

Plug-In Electric Vehicle Lithium-Ion Battery Cost and Advanced Battery Technologies Forecasts

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Technical Update, December 2012

EPRI Project Manager

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ABSTRACT

Batteries are a critical cost factor for plug-in electric vehicles, and the current high cost of lithium ion batteries poses a serious challenge for the competitiveness of Plug-In Electric Vehicles (PEVs). Because the market penetration of PEVs will depend heavily on future battery costs, determining the direction of battery costs is very important. This report examines the cost drivers for lithium-ion PEV batteries and also presents an assessment of recent advancements in the growing attempts to establish a technical basis for development of lithium –sulfur batteries.

Improvements in vehicle efficiencies and battery technology are likely to result in smaller batteries for the same given range. These changes, coupled with decreasing material costs will result in smaller, lower cost packs in the future. PEV-10 battery packs are expected to decrease from 4.4 kWh today to 3.4 kWh in 2020 (a decrease of 23%); PEV-40 battery packs will decrease from 16 kWh today to 11 kWh and PEV-70 battery packs will decrease from 24 kWh today to about 17 kWh by 2020, both decreases of about 30%. Corresponding increases in specific energy density and volumetric energy density are also expected for each vehicle type. By 2020 PEV-10 battery costs will decline from today's \$740/kWh to \$667/kWh; PEV-40 battery costs will decline from today's \$525/kWh today to \$364/kWh; and PEV-70 battery costs will decline from today's \$366/kWh to \$203/kWh. .

The differences in the \$/kWh battery costs of these vehicle types reflects the fact that battery specific (\$/kWh) costs strongly depend on battery specific power and the P:E ratio because higher power capability requires lower electrode loadings which, in turn, increases battery areas for a given battery capacity and thus also battery costs. Because this important cost factor depends on battery cell design, the impact of cell designs must be considered explicitly when projecting future battery costs. This aspect will be a key topic of study in 2013.

This report presents a first attempt to assess recently reported R&D advances for their potential to become the basis of lithium-sulfur battery technology that can meet the requirements for EV propulsion. Realistic upper bounds to the energy storage potential of Li-S were estimated and the prospects for overcoming current cycle life and discharge rate limitations were examined.

Estimates based on experimental data and a simple cell section model indicate good potential for Li-S specific energies to exceed those of Li Ion by about 50% but possible energy density increases are likely to be small. Substantially larger increases, especially of energy density, are possible in principle, but practical solutions to the required increases in sulfur cathode utilization and discharge capacity are not in sight and appear extremely difficult to achieve.

The largest impediment facing the development of practical Li-S batteries for EV applications is inadequate cycle life caused by the irreversible reaction of polysulfides, partial discharge products of the sulfur cathode, with the lithium anode. Recent R&D to mitigate this problem has helped achieve stable cycling of Li-S cell for 100+ deep cycles at promising cathode capacities but only rather low current densities and C rates. Achieving the 1000+ cycles goal for EV applications will require further reductions of polysulfide flux to the Li anode surface.

The currently most promising strategies used to achieve better polysulfide control– retaining polysulfide discharge products within the cathode structure, or/and using barriers in the cell to prevent polysulfides from reaching the lithium anode –increase cell resistances and decrease

already inadequate discharge rates. The development of stable, high-conductivity liquid electrolytes or lithium ion-conducting glasses could become part of solution to the low-rate discharge limitation of Li-S cells (and batteries). In the case of glass electrolytes the solution might be an all-solid Li-S cell if the anticipated large cathode volume changes with cycling can be accommodated.

The study makes clear that a number of major, technically diverse advances are needed to realize the energy storage potential of lithium-sulfur batteries for electric vehicle applications, quantifies some of them and identifies promising research direction. Although no truly fundamental barriers to these advances appear to exist, the author believes that it will take more than a decade of intense R&D, engineering and innovative manufacturing development to overcome the current life and rate limitations and establish a successful high energy Li-S battery technology.

Keywords

Lithium-ion

Lithium sulfur

Cost Model

Battery

Plug-In Electric Vehicle

Forecast

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1

INTRODUCTION

The current high cost of lithium ion batteries poses a serious challenge for the competitiveness of Plug-In Electric Vehicles (PEVs). Because the market penetration of PEVs will depend heavily on future battery costs, determining the direction of battery costs is very important.

Unfortunately, projecting the future costs of lithium ion batteries with confidence is hardly trivial: projections developed by a number of credible organizations over the past 5 years or so differ a great deal, so that various analysts draw rather different conclusions on whether and when PEV become economically competitive with conventional vehicles.

