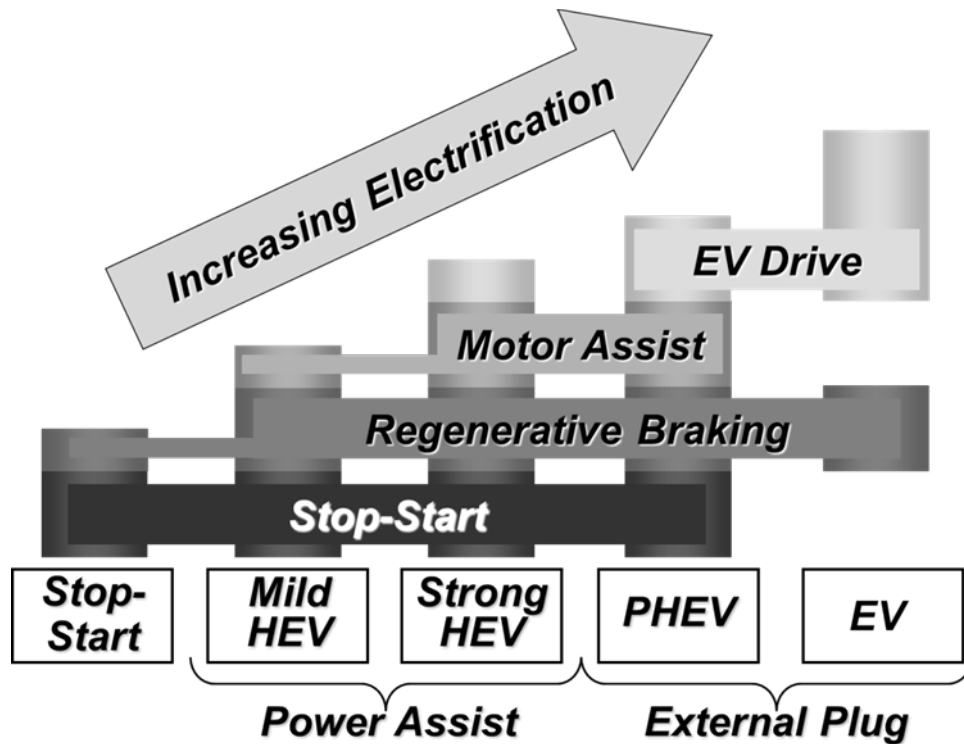


Figure 1: Electrified Vehicles Types as a Function of Electrification [2]

The performance and maturity of various battery chemistries has shaped their electrified vehicle type suitability and commercialization over the last twenty years. In recent years the maturation of lithium ion technology is actively driving a migration away from nickel metal hydride batteries for most HEV and EV applications. However, due to remaining low temperature and cost challenges, it is predicted that lithium ion technology will have a difficult time wholly supplanting lead acid chemistries in the stop-start market (Table 1).

Vehicle Type	Past (1990-2010)	Near Term (2010-2015)	Future (2015+)
Stop-Start	Lead Acid	Lead Acid	Lead Acid & Lithium Ion
HEV (Mild & Strong)	Nickel Metal Hydride	Lithium Ion & Nickel Metal Hydride	Lithium ion & Nickel Metal Hydride (Toyota)
PHEV	N/A	Lithium Ion	
EV	Lead Acid & Nickel Metal Hydride	Lithium Ion	

Table 1: Commercialized Battery Chemistry as a Function of Vehicle Type

The various electrified vehicle types place very different power, energy and cycle life demands on their batteries. Supporting the large variety of electrified feature requires the availability of a wide range of power, energy and cycle life as shown in (Table 2). Cycle life is strongly affected by the extent of the battery's capacity which is used in each cycle. Likewise, designing for high energy is well known to have a direct impact on power delivery as a tradeoff.

Vehicle Type	Power (kW)	Energy (kWh)	Cycles (1,000)
Stop-Start	< 10	< 0.4	75 – 450 (Charge Sustaining)
HEV (Mild & Strong)	Mild: 10-20 Strong: 20-40	Mild: < 1 Strong: 1-2	300 (Charge Sustaining)
PHEV	> 40	5 – 16	300 (Charge Sustaining) 5 (Charge Depleting)
EV	> 80	> 12	5 (Charge Depleting)

Table 2 Battery Requirements as a function of Vehicle Type

Use cycles can be defined by the state of charge (SOC) that is used which commonly differ depending on the application. The SOC % swept is typically narrow (charge sustaining, CS) in high power or wide (charge depleting, CD) in high energy applications (Figure 2). The size of the SOC range used and cycle life are known to be inversely proportional for all battery chemistries and this tradeoff drives another important vehicle battery design choice.

