



A Technical Assessment of High-Energy Batteries for Light-Duty Electric Vehicles

GCEP Energy Assessment Analysis
Fall 2006

Abstract

Widely successful electric vehicles could allow low-carbon electricity to replace fossil hydrocarbons as the primary energy carrier of the transportation sector, but battery technology is a major limitation to electric vehicles supplying an energy service comparable to hydrocarbon-fueled vehicles. New battery technologies with higher specific energy, lower cost, and longer calendar and cycle lifetimes may be required to enable a successful electric vehicle. Current research efforts towards these goals include high-capacity and low-cost lithium intercalation cathode materials, anodes with higher lithium capacity, and alternative approaches involving redox couples, polyvalent cations, and oxide electrodes undergoing conversion or displacement reactions. Fundamental materials exploration is required to achieve a new generation of battery technology and a new, widely accepted generation of electric vehicles.

Table of Contents

Foreword	3
1. Introduction	4
2. Light-Duty Vehicles as an Energy Service.....	4
Range	4
Power.....	5
3. Electric Vehicle Performance.....	6
Energy Storage.....	6
Electric Vehicles as an Energy Service.....	8
4. High-Energy Battery Performance.....	10
Specific Energy.....	10
Volumetric Energy Density.....	11
Specific Power.....	11
Efficiency.....	11
Lifetime.....	12
Costs.....	12
5. High-Energy Battery Research and Opportunities.....	13
Lithium Intercalation Cathodes.....	14
Lithium Intercalation Anodes.....	15
Alternative High-Energy Chemistries.....	16
6. Conclusions	16
References	18
Appendix	21

Foreword

This report is one of a series of assessments on various areas of the energy landscape prepared by GCEP staff. The assessments are intended to provide an introduction to the energy area as well as context for future fundamental research towards reducing greenhouse gas emissions. By examining the goals and potential of energy transformation technologies as well as current progress and research towards these ends, the assessments take a step toward elucidating promising areas for future research. This report, produced by GCEP Energy Analysis staff, was written by Wes Hermann with contributions from Paolo Bosshard, Emilie Hung, Rebecca Hunt, and AJ Simon. Electronic copies of this and other GCEP assessments can be found on the GCEP website: <http://gcep.stanford.edu>. Please address all correspondence to gcep@stanford.edu.

1. Introduction

A large and growing fraction of global energy use and greenhouse gas emissions is directly associated with transportation. Worldwide, CO₂ emissions from the combustion of carbon-based fuels in vehicles account for 24% of global energy-related emissions and transportation's fraction of global greenhouse gas emissions is expected to approach one third in the coming decades without significant changes in transportation energy requirements or carbon intensity [1,2]. The substitution of low net carbon emissions energy carriers for fossil hydrocarbons has the potential to decouple transportation energy use from greenhouse gas emissions.

One option for providing low-carbon energy for transportation is electricity derived from renewable, nuclear, or fossil resources with carbon capture. However, without a viable method to transmit electricity directly to moving vehicles, electric energy must be reversibly stored onboard the vehicle. An electrochemical energy storage cell, or battery, is one promising option for onboard energy storage. While a number of battery-electric vehicles have been developed in the past, none have been widely successful due in part to the limitations of battery technology.

This report connects the light-duty transportation energy service, battery performance requirements for use in a successful light-duty electric vehicle, and current research toward new high specific energy battery concepts. Fundamental research could enable a significant technical advance in battery specific energy that could help battery-electric vehicles significantly impact global greenhouse gas emissions.

2. Light-Duty Vehicles as an Energy Service

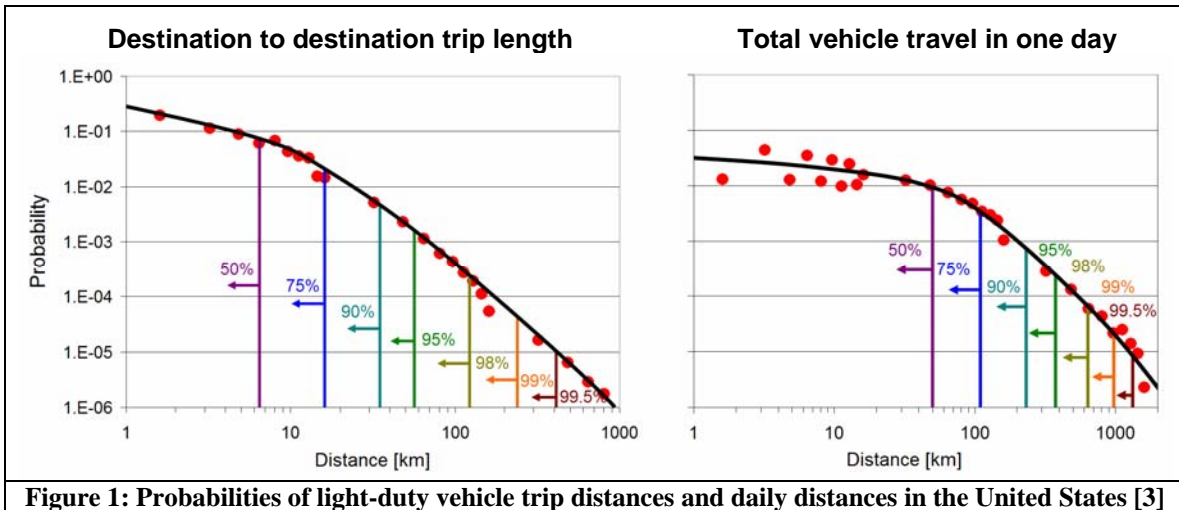
Light-duty vehicles provide a unique energy service, allowing direct destination to destination access at moderate speed. The majority of travel worldwide and over 85% of travel in the United States is in light-duty vehicles [3,4]. The fraction of global mobility performed by light-duty vehicles worldwide is expected to increase as more of the world's population gains access to modern transportation technology. Light-duty vehicles as they are now used must be able to travel certain distances without refueling and need sufficient power to perform maneuvers required by the existing transportation infrastructure. By examining standard driving cycles and statistical data about the use of light-duty vehicles, the energy service they provide can be quantified.

Range

Travel distances extracted from usage data can help indicate the required travel distance before refueling, or range, of a light-duty vehicle. In the United States, about which detailed transportation data are readily available, the average personal vehicle trip distance is 23 km and 99.5% of trips are shorter than 410 km [3]. A trip is defined as a vehicle traveling one leg between destinations not including refueling. However, many trips are often joined together in a given outing to reach multiple destinations without stopping for significant periods of time. In addition, multiple outings are often made in a single day in the same vehicle. If individual inter-destination trip lengths are the lower

bound on required range, an upper bound might be the distance a vehicle travels during one day. A vehicle that can travel 400 km is capable of accomplishing 95% of daily trips. The vehicle outlined in Table 3 of the following section would require about 120 MJ of mechanical work to travel this far.