The tremendous increase in interest in electric vehicles in the last five years has resulted in large efforts on and substantial progress in the technology and economic business case for batteries. Manufacturers across the world have invested billions of dollars into new production facilities, which has more than doubled the total manufacturing capacity for lithium ion batteries in just three years. While a good percentage of this capacity was supported by government spending and subsidies, automotive OEMs and suppliers have also invested substantially in the supply chain in the anticipation of high demand for electrified vehicles as the decade proceeds. On the other hand, skeptics have questioned PEV prospects, in good part because of high costs especially of batteries.

In an effort to project the future direction of PEV battery costs, EPRI has initiated a continuing program to understand and quantify the main drivers for battery costs based on data from industry sources on developments in material science, battery design, and manufacturing technology. In addition to examining present-day lithium ion batteries, the program has also initiated studies into future technologies, such as lithium-air and lithium sulfur which are increasingly mentioned as possible future high energy electric vehicle batteries. The program also examines other important vehicle technologies, such as advanced permanent magnet motors, which may present cost reduction opportunities in the future.

This report examines the cost drivers for lithium-ion PEV batteries and also presents an assessment of recent advancements in the growing attempts to establish a technical basis for development of lithium –sulfur batteries.

2011 was the first full year for volume manufacturing of the large format lithium ion batteries that are likely to dominate the electric vehicle battery market for at least the next decade. In 2012 a series of Plug-in electric vehicle (PEV) with ranges varying from 10 to 100 miles have been introduced into the automotive market. To date sales for some best-selling PEVs reflect the increasing popularity trend - Chevrolet Volt has sold almost 19300 units so far, the Nissan leaf has sold about 7000 units to date, and the Prius Plug-in about 8000 units. In addition new PEVs such as the Prius Plug-in and the Ford C-Max Energi were introduced.

Even as PEV sales increase and new models are introduced, the battery remains the single biggest component and future uncertainty in terms of cost. The scale manufacture of batteries has resulted in substantial reductions in cost at the battery level. While precise data are kept closely secret by OEMs and battery suppliers alike, it is believed that the cost to OEMs of vehicle

battery packs in 2011 for PHEV-40 and BEV-100 vehicles, (including the structure and battery management system, but not including thermal management or power electronics) has fallen to between \$450 to \$750/kWh. This is substantially lower than the costs of \$1000 to \$1500/kWh that were reported as recently as 2009. The interest in batteries has generated substantially increased investment in battery-related technologies. Progress with layered cathodes, silicon anodes, and high-voltage electrolytes suggests a promising future for electric vehicle batteries, with most investigators agreeing that by 2020, lithium batteries with roughly double the specific energy (250 Wh/kg, up from about 125 Wh/kg in 2011) will be widely available at half of today's cost (\$250/Wh, down from around \$500/Wh in 2011)¹. To gain an understanding whether and how these trends can be expected to continue is of high interest and a major motivation to EPRI's transportation program and battery cost studies.

With this purpose in mind, an analytic study was conducted to try and forecast battery costs into 2020 and study the influence of various cost drives with the help of the Argonne National lab (ANL) BatPac 1.1 cost model. The selection of this tool and its usage has been explained in detail in the 2011 EPRI report: *Advanced Components for Plug-in Electric Vehicles: 2011 Status and Prospects for Battery and Propulsion Technologies*. EPRI, Palo Alto, CA: 2011. 1021740.

This report is organized as follows:

Chapter 2 describes the main assumptions used in this study.

Chapter 3 discusses the cost analysis performed using the ANL cost model, to understand how various factors are likely to affect battery prices into the future.

Chapter 4 quantifies the influence of key battery variables on cost.

Chapter 5 summarizes the findings of the cost study.

Chapter 6 presents a first assessment of lithium-sulfur-based battery progress and prospects.

¹ Spotnitz, R. "Large Lithium-Ion Battery Design Principles," presented at the Advanced Automotive Battery Conference 2011, January 24, 2011.

2

ASSUMPTIONS

The cost projections of the study are for three milestone years – 2012, 2016, and 2020. The key drivers affecting battery cost that covered by the analysis are:

- Expected driving distance of the plug-in vehicle (PEV) under electric power
- Vehicle efficiency
- Battery Size (Storage Capacity)
- Useable battery capacity and state-of-charge (SOC) limits
- Battery Power
- Battery pack configuration
- Battery chemistry
- Material costs
- Annual production volumes
- Labor costs
- Yield

The assumptions for these key cost drivers over the three milestone years (2012, 2016, and 2020) are explained below.

PEV Choices

The PEVs sold today can be categorized into vehicles with three ranges: 10 miles, 40miles, and 70 miles (PEV-10, PEV-40, and PEV-70 respectively). The most important representatives for these classes are the Prius Plug-In (10 mile nominal electric range), the Chevy Volt (nominal 40 mile electric range, and the Nissan Leaf (approximately 70 miles electric range). Table 2-1 shows the vehicles and their approximate nameplate (that is, total as opposed to usable) battery capacities today.