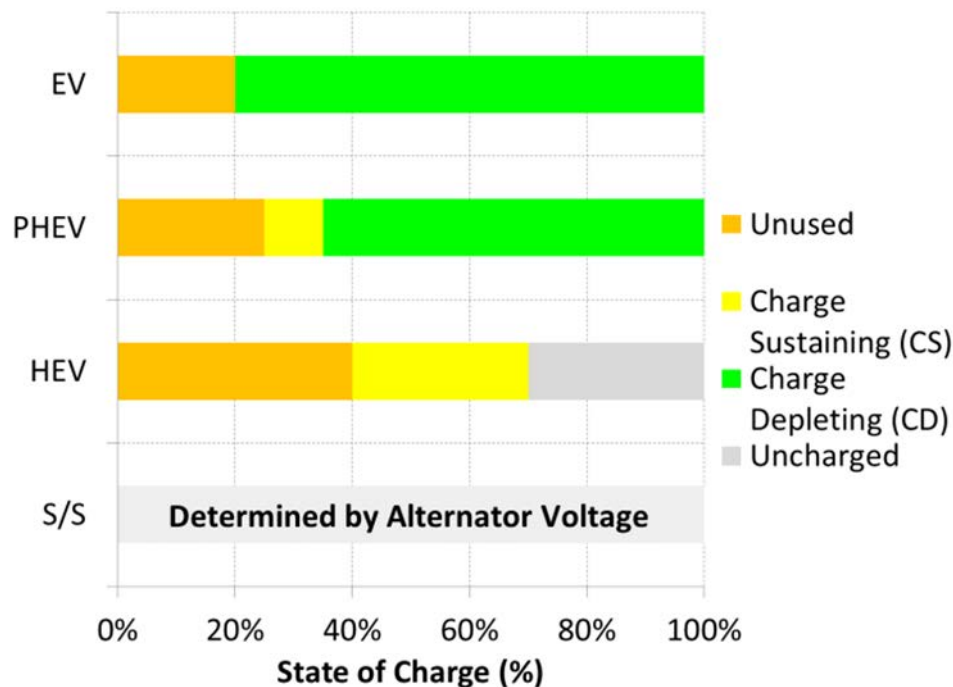


Figure 2 SOC used as a function of Vehicle Type [3]

Clearly, designing a vehicle battery involves balancing the competing performance figures, including energy and power. As a result, a variety of automotive industry/government organizations such as the United States Advanced Battery Consortium (USABC) [4], the European Council for Automotive Research & Development (EUCAR) [5] and the New Energy and Industrial Technology Development Organization (NEDO) [6] have created a set of electrified vehicle performance targets including energy and power. Comparing the goals of these organizations to the performance of various EV and consumer electronics packs, based on the well-known 18650 cell, is instructive regarding these interactions (Figure 3).

In Figure 3, the pack level specific energy (energy by weight) and specific power (power by weight) targets of various organizations and performance achieved by various designs is shown. The goals of each of the organizations listed above (USABC, EUCAR and NEDO) are shown in pink, green and red respectively. The dark blue points represent current commercial 18650 cell performances, downgraded

as they would function in a pack design. Those cells are typically designed as either high power or high energy due to the inherent tradeoffs involved in optimizing for either application. A triangle showing the design possibilities for the 18650 approach is shown. For context, the historical performance of various Ford Electric Vehicle battery packs are shown in Orange, ranging from the Lead Acid Ford Ranger in 1998 to the Lithium Ion Ford Focus in 2011. The performance of other carmaker's electric vehicles, Nissan and Tesla, are also shown for comparison.

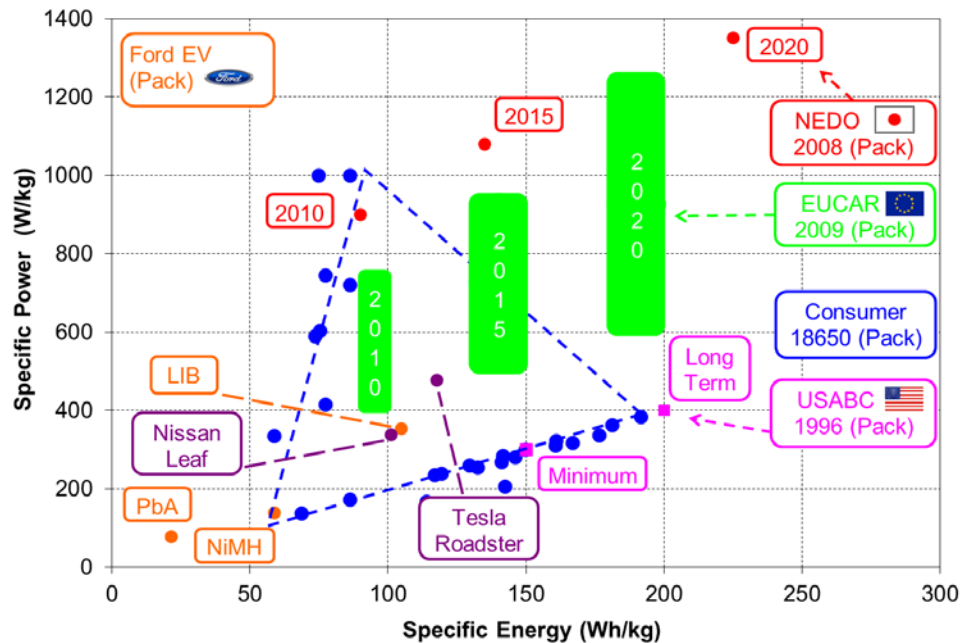


Figure 3 Energy and Power EV Performance and Targets [4, 5, 6]

Life Prediction

When determining the ability of a battery technology to meet future life requirements a high level of confidence is required. Consequently, qualifying a new technology for production can take several years of validation testing to ensure the typical 10 year / 150,000 mile vehicle life requirement.

Calendar ageing mechanisms are often accelerated by high temperature protocols that take advantage of a battery's Arrhenius kinetic mechanisms. Cycle life acceleration is more problematic, as its decay mechanism is more difficult to replicate through established techniques. Recently, an emphasis on high precision battery testing has been proposed as a method to accelerate the understanding of cycle life based decay mechanisms [7]. The impact of improvements in battery testing precision hinges on the error propagation of imprecise measurements used as the basis for future predictions as is shown in Figure 4.