Probability curves for both vehicle trip distance and daily vehicle distance traveled are provided in Figure 1. These curves derive from a data set of 640,000 trip records in the United States over a 12-month period in 2001 and 2002. The vertical lines under each probability curve represent fractions of the total travel data below a given distance value on the horizontal axis.



About 1% of travel days and about 20% of miles driven in the United States are long trips during which a vehicle travels more than 1000 km in one day, usually at highway speed [3]. These types of trips present a special challenge for electric vehicles, as the distance between stops is long, the energy requirement per unit distance is high, and the expected time at each stop is short.

Power

Hill climbing and acceleration, especially at highway speed, are two aspects of driving that require a large amount of power and can define the upper limit of power required by the vehicle. The power required is a function of several vehicle characteristics, but the most important variable during these maneuvers is mass. The maximum power required on the constant-elevation US06 highway drive cycle (see Appendix) is during an acceleration maneuver of 0.75 m/s^2 at 35 m/s^1 , which requires about 50 kW for the vehicle outlined in Table 3 of the following section. Performing this same maneuver on a 5% grade could double the required power. Steeper grades up to 15% are often only driven at a speed of under 15 m/s. Extreme grade climbing such as this requires an amount of power comparable to the zero-grade highway acceleration maneuver.

¹35 m/s = 126 km/hr = 78 miles/hr

In addition to energy output rate, the rate of energy input determines refueling time, which is a component of the transportation energy service. Together with the availability of refueling infrastructure at and on the way to destinations, refueling time has practical consequences for available destinations and the time it takes to reach them. Light-duty, hydrocarbon-fuelled vehicles currently refuel at up to 38 L/minute, the power equivalent of 22 MW. The technical ability exists to refuel much faster, but refueling time is not considered a major constraint for these vehicles. Since battery electric vehicles require reversing the same chemical processes during charging that normally release energy when the vehicle is moving, refueling time is governed by many of the same limitations as the forward processes and is significantly longer.

3. Electric Vehicle Performance

In order for an electric vehicle to provide an energy service comparable to a light-duty gasoline-fueled vehicle, it must attain acceptable levels of performance in terms of range, power, lifetime, and cost. The battery is now a major limitation in many of these respects. Advances in battery technology could allow electric vehicles to accomplish a larger portion of the energy service currently provided by hydrocarbon-fueled vehicles.

Energy Storage

Electric vehicle batteries must be able to deliver an amount of mechanical work to the vehicle wheels comparable to other energy storage strategies while not allowing the mass or size of the battery to dominate the vehicle platform. The specific energy and volumetric energy density of various energy storage systems are compared in Table 1. The final two columns use system conversion efficiency assumptions to compare the energy storage mass and volume required for a given mechanical energy output. Advanced batteries could attain a storage mass and volume similar to advanced hydrogen storage strategies for a given amount of mechanical work provided but without requiring the added mass and volume of a fuel cell system.

Table 1: Specific energy and energy density of various portable energy storage strategies [5-7]

Energy storage strategy	Specific energy [MJ/kg]	Energy density [MJ/L]	Storage mass ¹ [kg]	Storage volume ¹ [L]
Gasoline and tank	30	30	16	16
Ethanol and tank	19	20	25	24
CNG and tank ²	11	11	44	44
Hydrogen storage strategies	2.0-6.0	2.0-3.5	40-120	70-120
Advanced battery module (hypothetical)	0.5-1.0	1.0-2.0	150-300	75-150
LiCoO ₂ cathode Li-ion battery module	0.5	1.0	300	150
NiMH battery module	0.2	0.5	750	300
Pb-Acid battery module	0.1	0.3	1500	500

¹Sufficient to provide 120 MJ mechanical work on an advanced light duty vehicle with regenerative braking; Assumed conversion efficiencies to mechanical work: Gasoline, ethanol, CNG 25%; Hydrogen PEM 50%; Batteries 80%.

²25 MPa.

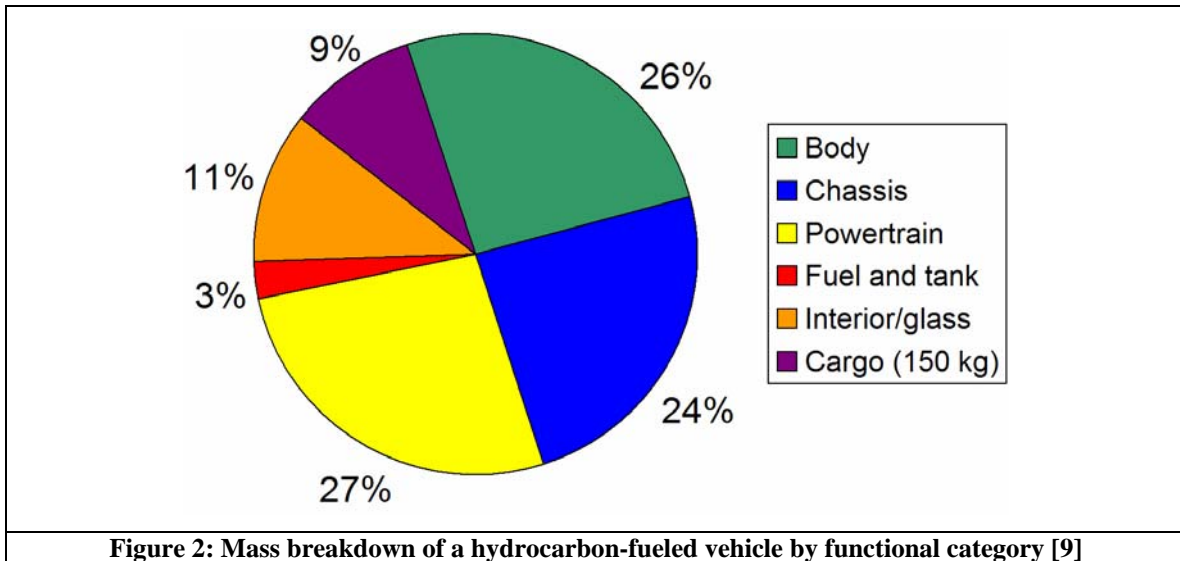
The specific energy of the energy storage system directly impacts the energy service the vehicle can provide. Commercial mass-market, light-duty electric vehicles have used lead-acid and nickel metal-hydride battery chemistries. Table 2 lists performance characteristics for the batteries of a number of electric vehicles, the battery module mass, and the vehicle's range on an urban driving cycle. While the maximum power of many of these vehicles is directly comparable, their range is several times less than that of an equivalent hydrocarbon-fueled car. With a range of about 200 km or less, these vehicles are capable of performing 75-90% of the travel days in Figure 1 without recharging, but the combination of short range and long recharging time makes longer trips less feasible. Low battery specific energy is a primary factor limiting the range of these vehicles.