Table 2-1
Vehicle Selection for Cost Study

Vehicle	Range (miles)	Nameplate Battery Capacity (kWh)
PEV-10	10	4.4
PEV-40	40	16
PEV-70	70	24

Battery Chemistry

Important battery chemistry assumptions are shown in Figure 1-1. Survey of most PEVs on the market today reveals that LiMn_2O_4 (LMO) is the predominant cathode chemistry today, and the anode material is carbon-based, usually graphite. The cell voltages for LMO-based cells is approximately 3.7 V. The specific storage capacities (“loading”) are around 100 mAh/gm for LMO, approximately 330 mAh/gm for graphite. The maximum electrode coating thickness permissible is assumed to be 100 μm , with the actual thickness governed by power requirements.

It is expected that by 2016, cathode chemistries will move towards low cobalt chemistries, with the consensus opinion among battery manufactures being that NMC will be the pre-dominant chemistry going forward. The cell voltage for NMC-based cells will be around 3.6 V and NMC loading is likely to be around 175 mAh/gm. The anode material will continue to be predominantly graphite. The maximum electrode coating thickness permissible is assumed to be 125 μm , limited, however, by power requirements.

Going further, it is expected that by 2020, advanced mixed metal oxides will be available as cathode materials. Graphite-based cells with these materials will have significantly higher cell voltages (> 4 V), assumed to be 4.1 V in this analysis. It must however be cautioned that these materials, which include the layered manganese rich cathodes of composition $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M}=\text{Mn}, \text{Ni}, \text{Co}$), developed originally at Argonne National Lab, are still in the technology development stage.. Difficult issues such as voltage fade, high voltage electrolyte stability and safety, and others aspects still need to be resolved. Once available such materials offer loadings up to 290 mAh/gm, the assumption in this study. By 2020 silicon/carbon/lithium alloys are assumed to be available as anode materials. These advanced materials offer very high electrode loadings, with 600 mAh/gm assumed for this study. The highest permissible electrode coating thickness is assumed to be 150 μm , again limited by maximum power requirements

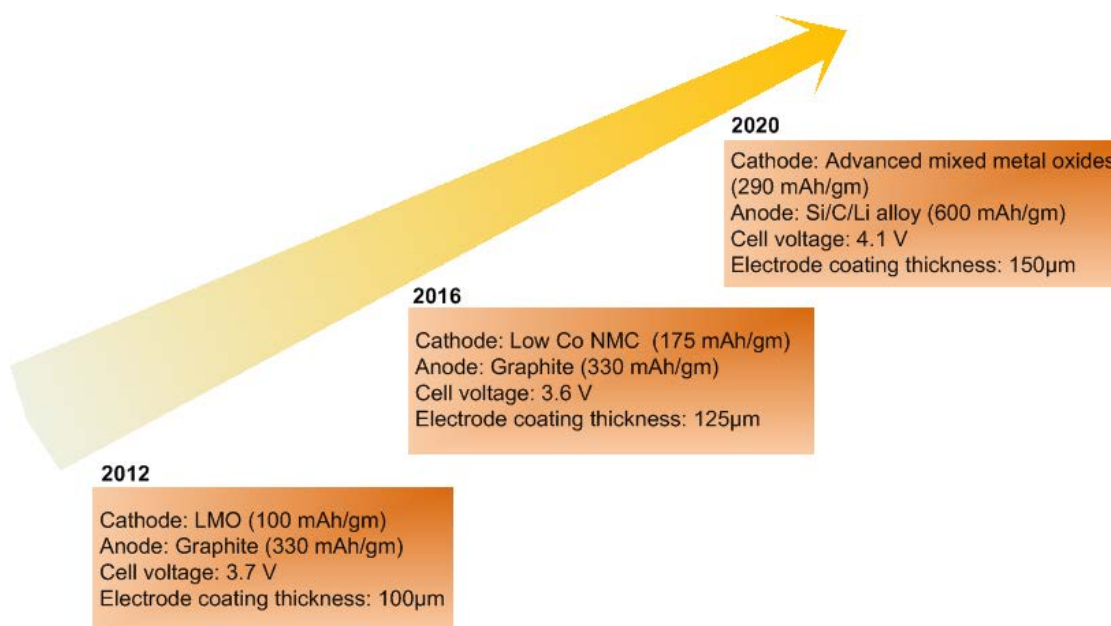


Figure 2-1
Battery Chemistry Assumptions, 2012-2020

Material Costs

LMO costs were obtained from the ANL BatPac 1.1 model. The cost (price) of the low-Co Ni-rich NMC is assumed to be 50% lower than that of 1:1:1 NMC which costs about \$40/Kg at present. This actually causes a slight increase in cathode costs going from 2012 to 2016 as it is expected that chemistries move to NMC from the lower- cost LMO used today. No reliable cost numbers are available for the advanced mixed-oxide materials and forecasts are difficult. However, based on the fact that these materials pre-dominantly use low-cost metals, a reasonable assumption of \$15/kg in 2020 is made. The basic cost assumptions are tabulated in Table 2-2.