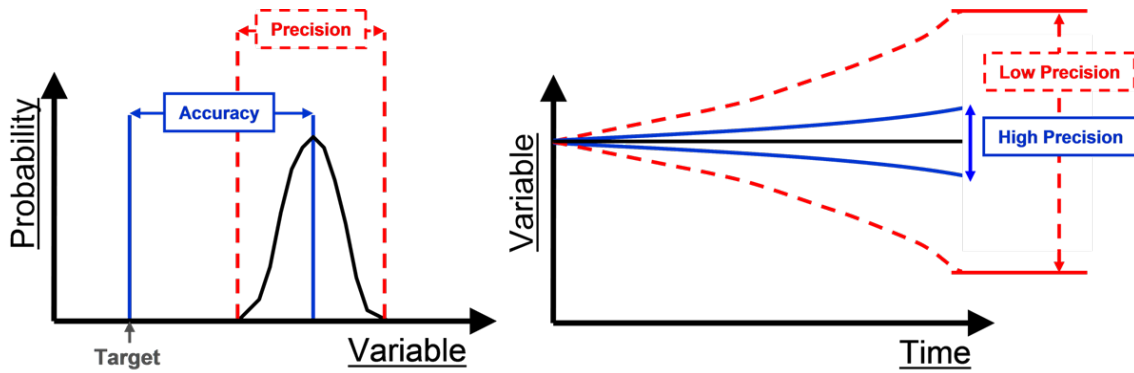


Figure 4 Precision vs. Accuracy (L) and Time (R)

Low Current

To understand the specific impact of imprecise battery capacity measurements, the example of columbic efficiency (CE) in consumer electronic cell life requirements is shown in Figure 5. Columbic efficiency is defined as the number of electrons that leave a battery, divided by the number that entered. Based on this definition, a theoretically perfect battery would have a CE value of unity or 100%. If a cell was to deliver the exact amount of columbic efficiency (99.954% or a deviation of 446ppm from ideal) required to achieve 20% capacity decay in 500 cycles, the curve shown in Figure 5L would be achieved. Existing battery test equipment is capable of columbic efficiency errors of approximately this order of magnitude or 350ppm. To be relevant to EVs, where an order of magnitude improvement in cycles to 5,000 is required, testers would need a corresponding order of magnitude improvement to approximately 50ppm error. By looking at the consumer electronic example in Figure 5R, when the error is on the same order of magnitude (350ppm) of the allowable deviation (446ppm), the wide impact on predicted future capacity can be observed clearly and compared to the improved predictability at 50ppm.

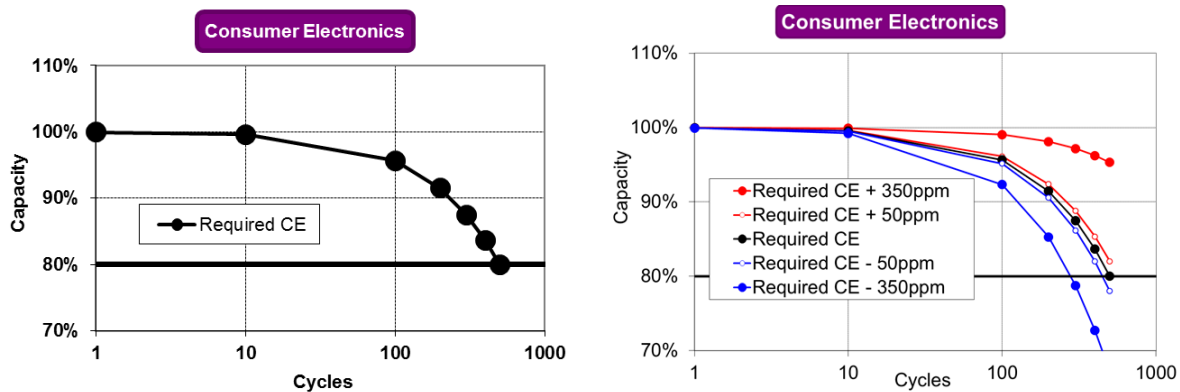


Figure 5 Columbic Efficiency Required (L) and Uncertainty (R)

Recognizing this opportunity for improvement, there has been a rising interest in academia in high precision battery testing. Current academic systems have been report to achieve 100ppm error in terms of columbic efficiency, with a stated goal of achieving 10ppm in future systems [7, 8]. It should be noted that each of these systems is at low current rates of single digit amps at the most. The impact of using a 100ppm system on the imprecision of columbic efficiency measurements is seen in Figure 6. As can be seen in Figure 6, the closer that a battery's CE gets to unity (Right side), the flatter its capacity decay cycle becomes over time (Left side).