Table 2: Performance characteristics for various electric vehicles [8]

Electric vehicle platform	Battery specific energy [kJ/kg]	Battery specific power [W/kg]	Battery mass [kg]	Vehicle Urban Range [km]
Chevrolet S-10 (lead-acid)	80	181	575	71
Toyota RAV4 (lead-acid)	105	106	550	110
Toyota RAV4 (NiMH)	180	124	461	151
GM EV1 (NiMH)	188	216	481	226
Chevrolet S-10 (NiMH)	193	201	491	153
Ford Ranger (NiMH)	193	173	485	134
Dodge Caravan (NiMH)	199	172	532	127

The relatively low specific energy of batteries indicates that in order to attain comparable energy storage to liquid fuels, the energy storage mass must be a larger portion of the total vehicle mass. Figure 2 illustrates the mass breakdown of a modern passenger vehicle with respect to major system components. A small fraction (3%) of vehicle mass is devoted to transporting energy. This suggests that a higher percentage of vehicle mass could be diverted to energy storage before the amount of energy spent transporting the energy carrier would begin to significantly increase the overall energy requirement of the vehicle. Increasing the mass of the energy storage component on a 1600 kg vehicle from 40 to 300 kg with no further changes would push the fraction of total vehicle mass devoted to storing energy to 15%. In addition, the power train component of electric vehicles may require significantly less mass than a comparable internal combustion engine system. Performance electric vehicle motors can have a specific power of 6 kW/kg while performance internal combustion engines attain about 2 kW/kg².

² Tesla Motors Roadster motor: 3-phase, 4-pole, 185 kW, 32 kg; Porsche Carrera GT engine: 5.7-liter, V10, 450 kW, 205 kg.



Electric Vehicles as an Energy Service

Connecting battery performance parameters to the light-duty vehicle transportation energy service requires relationships between vehicle range, mass, battery specific energy, and other battery and vehicle parameters. Many of these relationships can be illustrated through a simple model. While not purporting to be a rigorous representation of electric vehicle systems or behavior, a model has been developed that uses reasonable assumptions for the characteristics and resistance parameters of an electric vehicle to determine the vehicle energy requirement. The results are useful for illustrating the relationships between battery performance and the light-duty vehicle energy service. Table 3 lists parameters and results from a particular model scenario run on both an urban and highway drive cycle.

While a hybrid gasoline-electric vehicle today carries about 1.5 GJ and can have a range exceeding 700 km, an electric vehicle with the parameters outlined in Table 3 can travel 400 km on the UDDS cycle using 150 MJ according to the present model. This difference in distance-specific energy use is primarily due to the increased power train efficiency of an electric vehicle. The maximum battery power available in this model is 60 kW, exceeding the maximum power demand on both the UDDS and US06 cycles and sufficient power for the vehicle to climb a 15% grade while traveling at 20 m/s. If battery charging can take place at the maximum sustained battery power, the charging time for this vehicle would be approximately 40 minutes.

The accessory load of 200 W used in the model does not include the use of air conditioning (cooling), which can require up to 1 kW. This value in addition to the power consumption of other accessories amounts to a significant fraction of the average battery power requirement on the urban drive cycle and would reduce the urban cycle driving range to 300 km if operated continuously.

Table 3: Model parameters and results for an electric vehicle on urban and highway drive cycles

Battery		
Mass	300	kg
Specific energy	500	kJ/kg
Specific power	200	W/kg
Total energy storage	150	MJ
Maximum sustained power	60	kW
Discharge efficiency	0.80 – 0.95 ¹	
Vehicle platform		
Total loaded vehicle mass	1450	kg
Aerodynamic drag coefficient	0.26	
Frontal area	2.16	m ²
Coefficient of rolling resistance	0.007	
Electrical-mechanical conversion efficiency	0.88	
Accessory load	200	W
Results		
	U.S. federal urban dynamometer drive schedule (UDDS)	
Average speed	9.5	m/s
Range	400	km
Average battery power requirement	4.7	kW
Maximum battery power requirement	20	kW
Distance-specific energy requirement	375	kJ/km
Battery mass energy use fraction ²	14	%
	Modified highway US06 federal drive schedule (US06) ³	
Average speed	30	m/s
Range	250	km
Average battery power requirement	19.3	kW
Maximum battery power requirement	50	kW
Distance-specific energy requirement	600	kJ/km
Battery mass energy use fraction ²	8	%

¹Linear function of power output

²Fraction of total energy use expended moving the mass of the battery

³Provided in the Appendix

Comparing the results in Table 3 to the energy service values illustrated in Figure 1, this combination of vehicle platform and battery could perform 90-95% of the United States travel days without recharging and 99% of the inter-destination trips. However, the relatively shorter range at highway speed could pose a challenge for long-distance driving. A battery with twice the specific power could reduce recharging time from 40 minutes to 20 minutes, making en-route recharging more feasible.

An electric vehicle's range could be increased by further improving the specific energy of the battery or increasing battery mass. While a larger battery would also mean higher costs, there is some room for increase from an energy perspective as moving the battery mass itself accounts for 8% and 14% of the energy consumed on the modified US06 highway and UDDS cycles respectively. The electric vehicle platforms listed in Table 2 have battery masses from 460 to 575 kg. A 450 kg battery in the vehicle platform of Table 3 would raise the battery mass energy use fractions to 12% and 20% on the two cycles respectively, with ranges increasing to 350 and 550 km. The battery specific energy in Table 3, 500 kJ/kg, is already a factor of 2.5 greater than that of the best commercial electric vehicle batteries listed in Table 2, but some proposed chemistries have the potential to achieve even higher values.