Table 2-2
Basic material cost assumptions for active materials

Material	Cost (\$/Kg)		
	2012	2016	2020
Cathode (Active material)	10 (LMO)	20 (Low-Co NMC)	15 (Advanced mixed oxides)
Anode (Active material)	19 (Graphite)	15 (Graphite)	15 (Si/C/Li)

Vehicle Efficiency Improvements, Battery Capacity and Useable Battery SOC,

Vehicle Efficiency Projections

As vehicle efficiencies improve through a combination of weight reductions, better aerodynamics and drive train efficiency improvements, we expect that in the future batteries with smaller capacities will be able to deliver the same vehicle performance and range as today. Furthermore, the smaller battery capacities are likely to be utilized more fully because technology advances will permit the use of larger SOC windows. In combination these factors are expected to permit substantial reductions in the capacities of PEV-10, PEV-40 and PEV-70 batteries as discussed in the following.

To project the Wh/mile vehicle efficiency improvements going forward, the 3-2-1 rule was applied. Assuming that today's vehicles could deliver approximately 4miles/kWh (specific consumption of 250 Wh/mile), projections of Wh/mile specific consumption (Figure 2-2) were made assuming a 3% improvement for 2 years, followed by a 2% improvement for 2 years, and a 1% improvement in the subsequent four years. Table 2-3 shows the Wh/mile improvement forecasts.

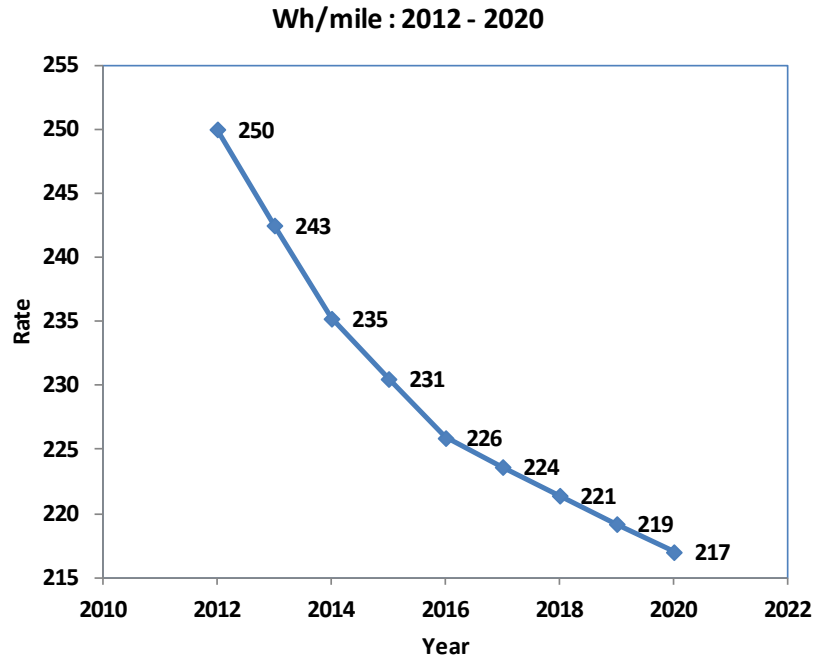


Figure 2-2
Wh/mile: 2012 - 2020

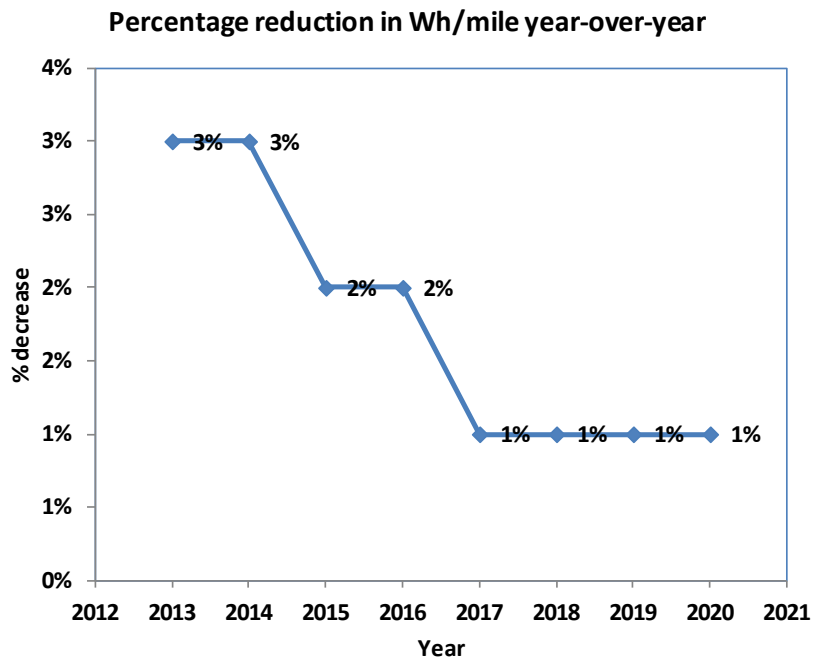


Figure 2-3
Wh/mile reduction year-over-year

Table 2-3
Wh/mile projections: 2012 - 2020

Year	2012	2013	2014	2015	2016	2017	2018	2019	2020
Wh/mile	250	243	235	231	226	224	221	219	217