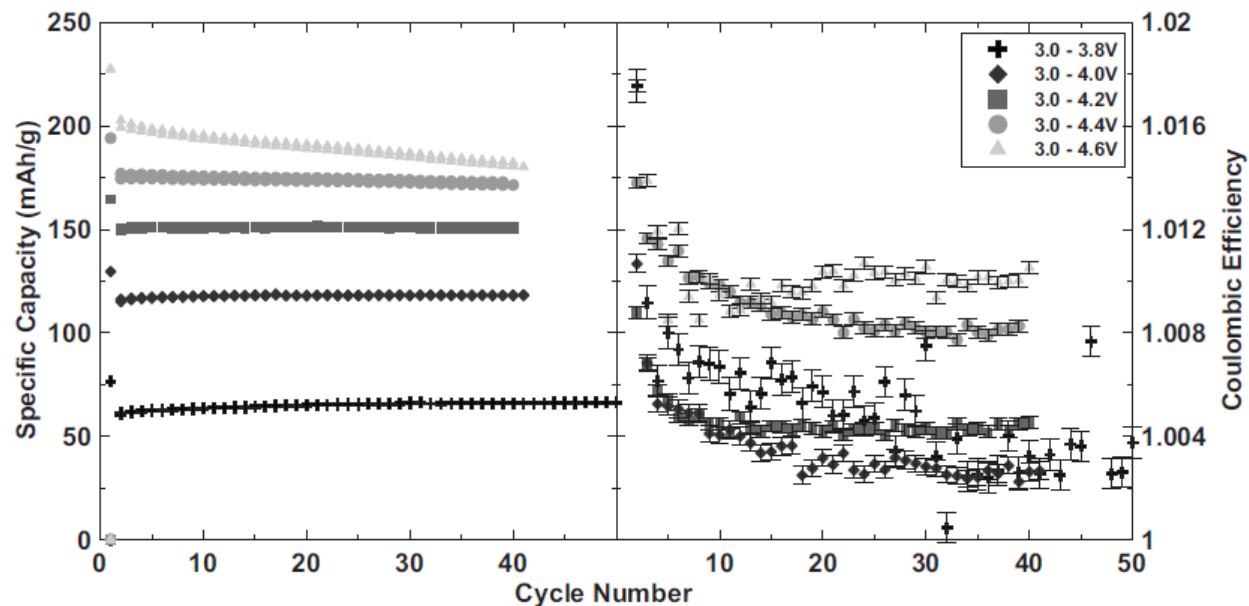


Figure 6 Capacity and High Precision Coulombic Efficiency as a function of Charge Voltage [7]

High Current

To be relevant to automotive testing, currents of at least several hundred amps, as would be seen during traditional product validation condition, must be supported. The range of power and corresponding current demands seen in representative vehicle duty cycles are shown in Figure 7. These curves represent life cycling patterns. Higher currents are achieved in power characterization patterns, and these curves show values ranging from +300 to -120A for the various applications. To address the challenge associated with improving the precision of capacity predictions at these higher current and power levels, the DOE ARPA-E office has awarded a research contract to Ford, Arbin and Sandia National Labs to build a commercially viable 50ppm 200A tester [9].

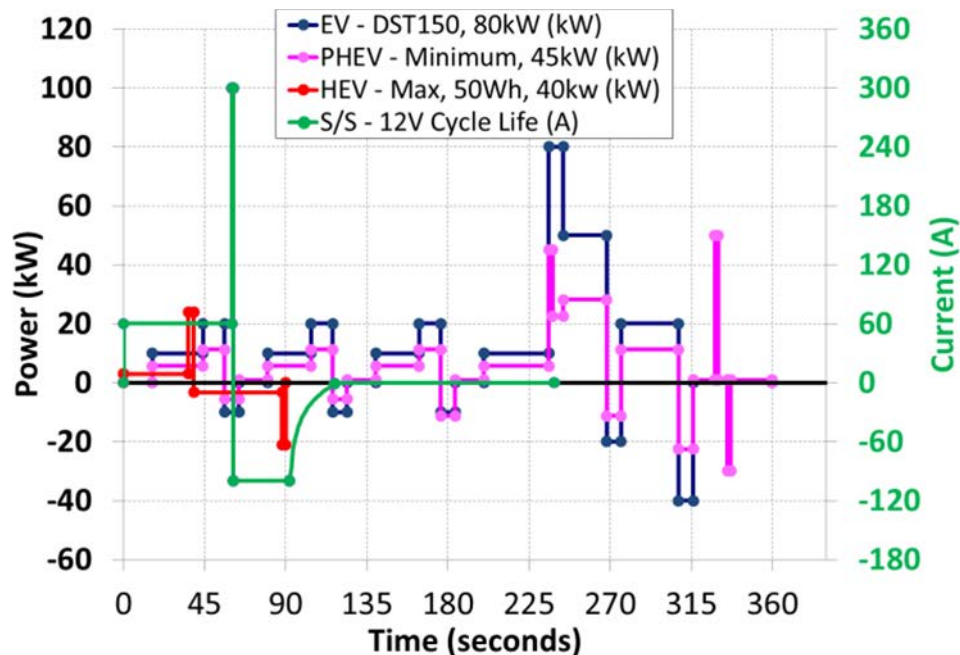


Figure 7 Power and Current Levels of USABC Duty Cycles by Vehicle Type [10, 11, 12, 13]

Temperature

Another of the biggest challenges in testing at high currents is mitigating the resulting temperature changes which can occur in the test cells as well as the tester itself (such as shunts and amplifiers). When focusing on the test cell, a thermal image of an automotive cell as in Figure 8 shows the thermal gradients which can be created. The top of the cell is affected by having access to the connecting terminals which serve as excellent thermal wicks given the strong thermal conductivity behavior of the highly electronically conductive metals used. The order of magnitude of the gradient can vary widely depending on cell design and test pattern run, but its orientation remains the same.