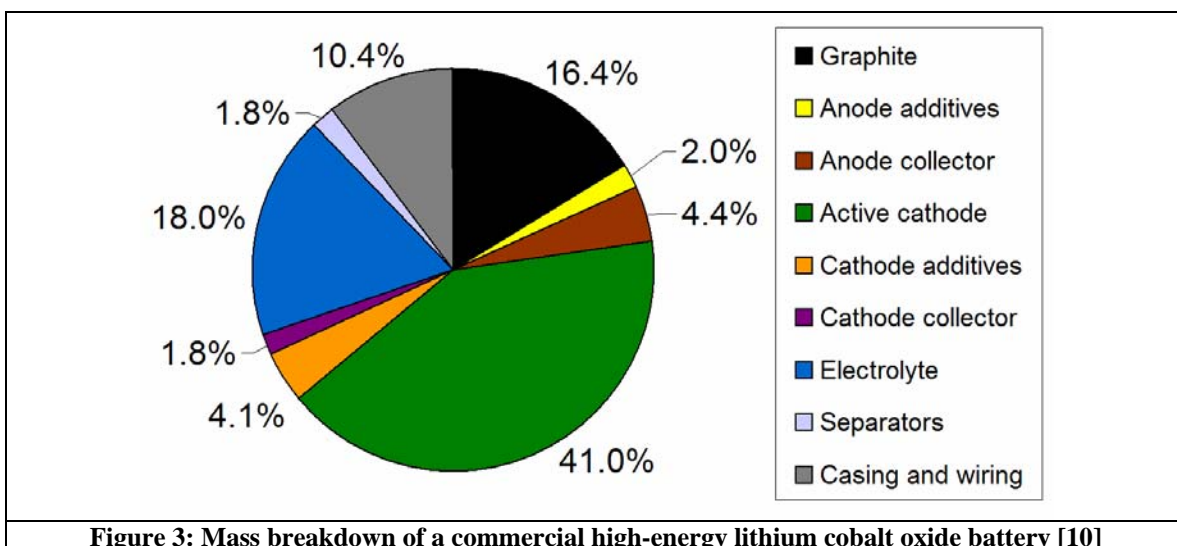
4. High-Energy Battery Performance

The energy service provided by an electric vehicle is closely linked to the performance of its battery. In particular, the energy, power, efficiency, lifetime, and cost of a battery directly impact the value, price, and therefore large scale acceptance of the vehicle. By a general comparison with the energy service provided by hydrocarbon-fueled, light-duty vehicles, quantitative estimates can be made for the required performance of an electric vehicle battery in each of these respects.

Specific Energy

In order to store enough energy to move a vehicle long distances while keeping the battery mass low enough to not significantly affect vehicle performance, batteries must have high specific energy, or energy stored per unit mass. The specific energy of a battery is determined by integrating the voltage difference between the electrodes over the quantity of electron transfers during discharge and dividing by the total mass of all battery module components. Approaches to increasing specific energy must provide high electron capacity at substantial voltages using the lightest possible materials.

A battery module capable of powering an electric vehicle consists of electrochemically-active materials as well as conductors and packaging. As illustrated in Figure 3, a mass breakdown of a commercial deep-cycle battery with a lithium cobalt oxide cathode and a graphite anode shows that the electrodes make up a large portion of the battery mass. The cathode makes up the largest fraction due to its low specific ion capacity relative to graphite. For reference, Figure 5 in the next section illustrates the physical structure of a Li-ion type battery.



An acceptable specific energy for a battery module powering an electric vehicle depends on the vehicle characteristics and the energy service it must provide. For the vehicle characteristics and driving cycles outlined in Table 3, a 300 kg battery module with a

recoverable specific energy of 500 kJ/kg at the end of its useful life would allow an electric vehicle to perform nearly all the energy services of a hydrocarbon-fueled vehicle, with the exception of extended inter-city travel with only short stops between travel legs.

Volumetric Energy Density

The amount of energy a battery stores in a finite volume, while a primary concern for portable electronics applications, will not likely be a fundamental limiting factor for electric vehicle batteries from an energy use perspective. Due to the high density of batteries (2-3 kg/L in Table 1), battery volume does not threaten to dominate the on-road energy requirement of vehicles as does battery mass. The battery in Table 3 accounts for approximately 2% of vehicle volume. For example, consider the worst case scenario of making a vehicle taller to accommodate extra battery volume. If the frontal area and mass of the vehicle in Table 3 were increased from 2.16 m² and 1450 kg to 2.2 m² and 1467 kg respectively to accommodate a doubling of battery volume from 150 L to 300 L, the urban range would decrease by 1.4% due to slightly increased aerodynamic drag and structure weight. In addition, the higher volumetric power density of the remainder of the electric vehicle power train relative to other vehicle types allows more room in the vehicle platform.

Specific Power

The power required to perform the most demanding driving conditions of the basic energy transportation service is about 60 kW (80 hp) for a mass-market light-duty vehicle. If 300 kg of batteries are required for an electric vehicle to have sufficient range, then a specific power of 200 W/kg can achieve the desired overall power. An electric vehicle with more batteries would require a lower specific power, but recharging time could benefit from a higher value. Most modern batteries easily achieve 200 W/kg, suggesting that specific energy is a greater limitation and a greater research challenge for application in electric vehicles. However, new materials providing high specific energy at low cost must maintain this standard of specific power such that battery power does not become a limitation.

Battery specific power is determined in large part by the rate at which desirable chemical reactions can occur in the cell at high efficiency. One major limitation to reaction rate is the transport of ions and electrons. If the migration pathways of ions and electrons are narrow, long, or difficult due to the conductivity of the materials, it takes a larger driving force to transport charge and more useful energy is converted to thermal energy instead of electric energy. For this reason, most efforts towards increasing specific power are aimed at finding high-conductivity materials, increasing contact at interfaces, and engineering cell geometry to provide short conduction paths for ions and electrons.

Efficiency

Battery efficiency is a measure of the amount of electrical energy discharged from a battery divided by the amount of electrical energy transferred to the battery during charging. The remaining energy that is not extracted as electricity is converted to thermal

energy through kinetics and transport losses. Closely related to the limitations on specific power, battery efficiency decreases with increasing charge and discharge rate.

In order for high-energy batteries to be a practical link in an integrated energy conversion chain, a reasonable efficiency should be maintained such that the final delivery of energy to the vehicle wheels does not require an undue amount of low-carbon primary energy. A minimum value of 75% efficiency is readily achievable by current battery technology and is not an unreasonable requirement for future high-energy chemistries.

Lifetime

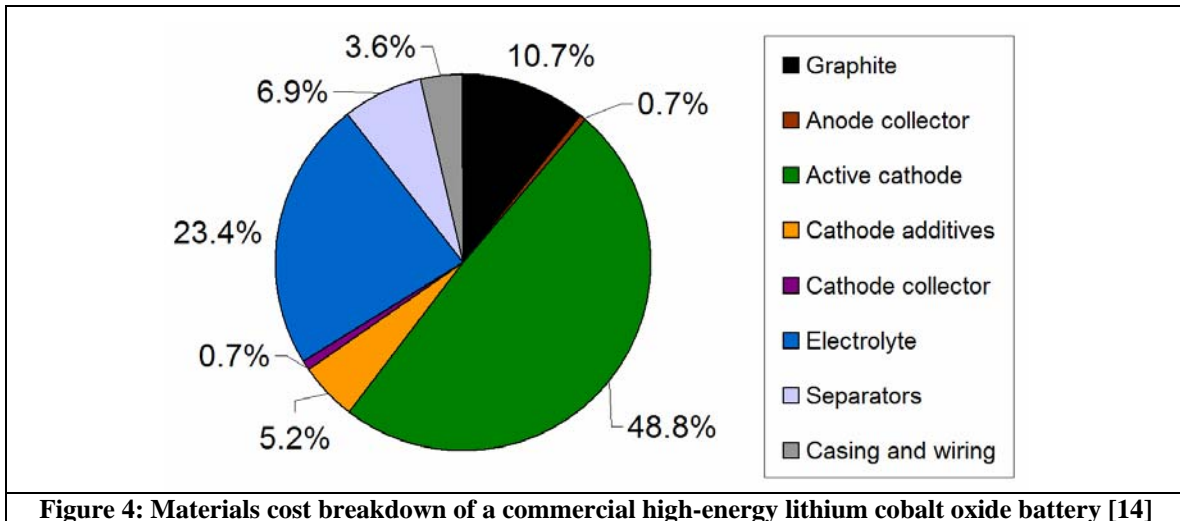
The lifetime of a battery depends on the inherent susceptibility of its active components to irreversible change and the usage and environmental conditions that exacerbate these changes. These changes can decrease the energy capacity of cells by irreversibly forming stable compounds within the electrodes or degrading the power capability of cells by increasing transport barriers and losses [11-13]. While most batteries undergo irreversible change on every charge and discharge cycle, even under ideal conditions, extreme values of temperature, voltage, and mechanical stress can greatly accelerate these processes.