For the purpose of this analysis, similar electric efficiencies are assumed for all the three vehicles. The Wh/mile figures for 2012, 2016, and 2020 are reproduced in Table 2-4.

Table 2-4
Wh/mile assumptions (from Table 2-x): 2012 - 2020

Year	2012	2016	2020
Wh/mile	250	226	217

Useable Battery State-of Charge (SOC)

As battery technology improves, a reasonable assumption can be made that the allowable depth of discharge or the useable SOC of the batteries will continue to increase in the future. The 2012 useable SOC are estimated from the nameplate and useable battery capacities quoted by OEMs. The typical nameplate capacities for PEV-10, PEV-40, and PEV-70 batteries based on vehicles in production today are 4.4, 16, and 24 kWh. Usable capacities for the PEV-40 and PEV-70 are quoted by OEMs as 10.8 and 18 kWh, respectively. Based on this information typical SOC for 2012 PEV-40s and PEV-70s are around 0.65 and 0.70, respectively. For the 2012 PEV-10, no data is available on usable battery capacity. Assuming 250 Wh/mile (from Table 2-4), the allowable SOC range is estimated to be 0.57 $(= (250 \times 10)/(1000 \times 4.4))$.] By 2016, the permissible SOC ranges are assumed to widen to 0.6, 0.7 and 0.8 for a PEV-10, PEV-40, and PEV-70, respectively. Further improvements by 2020 should result in deeper depth of discharge capabilities, with 0.65, 0.8, and 0.9 assumed for the three vehicles. The useable SOC assumptions are summarized in Table 2-5.

Table 2-5
Vehicle allowable SOC range projections: 2012 - 2020

Vehicle	2012	2016	2020
PEV-10	0.57	0.6	0.65
PEV-40	0.65	0.7	0.8
PEV-70	0.7	0.8	0.9

Battery Capacity

The 2012 nameplate sizes are based on PEVs in production today as explained in the previous section. Based on the Wh/mile and allowable SOC range assumptions in Tables 2-4 and 2-5, the nameplate battery capacities for 2016 and 2020 can be estimated using the equation below.

$$\text{Nameplate battery capacity} = (\text{Wh/mile} \times \text{PEV range}) / \text{allowable SOC range}$$

The nameplate capacities are rounded to the nearest integer.

Table 2-6
Battery Size: 2012 - 2020

Vehicle	2012	2016	2020
PEV-10	4.4	3.8	3.4
PEV-40	16	13	11
PEV-70	24	20	17

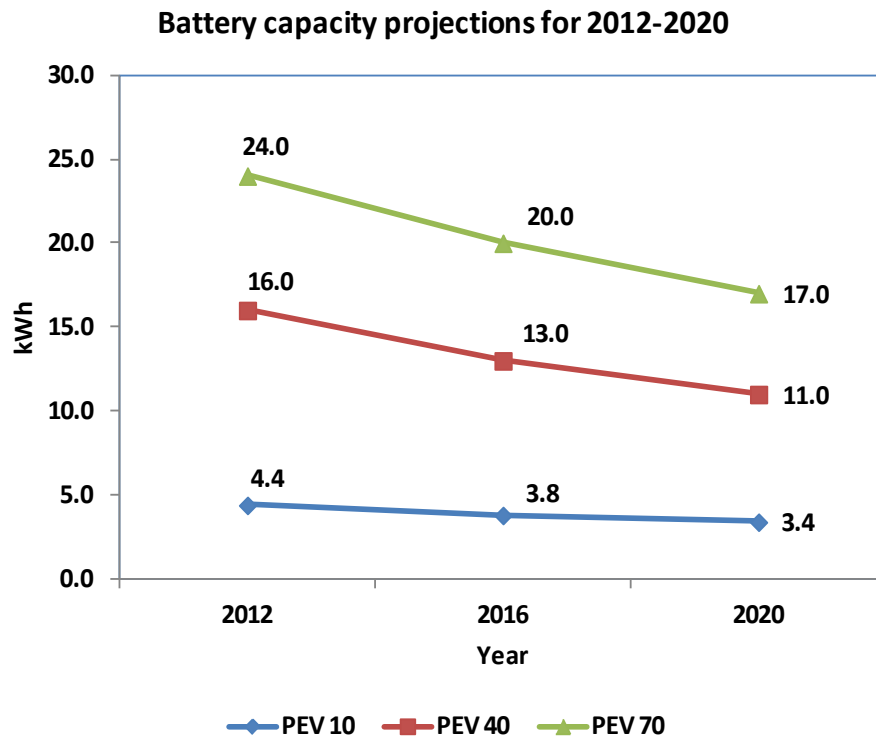


Figure 2-4
Battery capacity projections for 2012-2020

Battery Pack Configuration

Several pack electric configurations are considered in the study to allow for possible cost reductions:

- Series-parallel configurations of 2012 PEVs remaining unchanged in 2016 and 2020
- Migration to single string electric configurations to capture the cost reductions arising from the associated increases in cell size

Pack electric configuration unchanged from 2012

Table 2-7

Scenario 1: Battery Pack Assumptions

Vehicle	Number of cells/string	Number of parallel strings
PEV-10	56	1
PEV-40	96	3
PEV-70	96	2

These configurations provide a reasonable baseline for estimating battery costs in 2016 and 2020. However, there are two implications of this scenario that argue against its future use. Because of declining battery capacities, retaining these electric configurations would result in decreasing cell Ah capacities over the years. This approach thus would fail to take advantage of the fact that going to larger Ah cells offers very significant reductions in cell and battery specific (i.e., \$/Ah and \$/kWh) costs (EPRI report 2010).

Single-string battery electric configurations permit use of less complex battery performance and safety management systems besides offering the cost advantage of larger-capacity cells. It is therefore reasonable to assume OEMs will push towards single-string arrangements in future battery technology generations.

Table 2-7 shows the battery pack assumptions that remain the same through 2020.

Migration to single string structures with pack voltage remaining same

Table 2-8

Scenario 2: Battery Pack Assumptions (2012 -2020)

Vehicle	2012			2016			2020		
	No. of cells per string	No. of parallel strings	Pack Voltage	No. of cells per string	No. of parallel strings	Pack Voltage	No. of cells per string	No. of parallel strings	Pack Voltage
PEV-10	56	1	207	56	1	202	50	1	205
PEV-40	96	3	355	100	1	360	88	1	360
PEV-70	96	2	360	100	1	361	88	1	361

This scenario assumes that going forward to 2016 and 2020 the PEV-40 and PEV-70 battery packs will have migrated to single string arrangements (PEV-10 already has a single string battery configuration in 2012.), with unchanged pack voltages throughout the years. The corresponding pack configuration details are shown in Table 2-8. This scenario results in a migration to larger format cells that allow significant cost reductions. Note that the Ah capacities decrease slightly from 2016 to 2020 because the battery capacities decrease while the number of cells stays the same for each vehicle.

Battery Power

Battery power assumptions were made after review of vehicle power requirements and US DRIVE targets. The motor powers in today's PEVs are approximately 38 kW, 110 kW, and 80 kW for PEV-10, -40, and -70 respectively. Battery power is assumed as approximately 1/0.75 times motor power assuming a converter efficiency of 75%. An additional 10% overhead is added to factor in degradation of battery power over calendar life. The final battery power assumptions are shown in Table 2-9; these numbers are roughly in line with US DRIVE targets. It is assumed that this battery power does not change over time.

Table 2-9
Battery Power Assumptions (2012 -2020)

Year	2012	2016	2020
Power (kW)	50	150	110

Other Assumptions

Other key assumptions are:

- The annual production of battery packs is assumed to vary over 10,000 to 250,000 range.
- The labor cost is fixed at \$18/hr.
- It is assumed that technology and process improvements through scale will result in high yields, fixed at 99% for all cases.

3

BATTERY COST ANALYSIS

Analysis Framework

The objective of this analysis is to generate cost forecasts for Lithium-ion PEV batteries. Two cases are simulated here:

- Case 1: Battery nominal capacities are projected to be the same throughout the years with battery packs migrating to a single string arrangement in 2016 and 2020 and pack voltages remaining the same.
- Case 2: Battery capacities are projected to decrease through 2020, accompanied by a migration to single string structures and unchanged pack voltages.

For both cases, pack costs are estimated for production of 10,000, 20,000, 30,000, 50,000, 100,000, and 250,000 packs per year. All other assumptions are as specified in the previous chapter. Cost, weight, volume, specific energy, and energy density projections for the three vehicles were made using the ANL BatPac 1.1 cost model.

Case 1: Fixed Battery Capacities through 2020

This case assumes that, for each of the vehicle types analyzed, battery size will not change over the next eight years, see Figure 3-1. However, there will be migration to single string batteries with larger cells, with voltages remaining at 2012 levels (see Table 2-8). Pack kWh and cell Ah capacities are as shown in Table 3-1 and 3-2. The P:E ratios of the three packs are shown in Table 3-3. All other assumptions are detailed in chapter 2.