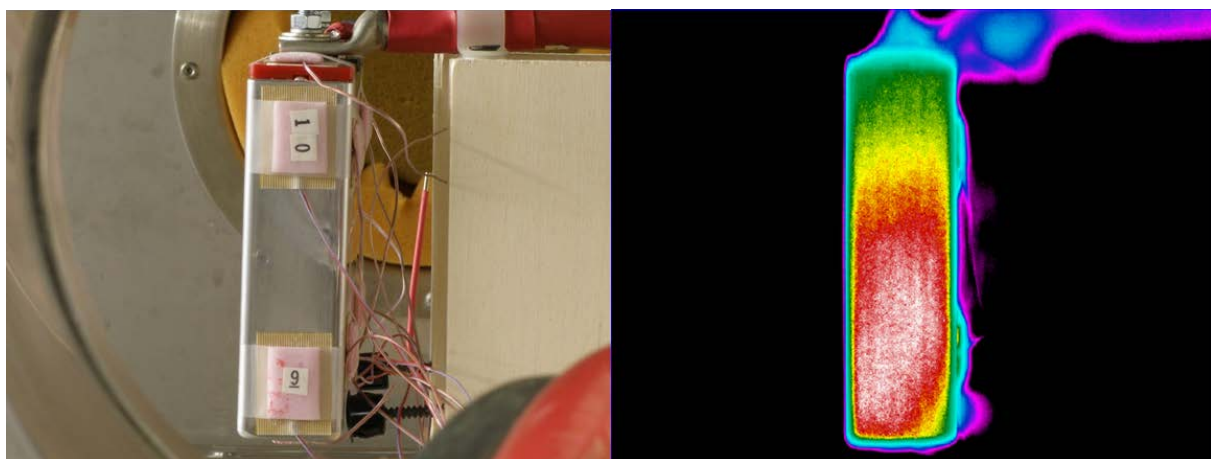


Figure 8 Thermal Imaging of an Automotive Lithium Ion Cell

To explore the impact of high current driven thermal gradients during high precision testing, the Ford ARPA-E team has been developing various thermal control strategies. An example of one such strategy is shown in Figure 9 involving two thermoelectric (TE) heater/cooler assemblies surrounding a single cell.

By coupling the intimate cooling capacity of the TEs with feedback (cell temperature) and feedforward (current delivery pattern and its resulting cell driven temperature change), it is possible to effectively neutralize temperature fluctuations during the testing and to study its effects, for example, (dV/dT) on precision.

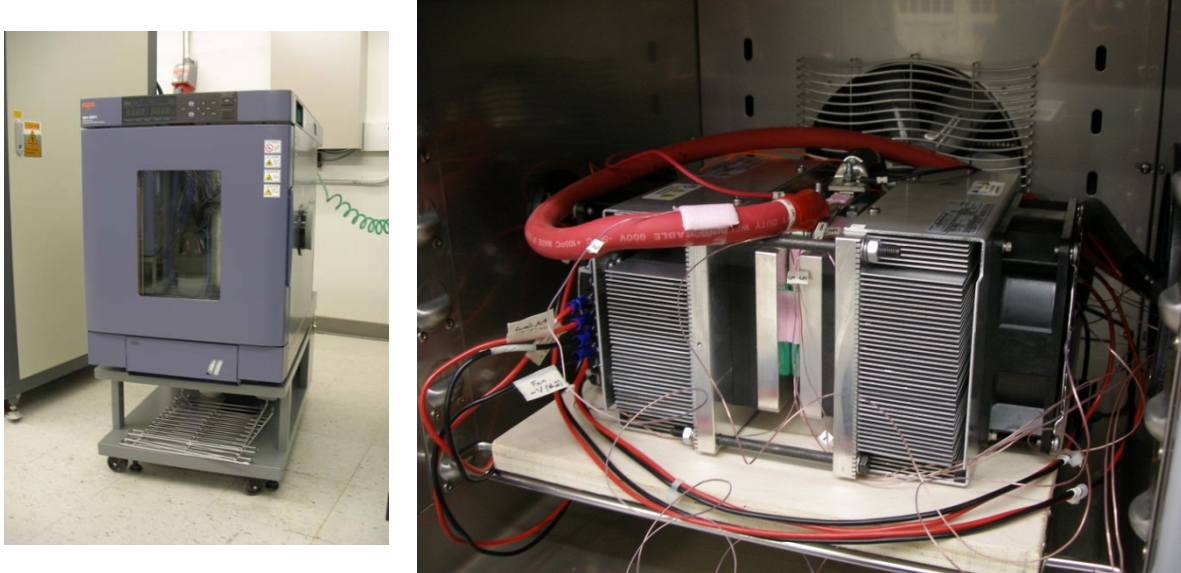


Figure 9 Thermal Chamber (L) and Thermoelectric Cell Controller (R)

Battery life decay mechanisms can be subdivided into those which are use and calendar dependent. As mentioned previously, the Arrhenius based mechanisms of calendar aging lend themselves well to accelerated testing. It is the hope that high precision battery testing will provide similar insights and tools to understand and accelerate use-aging mechanisms.

Safety Prediction

Modern electrified vehicles have been sold for the last twenty years. A wide range of current and evolving government regulations and industry standards cover all aspects of automotive design. In the US, government automotive regulations take the form of Federal Motor Vehicle Safety Standards (FMVSS) requirements, with FMVSS 305 primarily focusing on electrified vehicles. The three main requirements of FMVSS 305, electrolyte spillage, physical retention and electrical isolation are described in Table 3.

Section		Requirement
S5.1	Electrolyte Spillage from Propulsion Batteries	<5L Spillage Total, 0 into Passenger Cabin 30 minutes after barrier test
S5.2	Electrical Energy Storage / Conversion Device Retention	Energy Device shall remain attached to vehicle and out of passenger cabin
S5.3	Electrical Safety	Maintain Isolation >100ohm/volt with monitoring or >500 ohm/volt without monitoring

Table 3 US Federal Motor Vehicle Safety Standard 305 Requirements [4]

As the technology and systems have evolved, FMVSS 305 has been revised numerous times since it was first issued in 2000. With the recent application of lithium ion batteries to automotive applications, the US automotive regulator, the National Highway Traffic Safety Administration (NHTSA), has performed a

variety of research projects to study the safety behavior of the technology. This research topic is one of global concern and impact, as is evidenced by the launching of a Global Technical Regulation (GTR) development committee by the UNECE [15]. The GTR action has seen active participation from the industry and regulatory bodies of Europe, Asia and North America.

One of the NHTSA sponsored research projects has been performed by Ford in collaboration with Ricardo, an engineering consultancy. The goal of this effort was to develop a set of recommendations for vehicle level safety tests and performance metrics for possible future NHTSA consideration. The Ford approach to NHTSA's research request has been to study parts level (cell strings, modules and packs) behaviors as a means to arrive at quantifiable vehicle level recommendations. The most common way to describe the response of a lithium ion battery to abuse is to use the EUCAR rating system shown in Table 4. The EUCAR system assigns a response score from 0 to 7 across the range of increasingly severe battery responses. For example a EUCAR score of 5 denotes a battery experienced a fire or flame event.