As the battery is the largest and likely most expensive component of an electric vehicle, a long lifetime is critical to its practicality. For all but the most inexpensive battery chemistries, a lifetime as long as the expected vehicle lifetime may be required. In order to achieve expectations similar to current light-duty vehicles, a successful electric vehicle battery should remain above its rated energy capacity and power capability for a calendar lifetime of at least 10 years. During this time, the battery could be expected to undergo at least 2000 charge and discharge cycles.

Costs

In order for an electric vehicle to be successful, the cost of the battery must not dominate the overall cost of the vehicle platform. Commercial high-energy cells with a lithium cobalt-oxide cathode, graphite anode, and a liquid lithium salt electrolyte cost about US\$45/kg to manufacture [14]. At this price, the 300 kg battery for the scenario examined in Table 3 would exceed US\$13,500. This value is large compared to the manufacturing cost of the drive train of mass-market hydrocarbon-fueled vehicles.

Because precursors for the active materials make up most of the cost of current lithium-ion batteries [14], the search for better battery materials should be guided in part by the long term prospects for inexpensive production. As illustrated in Figure 4, materials for the cathode and electrolyte make up a large portion of the cost. New battery technologies could utilize less expensive materials including more abundant metals.

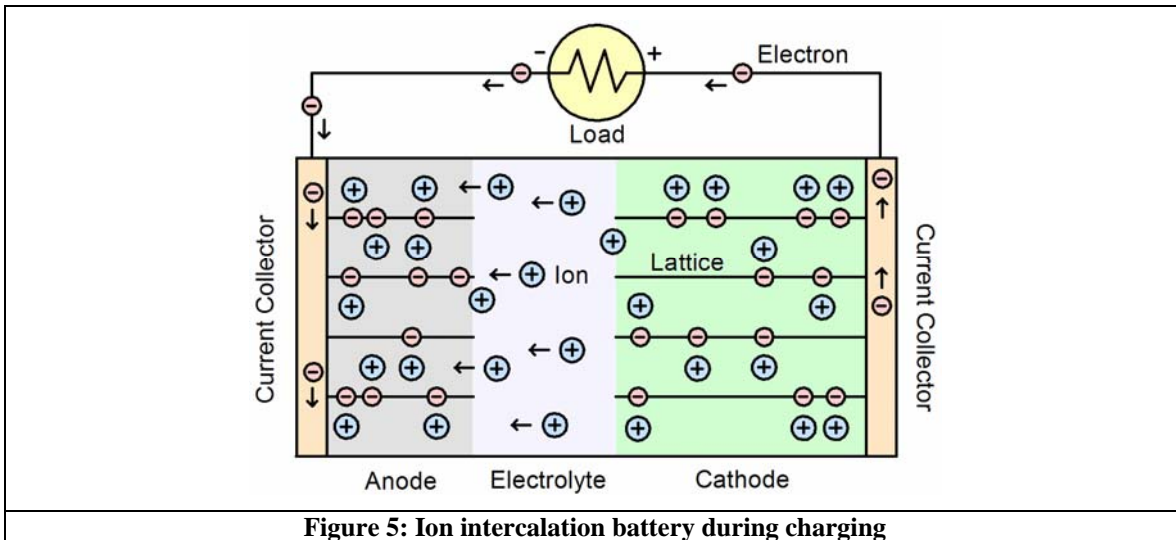


While there are few fundamental barriers to reducing the cost of production for a given material, elements and compounds that are either more abundant and at high concentration in the Earth’s crust or are waste products of other large-scale industrial practices tend to have lower cost. Though the classification of mineral reserves is subject to economic activity and conditions, the stated world reserve base of 13 Tg cobalt is small compared to 140 Tg nickel and 1000 Tg copper³ [15]. As cobalt comprises one quarter of the mass of the battery represented in Figures 3 and 4, global annual production of 30 million 300 kg battery packs of this chemistry would deplete the currently stated cobalt reserve base in six years.