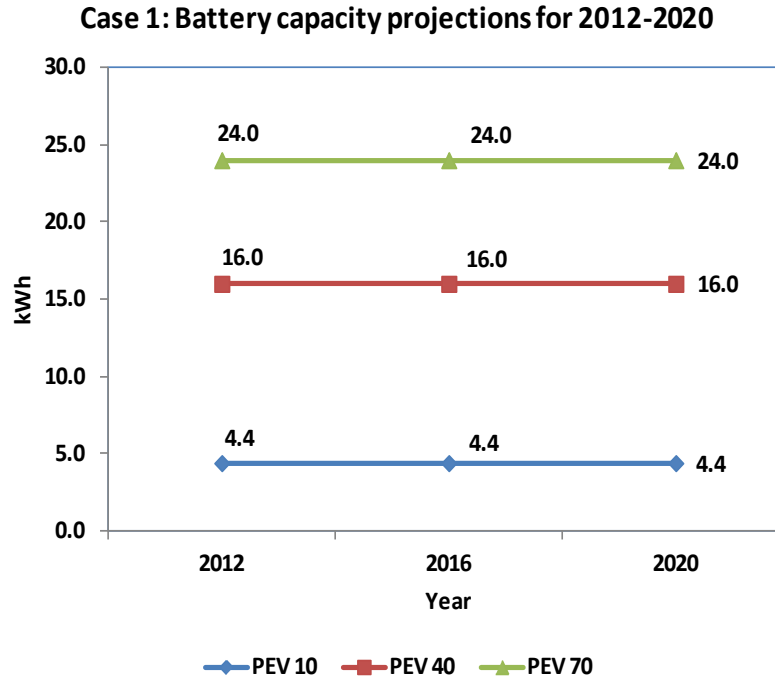


Figure 3-1
Case 1: Battery capacity projections for 2012-2020

Table 3-1
Case 1: Battery size assumptions (2012 -2020)

	Battery Size (kWh)		
Vehicle	2012	2016	2020
PEV-10	4.4	4.4	4.4
PEV-40	16	16	16
PEV-70	24	24	24

Table 3-2
Case 1: Cell Ah (2012 -2020)

	Cell Ah		
Vehicle	2012	2016	2020
PEV-10	21	21	21
PEV-40	44 (3 x 15)	44	44
PEV-70	67 (2 x 33)	67	67

Table 3-3
Case 1: Battery P:E ratios (2012 -2020)

Vehicle	P:E ratio
PEV-10	11.4
PEV-40	9.4
PEV-70	4.6

Battery Pack Costs

Figure 3-2 shows the cost curves as a function of volume calculated for the three vehicles using the ANL model. The curves show several interesting features. The battery pack cost for a PEV-10 actually increases from the 2012 to 2016 because the NMC material assumed to be used by 2016 is slightly more expensive than the LMO used in 2012. The 2020 costs are lower than in 2012 but only slightly so because the 2012 battery already uses a single-string configuration, and cell Ah capacity actually decreases from 2012 through 2020. For the PEV-10 battery the main benefit from the migration to the more advanced chemistries is an increase in battery energy density, as will be discussed later. The PEV-40 and PEV-70 battery costs show a more significant decrease through 2020.

The PEV-40 and PEV-70 use parallel strings in 2012 but migrate to single string configurations in 2016 and 2020. As a result, there is a significant increase in the cell size from 2012 to 2016 (15 Ah to 44 Ah in the case of PEV-40 and 33 Ah to 67 Ah in the case of PEV-70) . Together with the lower battery capacity the benefit of increasing cell Ah capacities results in substantially lower battery costs in 2016 and again in 2020, as shown in Table 3-4.

A key observation is that the PEV-40 battery costs more than the PEV-70 of 50% larger capacity. This is the result of the substantially higher specific power capability of the PEV-40, and it points to the significance of the impact of specific power on battery costs.