Score	Title	Description
0	No Effect	No Effect. No loss of functionality
1	Passive Protection Activated	No defect; no leakage; no venting, fire, or flame; no rupture; no explosion; no exothermic reaction or thermal runaway. Cell reversibly damaged. Repair of protection device needed.
2	Defect / Damage	No leakage; no venting, fire, or flame; no rupture; no explosion; no exothermic reaction or thermal runaway. Cell irreversibly damaged. Repair needed.
3	Leakage (Δ mass < 50%)	No venting, fire or flame*; no rupture; no explosion. Weight loss <50% of electrolyte weight (electrolyte = solvent + salt).
4	Venting (Δ mass > 50%)	No fire or flame*; no rupture; no explosion. Weight loss of $\geq$ 50% of electrolyte weight (electrolyte= solvent + salt).
5	Fire or Flame	No rupture; no explosion (i.e., no flying parts).
6	Rupture	No explosion, but flying parts of the active mass.
7	Explosion	Explosion (i.e., disintegration of the cell).

Table 4 EUCAR Battery Abuse Response Rating [16]

A rigorous fault tree analysis (FTA) was performed by the Ford team to consider all the possible lithium ion specific faults a vehicle could experience. From the FTA process a ranked list of priority hazards was developed for further exploration. The three top priority faults of crush, overcharge and short circuit were selected for procedure and design of experiments development. A global survey of existing battery regulations and industry standards was then performed to serve as a starting point for the test procedure development process. These draft test procedures were then tested at three different locations in the US. These sites evaluated string, module and pack hardware built up with three different types of lithium ion cells. This wide ranging experimental testing and analysis allowed for significant test procedure refinement and confidence in battery responses.

Abuse Categories

Typically, battery abuse tests fall into one of three possible categories: mechanical, thermal and electrical. The following presents the range of testing in each test type and, where appropriate, the results and recommendations of Ford's research are provided.

Mechanical

The range of battery safety mechanical test methods throughout the world is shown in Table 5. As this table shows, there is often a lack of consensus amongst the various regulations and standards about which testing should be performed. The most common test type is the dual combination of mechanical shock and mechanical integrity testing, which typically features a mechanical crush event occurring to the battery.

Test Type		Industry Standard					Government Regulation			
		Freedom Car	SAE J2929	SAE J2464	ISO 12405-1	ISO 12405-3	UN 38.3	ECE R100	Q/C-T 743	KMVSS 1.48
Mechanical	Mechanical Integrity	•	•	•		•		•	•	
	Penetration	•		•					•	
	Immersion	•	•	•		•				•
	Roll-Over	•		•						
	Drop	•	•	•		•	•		•	•
	Mechanical Shock	•	•	•	•	•	•	•		
	Vibration		•		•	•	•	•	•	

Table 5 Mechanical Safety Test Matrix

Following the Ford FTA process, crush testing was also identified as a priority fault. The large number of existing crush related test procedures were reviewed leading to the selection of the Freedom Car procedure as a starting point. A notable modification to this procedure is the attempt to stratify the battery response by breaking up the crush motion into 20 5% increments. By crushing in many small steps over approximately one hour, it is possible to determine the impact on time in the progression of a fault.

The summary of the crush testing results as a function of crush direction and number of crush steps is show in Table 6. The displacement values shown are the degree of crush of all hardware units at which a EUCAR 5 point was first observed (green) and after which all hardware experienced EUCAR 5 responses (red). The yellow region therefore describes the zone of variability where some hardware experienced EUCAR 5 responses and others did not.

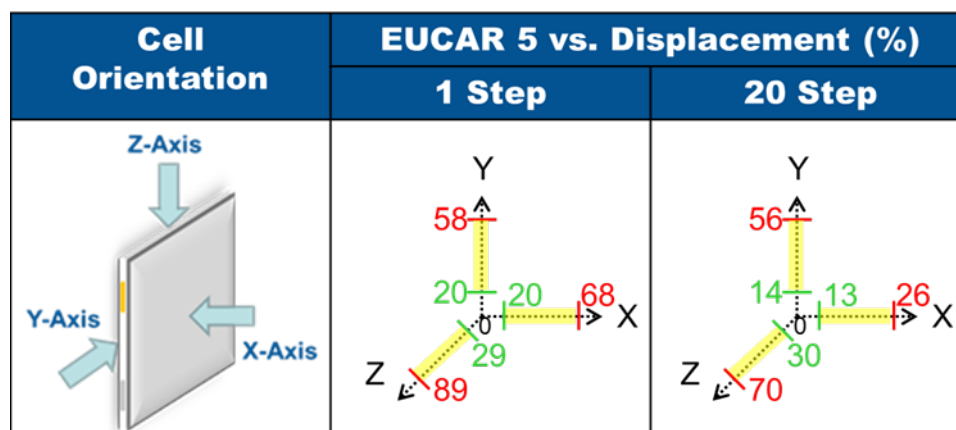


Table 6 Crush Orientation and Response

All hardware was able to be crushed to >13% displacement without a EUCAR 5 response. Additionally, the X-axis (the broad plane of the cell) had the smallest ranges of response, indicative of testing consistency. Designing a parts level crush test in the other axes (Y and Z) is non-trivial due to the tendency of hardware to move out of the plane of crush when not constrained in a vehicle. As a result, it was concluded that crush testing only be performed at the vehicle level and in the same manner as current FMVSS crash tests. If a battery was to experience mechanical damage during these tests, the test metrics shown in Table 6 could be used to assess the testing result.