5. High-Energy Battery Research and Opportunities

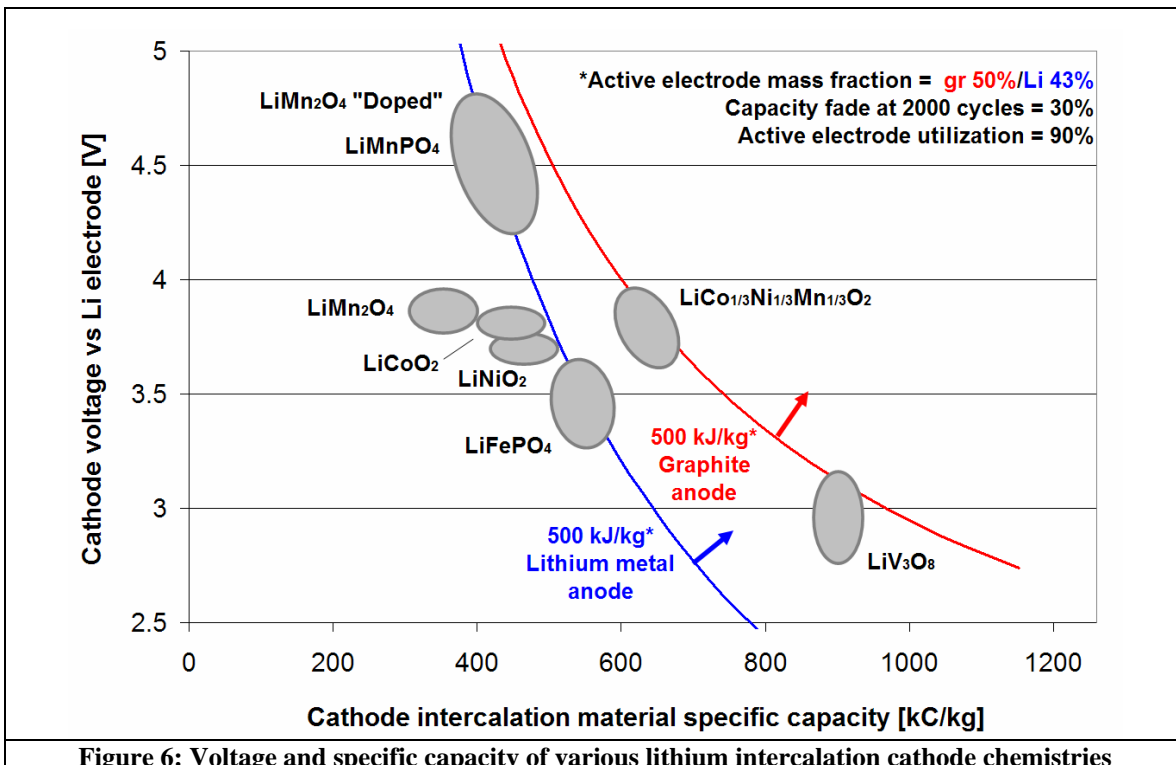
Battery research has made rapid progress over the last several decades. While there is now a spectrum of approaches being pursued, much of the focus of current research is on transporting a lithium ion between two intercalation electrodes, which act like storage shelves for ions as illustrated in Figure 5. Lithium is the lightest metal and therefore has an inherent advantage in terms of specific energy, though the lithium nuclei themselves only account for about 3% of the electrode active material mass. Each of the intercalation electrodes, the negative anode and positive cathode, is structured such that a lithium nucleus can be inserted into a crystalline lattice and neutralized. The difference in the insertion and neutralization chemical potential between the anode and cathode determine the voltage of the cell and the number of electrons that travel through the load determines the current. The number of electrons released is numerically identical to the number of ions traveling through the electrolyte for the alkali lithium, but can be more for polyvalent cations. The voltage is determined by the difference in crystalline lattice strain when the lithium is present or absent. Cell voltages below 3 V begin to significantly impact the amount of energy stored, while voltages above 5 V are difficult to sustain without compromising the electrolyte. The following sections discuss research progress in lithium ion intercalation cells and other proposed high-energy chemistries.

³ 1 Tg = 10⁹ kg = 10⁶ tonnes



Lithium Intercalation Cathodes

Since cathodes are the largest fraction of the total battery mass due to their low ion capacity relative to graphite, finding higher capacity cathode materials has been an active area of research. The most common lithium ion cathode approach is a structured crystalline transition metal oxide material capable of intercalating lithium ions at 3 to 5 V relative to a graphite anode. Figure 6 illustrates the voltage and recent progress in capacity for several cathode materials at low cycle numbers. The specific energy curves for graphite and lithium metal anodes include several assumptions about recoverable energy at end of life as noted in the illustration.



A range of materials combinations is currently under consideration to serve as higher specific energy and more cost effective crystalline cathodes: manganese oxide, vanadium oxide, iron or manganese phosphate, and varying mixtures of cobalt, manganese and nickel oxides [16]. Each of these approaches has specific challenges with respect to stability, safety, and cost [17-20]. Manganese oxide batteries are less expensive, environmentally inert, and relatively stable, but are more limited in the fraction of lithium ions that can be stored in the cathode structure than other proposed chemistries due to their octahedral, rather than layered, geometry. Adding small amounts of other metals can increase the intercalation voltage beyond 4.5 V, increasing the energy stored [21]. Cobalt and nickel can also be added to manganese oxide in various proportions to stabilize the oxides in layers. This prevents the octahedral structures from forming, leading to higher ion capacity. Recent efforts have successfully stabilized a combination of nickel and manganese oxide alone without requiring scarce and expensive cobalt [22].

Iron phosphate or manganese phosphate cathodes are relatively inexpensive and inert, but have low electronic and ionic conductivity [23]. Producing smaller particles, coating the particles in carbon, mixing the cathode material with conducting fibers, and optimizing small-scale architecture are approaches being pursued to increase ion and electron conductivity and therefore power capability with some success [24,25].

Vanadium oxide batteries have exceptionally high lithium capacity, but store it at a lower average voltage, leaving the overall energy density similar to other chemistries [26,27]. This material can be used in several arrangements including V_2O_5 , V_3O_8 , and V_6O_{13} with each capable of intercalating a number of lithium ions [28,29]. While multiple lithium ion storage increases capacity, the voltage available upon extraction of subsequent lithium ions decreases significantly, affecting the overall energy storage.

More recently, transition metal silicate cathodes have also been considered, promising high capacities and abundant precursor materials [30,31]. However, due to the insulating properties of silicates, electron and ion conductivity are very low. Nanostructuring for short diffusion distances or doping with various additives might improve conductivity.

Lithium Intercalation Anodes

Alternative anode materials to graphite are also under consideration to improve the specific energy of lithium ion batteries. While graphite already has high specific lithium ion capacity, 1.26 MC/kg^4 , it may be possible to achieve compounds or alloys with even higher capacities or use pure lithium metal. Alloys of lithium with tin or silicon have theoretical capacities of 3.6 and 14.4 MC/kg respectively. However, the large mechanical changes that take place over the course of cycling lead to instability and capacity loss [32,33].

⁴ MC/kg = 10^6 Coulombs per kg, a measure of specific ion capacity. Multiply by potential difference (V) to obtain specific energy in MJ/kg.

The central challenge of using pure lithium for the anode is the formation of thin metallic protrusions, or dendrites, when the lithium ions deposit onto the anode surface. These dendrites can pierce the soft electrolyte, causing a short circuit between the electrodes. Efforts are underway to develop electrolytes that are either strong enough to mechanically inhibit lithium dendrite growth or that chemically passivate the surface [34,35].

Alternative High-Energy Chemistries

Several alternative high-energy approaches are being considered including redox couples, polyvalent cations, and oxide electrodes undergoing conversion or displacement reactions. The redox couple between lithium and sulfur provides a much higher theoretical energy density than lithium ion chemistries, but raises serious challenges for reversibility [36,37]. With a theoretical energy density of nearly 10 MJ/kg active material, the energy storage density could approach that of many carbon-based fuels. However, current cell designs produce insoluble, non-conductive lithium sulfides that eventually destroy cell reversibility, especially at high rates of discharge. Electrolyte formulations and electrode geometry are currently being studied with a goal of allowing extended reversibility upon cycling and greater sulfur utilization. Current lithium-sulfur formulations have a cathodic capacity of 4.3 MC/kg at about 2.1 V, but have unacceptably low cycle lives for electric vehicle applications [19].