Thermal

The set of available thermal testing protocols (Table 7) shows an even larger spread of uses than the mechanical (Table 5) or electrical (Table 9) procedures. The tests closest to achieving a consensus position are either the thermal shock or the fire exposure test. Thermal shock testing typically involves exposing a battery pack to a cycle of warm and cold temperatures and evaluating its performance. Done in this manner, this test is more of a durability evaluation procedure than an abuse failure mechanisms investigation tool.

Test Type		Industry Standard					Government Regulation			
		Freedom Car	SAE J2929	SAE J2464	ISO 12405-1	ISO 12405-3	UN 38.3	ECE R100	Q/C-T 743	KMVSS 1.48
Thermal	Thermal Stability	•								
	Fire Exposure	•	•	•		•		•		•
	High Temperature Storage	•							•	•
	Cycle w/o Thermal Control	•	•	•		•		•		
	Thermal Shock	•	•	•	•	•	•	•		
	Humidity Exposure		•		•	•				
	Passive Propagation			•						

Table 7 Thermal Safety Test Matrix

To investigate fire exposure, an established ECE regulation which calls for a fire exposure test to be performed on plastic fuel tanks used in vehicles to evaluate their robustness has been referenced for battery abuse testing. This test from the ECE R34 regulation has been adapted by various groups to serve as the basis for a battery fire exposure test (Table 8). It involves directly exposing a battery to burning pool of liquid fuel (Phase B) and then indirectly through a screen of refractory bricks (Phase C) and evaluating the hardware response (Phase D).

Phase A: Pre-heating 60 seconds	Phase B: Direct Exposure to Flame 70 seconds
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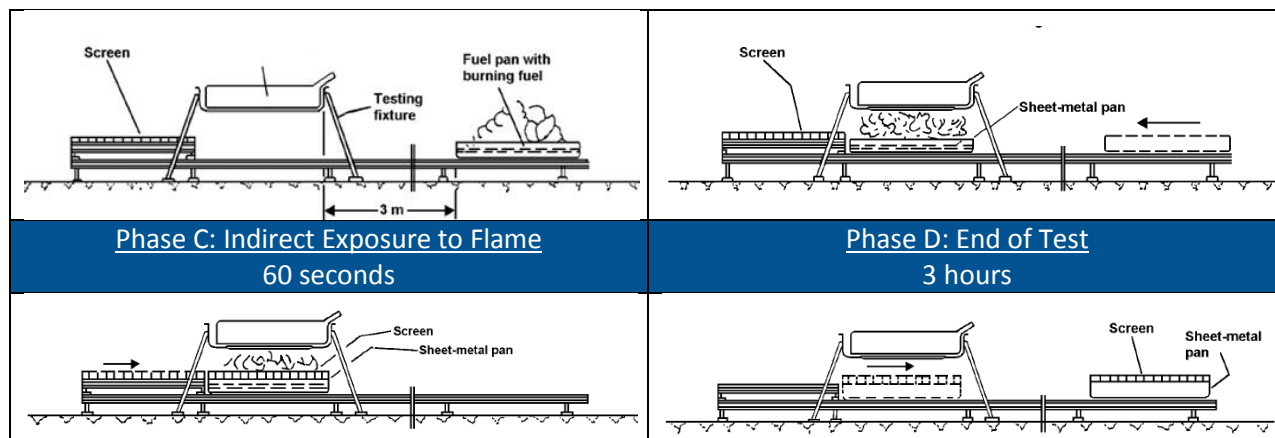


Table 8 ECE R100 Fire Exposure Test [17]

Electrical

The electrical subcategory of battery safety testing (Table 9) shows more consistency of application than the mechanical (Table 5) and thermal (Table 7) based procedures. All the reviewed regulations and standards feature overcharge, short circuit and over discharge test procedures. Although there are minor differences in test details (current, duration or resistance for example), the general procedures are also very similar.

Test Type		Industry Standard					Government Regulation			
		Freedom Car	SAE J2929	SAE J2464	ISO 12405-1	ISO 12405-3	UN 38.3	ECE R100	Q/C-T 743	KMVSS 1.48
Electrical	Overcharge	•	•	•	•	•	•	•	•	•
	Short Circuit	•	•	•	•	•	•	•	•	•
	Over Discharge	•	•	•	•	•	•	•	•	•
	High Voltage Exposure		•							
	Partial Short Circuit	•								
	Separator Shutdown			•						

Table 9 Electrical Safety Test Matrix

The Ford team investigated battery responses to both overcharge and short circuit, in addition to the previously described work done on crush. Similar to the mechanical tests, attempts at discretizing the moment of battery response led to a start/stop approach to overcharge electrical energy delivery using 20 5% state of charge (SOC) intervals. The results of both this start/stop and also continuous current delivery test patterns in terms of the SOC % at the EUCAR 5 event are shown in Table 10. It can be seen that no hardware had an event prior to 134% overcharge. As a result, in the unlikely event that a vehicle was able to allow an overcharge to occur, these figures of merit can be used to assess the test's outcome.