Batteries utilizing polyvalent cations such as Ca^{2+} , Mg^{2+} , and Y^{3+} in place of univalent lithium are being considered to increase the number of electrons transferred at the cell voltage per cation [38]. Since lithium accounts for a small portion of the active material mass in lithium ion batteries, substituting a heavier cation with over twice the charge capacity could increase energy storage disproportionately to the mass increase, allowing higher specific energy. Y^{3+} intercalation into V_2O_5 has shown a capacity of 1.0 MC/kg cathode material at 3 V, providing a higher specific energy cathode than any chemistry in Figure 4. However, diffusion of polyvalent cations through the cathode material is much lower than for lithium and suitable electrolytes and anodes have not been developed for these cations.

Conversion reactions include the reaction of a transition metal oxide or sulfide cathode with lithium to form a two phase mixture of lithium oxide or sulfide and metal nanoparticles stabilized by a layer of decomposed electrolyte material [39,40]. These reactions allow the transfer of multiple electrons per transition metal atom, increasing the ion capacity and therefore specific energy. Displacement reactions function by the lithiation of intermetallic alloys. Both approaches currently suffer from poor kinetics and low energy efficiency.

6. Conclusions

While current battery technology is able to provide electric vehicles with a range satisfying the majority of the light-duty vehicle energy service, fundamental research into new battery materials could help enable electric vehicles with nearly the same functionality as hydrocarbon-fueled vehicles. A battery module with a deliverable

specific energy of at least 500 kJ/kg at the end of life and a specific power of at least 200 W/kg would provide sufficient range for 99% of trips and 90-95% of total daily travel without recharging, while providing sufficient power for basic driving maneuvers. In addition, the use of abundant elements and materials could help reduce the cost of the battery to a smaller fraction of the vehicle package. A battery calendar lifetime of at least 10 years and a charge-discharge cycle life in the thousands may be necessary to avoid costly replacements.

Significant efforts are underway in the exploration of new high-energy battery materials, but fresh approaches may be required to make a significant advance. Loss of capacity over the battery lifetime and manufacturing trade-offs that may compromise energy storage performance in favor of safety and economy suggest that a successful battery enabled by fundamental research might require initial specific energy and power goals significantly exceeding those cited above in order to eventually achieve these values in practice. Previous generational changes in battery technology have resulted from fundamental materials exploration in areas once thought unlikely to yield results. The next advance may require such uncertain steps in new research directions.

References

1. Proost S, van Regemorter D. Are there cost-efficient CO₂ reduction possibilities in the transport sector? - Combining two modelling approaches. *Int. J. of Vehicle Design* 2001;26(2/3):116-130.
2. World Energy Outlook 2005. IEA, Paris, 2005.
3. 2001 National Household Travel Survey, Bureau of Transportation Statistics, US Department of Transportation. See also: http://www.bts.gov/programs/national_household_travel_survey/
4. Shafer A, Victor DG. The future mobility of the world population. *Transportation Research Record A* 2000;34(3):171-205.
5. Well-to-Wheels analysis of future automotive fuels and powertrains in the European context. WELL-to-WHEELS Report version 1b, 2004. European Commission Directorate General, Joint Research Centre. See also: http://www.enpc.fr/fr/formations/dea_masters/tradd/documents/Welltowheeleucar2004.pdf
6. National Hydrogen Energy Roadmap, Department of Energy 2002, p.17.
7. Energy Storage Systems Considerations for Grid-Charged Hybrid Electric Vehicles. Markel T, Simpson A. National Renewable Energy Laboratory, 2005, NREL/CP-540-38538.
8. EVAmerica Baseline Performance Testing Fact Sheets. Advanced Vehicle Testing Activity (AVTA). INL, NREL 2006. See also: <http://avt.inel.gov/fsev.shtml>
9. Kelkar A, Roth R, Clark J. Automobile bodies: Can aluminum be an economical alternative to steel? *JOM* 2001;53(8):28-32.
10. Costs of Lithium-Ion Batteries for Vehicles. Argonne National Laboratory (ANL) 2000, Report ANL/ESD-42, p. 7.
11. Vetter J, Novak P, Wagner MR, Veit C, Moller KC, Besenhard JO, Winter M, Wohlfahrt-Mehrens M, Vogler C, Hammouche A. Ageing mechanisms in lithium-ion batteries. *Journal of Power Sources* 2005;147(1-2):269-281.
12. Broussely M, Biensan P, Bonhomme F, Blanchard P, Herreyre S, Nechev K, Staniewicz RJ. Main aging mechanisms in Li ion batteries. *Journal of Power Sources* 2005;146(1-2):90-96.
13. Kanevskii LS, Dubasova VS. Degradation of lithium-ion batteries and how to fight it: A review. *Russian Journal of Electrochemistry* 2005;41(1):1-16.

14. Gaines L, Cuenca R. Costs of Lithium-Ion Batteries for Vehicles. Argonne National Laboratory, Center for Transportation Research, 2000. Report #ANL/ESD-42. See also: <http://www.transportation.anl.gov/pdfs/TA/149.pdf>
15. Mineral Commodity Summaries 2006. USGS, Reston, Va. See also: <http://minerals.usgs.gov/minerals/pubs/mcs/2006/mcs2006.pdf>
16. Whittingham, MS. Lithium batteries and cathode materials. *Chemical Reviews* 2004;104(10):4271-4301.
17. Vetter J, Novak P, Wagner MR, Veit C, Moller KC, Besenhard JO, Winter M, Wohlfahrt-Mehrens M, Vogler C, Hammouche A. Ageing mechanisms in lithium-ion batteries. *Journal of Power Sources* 2005;147(1-2):269-281.
18. Wohlfahrt-Mehrens M, Vogler C, Garche J. Aging mechanisms of lithium cathode materials. *Journal of Power Sources* 2004;127(1-2):58-64.
19. Akridge JR, Mikhaylik YV, White N. Li/S fundamental chemistry and application to high-performance rechargeable batteries. *Solid state ionics* 2004;175:243-245.
20. Kanevskii LS, Dubasova VS. Degradation of lithium-ion batteries and how to fight it: a review. *Russian Journal of Electrochemistry* 2005;41(1):3-19.
21. Aurbach D, Talyosef Y, Markovsky B, Salitra G, Kim HJ, Choi S. The study of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 5-V cathodes for Li-ion batteries. *Journal of Power Sources* 2005; 146(1-2):664-669.
22. Kang KS, Meng YS, Breger J, Grey CP, Ceder G. Electrodes with high power and high capacity for rechargeable lithium batteries. *Science* 2006;311(5763):977-980.
23. Yang SF, Song YN, Ngala K, Zavalij PY, Whittingham, MS. Performance of LiFePO_4 as lithium battery cathode and comparison with manganese and vanadium oxides. *Journal of Power Sources* 2003;119-121:239-246.
24. Kwon NH, Drezen T, Exnar I, Teerlinck I, Isono M, Graetzel M. Enhanced electrochemical performance of mesoparticulate LiMnPO_4 for lithium ion batteries. *Electrochemical and Solid-State Letters* 2006;9(6):A277-A280.
25. Chen JJ, Whittingham MS. Hydrothermal synthesis of lithium iron phosphate. *Electrochemistry Communications* 2006;8(5):855-858.
26. Chen CG, Liu YP, Li L. Development of vanadium oxide in lithium ion batteries. *Journal of Inorganic Materials* 2004;19(6):1225-1230.
27. Winny D, Sakamoto JS, Bruce D. Electrochemical properties of vanadium oxide aerogels. *Science and Technology of Advanced Materials* 2003;4(1):3-11.