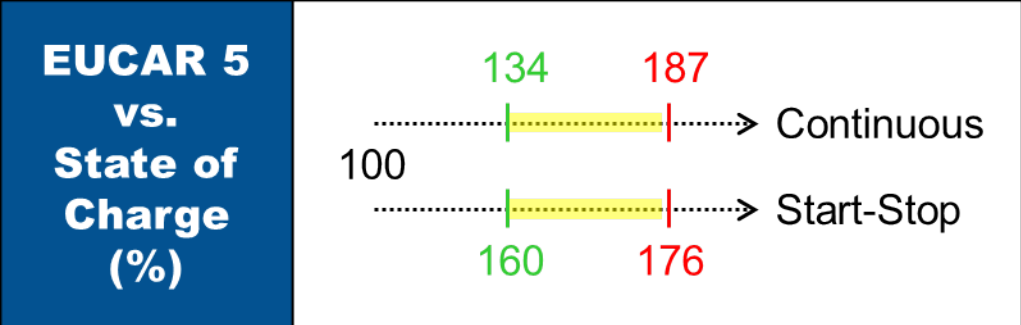


Table 10 Overcharge Pattern and Response

Short circuit abuse testing of batteries commonly uses shunts of various resistances. Typical procedures define specific shunt resistances (such as 10mΩ), irrespective of the test hardware details. This approach ignores the Ohms law behavior of the short circuit reaction which dictates that the severity of the short is dependent on the relative resistance of the hardware to the shunt. By exploring a range of relative resistance values it is possible to correlate the resulting test current and shunt resistance to the likely test outcome. The threshold currents and resistances for a EUCAR 5 event are shown in Table 11. Reviewing a vehicle battery’s internal resistance and the current limits imposed by the pack’s fusing is informative of the likely abuse response.

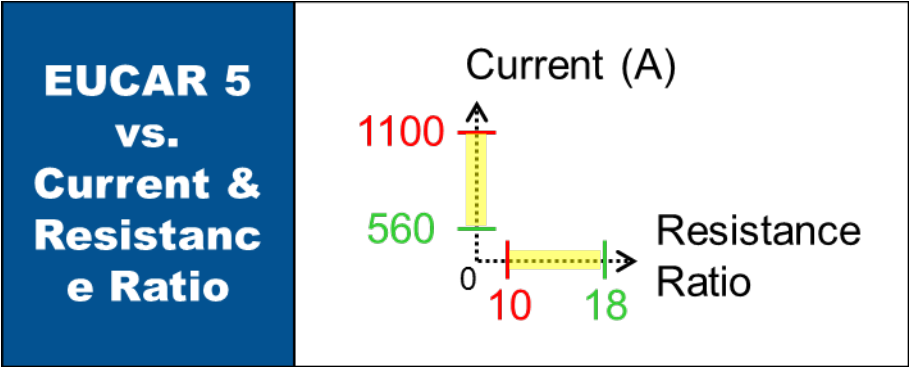


Table 11 Short Circuit Response

Over the last two decades, improvements in computing power and modeling capabilities have revolutionized automotive design and in particular crash performance development. A large number of experiments were performed to develop the crush, overcharge and short circuit metrics and boundary conditions as shown in Table 6, Table 10 and Table 11. Future research in this area should seek to couple experimental results with simulations (see Figure 10) in the hopes of supplanting the need for trial and error experimentation [18].

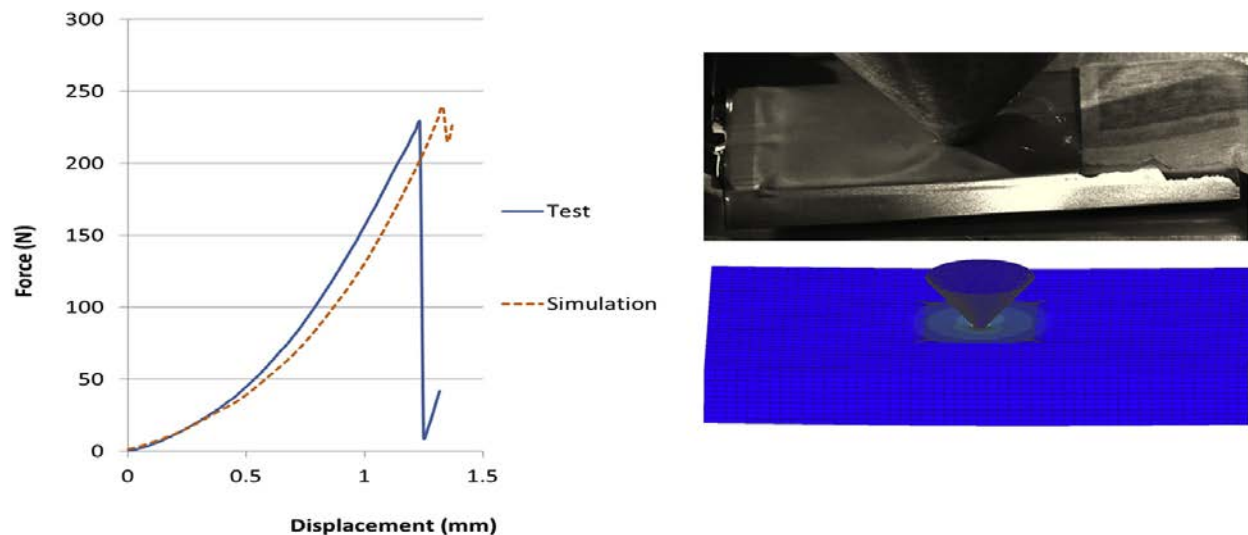


Figure 10 Cell Crush Modeling [18]

Conclusions

The success of long term vehicle electrification efforts will depend heavily on the performance of their requisite batteries and the current revival of electrified vehicles is being enabled by improvements in lithium ion batteries. The new opportunities provided by the increased energy and power capabilities of lithium ion technology also come with familiar uncertainties regarding battery life and safety. Batteries appropriate for automotive applications are required to pass extensive validation procedures to demonstrate durability. In the area of life, new testing tools to improve the prediction and identification of electrochemical failure mechanisms were described. Regarding safety and responses to abusive failures, the broad range of tests available globally were introduced and the results of recent industrial research were examined.

Acknowledgements

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