28. Kannan AM, Manthiram A. Synthesis and electrochemical properties of high capacity V_2O_5 cathodes. *Journal of the Electrochemical Society* 2003;150(7):A990-993.
29. Jouanneau S, La Salle AL, Verbaere A, Guyomard D. The origin of capacity fading upon lithium cycling in $Li_{1.1}V_3O_8$. *Journal of the Electrochemical Society* 2005; 152, no.8A1660-7.
30. Larsson P, Ahuia R, Nyten A, Thomas JO. An ab initio study of the Li-ion battery cathode material Li_2FeSiO_4 . *Electrochemistry Communications* 2006;8(5):797-800.
31. Dominko R, Bele M, Gaberscek M, Meden A, Remskar M, Jamnik J. Structure and electrochemical performance of Li_2MnSiO_4 and Li_2FeSiO_4 as potential Li-battery cathode materials. *Electrochemistry Communications* 2006;8(2):217-222.
32. Yoshio M, Kugino S, Dimov N. Electrochemical behaviors of silicon based anode material. *Journal of Power Sources* 2006;153(2):375-9.
33. Zhang JJ, Xia YY. Co-Sn alloys as negative electrode materials for rechargeable lithium batteries. *Journal of the Electrochemical Society* 2006;153(8):A1466-A1471.
34. Monroe C, Newman J. The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces. *Journal of the Electrochemical Society* 2005;152(2):A396-404.
35. Zhang XW, Li YX, Khan SA, Fedkiw PS. Inhibition of lithium dendrites by fumed silica-based composite electrolytes. *Journal of the Electrochemical Society* 2004;151(8):A1257-A1263.
36. Shim J, Striebel KA, Cairns EJ. The lithium/sulfur rechargeable cell. *Journal of the Electrochemical Society* 2002;149(10):A1321-5.
37. Zhu X, Wen Z, Gu Z, Lin Z. Electrochemical characterization and performance improvement of lithium/sulfur polymer batteries. *Journal of Power Sources* 2005;139:269-273.
38. Amatucci GG, Badway F, Singhal A, Beaudoin B, Skandan G, Bowmer T, Plitz I, Pereira N, Chapman T, Jaworski R. Investigation of Yttrium and Polyvalent Ion Intercalation into Nanocrystalline Vanadium Oxide. *J. Electrochem. Soc.* 2001;148(8):A940-A950.
39. Tarascon JM, Grugeon S, Morcrette M, Laurelle S, Rozier P, Poizot P. New concepts for the search of better electrode materials for rechargeable lithium batteries. *Comptes Rendus Chimie* 2005;8:9-15.
40. Debart A, Dupont L, Patrice R, Tarascon JM. Reactivity of transition metal (Co, Ni, Cu) sulphides versus lithium: The intriguing case of the copper sulphide. *Solid State Sciences* 2006;8(6):640-651.

Appendix

Truncated “highway-only” US06 drive cycle [m/s], 1 second intervals

24.4	28.1	28.0	31.0	31.7	31.2	30.0
25.2	28.2	28.0	32.1	30.2	31.1	29.7
25.4	28.7	28.1	32.2	29.7	31.3	29.8
26.0	28.6	28.1	33.5	29.8	31.4	29.6
26.1	28.7	27.8	32.5	29.6	31.4	29.7
26.7	28.8	27.9	32.3	29.5	31.4	29.5
26.8	28.8	27.9	32.3	29.6	31.8	29.6
26.9	29.0	27.9	32.2	29.6	31.7	29.3
27.1	29.2	27.9	32.4	30.0	31.7	27.8
26.7	29.5	27.8	32.6	30.1	31.6	27.8
26.1	29.5	28.0	32.5	30.5	31.7	27.5
26.0	29.7	28.1	32.1	30.5	31.8	27.3
25.8	28.7	27.9	31.9	30.7	31.9	27.5
25.6	28.4	27.9	31.8	30.5	31.7	27.3
25.7	28.6	27.9	31.8	30.5	31.8	27.5
25.3	28.7	27.7	31.7	30.4	32.1	27.5
25.5	28.5	28.1	31.8	30.0	32.2	27.6
25.3	28.8	28.1	31.8	29.7	32.5	27.6
25.3	28.7	27.9	31.8	29.6	32.3	27.6
25.1	28.6	28.1	32.2	29.4	32.3	
25.2	28.7	27.9	32.5	29.5	32.2	
25.3	28.4	27.8	32.9	29.7	32.2	
25.2	28.6	27.7	33.5	29.5	32.2	
25.1	28.6	27.6	33.9	29.7	32.5	
25.0	28.6	27.8	34.6	30.0	32.6	
25.0	28.5	27.8	35.1	30.2	32.7	
24.5	28.6	27.8	35.5	30.4	32.2	
24.2	28.3	27.7	35.0	30.5	32.0	
24.4	28.4	27.9	34.0	30.6	31.7	
23.3	28.6	27.8	33.8	30.8	31.5	
24.5	28.6	27.8	34.2	30.7	31.5	
24.9	28.8	27.9	34.7	31.0	31.7	
25.5	29.0	28.0	34.9	31.0	31.4	
25.9	29.1	28.0	35.4	31.0	31.8	
26.0	28.6	28.5	35.6	31.3	31.4	
26.6	28.7	28.8	35.7	31.5	31.4	
26.8	28.2	29.0	35.7	31.6	30.9	
27.3	28.5	29.1	35.9	31.7	30.8	
27.5	28.2	29.5	35.9	31.4	30.5	
27.7	28.5	29.6	35.6	31.6	30.5	
28.0	28.4	30.0	35.6	31.4	30.5	
28.0	28.2	30.1	35.4	31.2	30.3	
28.0	28.2	30.2	35.2	31.3	30.1	
27.8	28.2	30.5	34.7	31.4	30.2	
28.0	28.3	30.5	34.2	31.1	30.2	
28.2	28.4	30.8	33.2	31.0	30.2	
28.0	28.3	30.9	32.5	31.3	30.1	