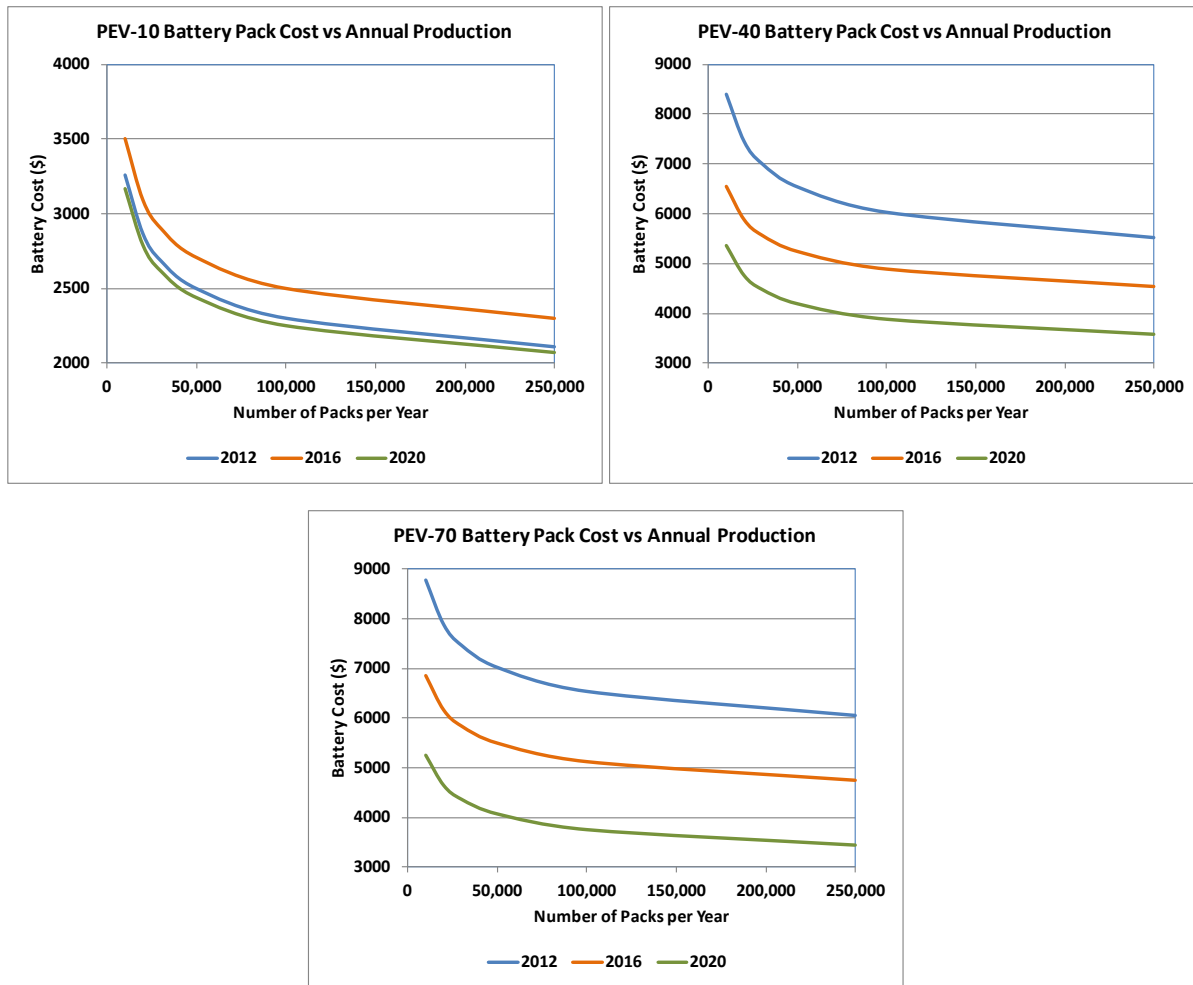


Figure 3-2
Case 1: PEV-10/-40/-70 battery pack costs: 2012-2020

Table 3-4
Case 1: PEV-10/-40/-70 battery pack costs (2012 -2020)

PEV-10	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$3,260	\$2,867	\$2,687	\$2,500	\$2,302	\$2,111
2016	\$3,503	\$3,091	\$2,902	\$2,707	\$2,500	\$2,300
2020	\$3,165	\$2,786	\$2,613	\$2,435	\$2,247	\$2,068

PEV-40	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$8,397	\$7,452	\$7,009	\$6,541	\$6,033	\$5,526
2016	\$6,550	\$5,882	\$5,571	\$5,245	\$4,892	\$4,542
2020	\$5,349	\$4,754	\$4,479	\$4,193	\$3,886	\$3,587

PEV-70	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$8,777	\$7,886	\$7,469	\$7,027	\$6,545	\$6,063
2016	\$6,849	\$6,161	\$5,839	\$5,498	\$5,127	\$4,755
2020	\$5,244	\$4,644	\$4,365	\$4,074	\$3,760	\$3,452

Battery Specific Costs (\$/kWh)

Figure 3-3 shows the \$/kWh specific cost for the three vehicle batteries. Again, the PEV-40 and -70 cases show significant reduction in costs over the course of the years. Table 3-5 shows the \$/kWh for all three vehicles. Key observations are as follows for production volumes of 10,000 packs per year today and 250,000 in 2020:

- PEV-10 costs are around \$740/kWh today and decrease to \$470-480/kWh by 2020.
- PEV-40 costs are around \$525/kWh today and decrease to \$225/kWh by 2020.
- PEV-70 costs are around \$366/kWh today and decrease to \$144/kWh by 2020.

As expected, battery specific costs depend significantly on battery capacity and P:E ratio. Batteries with smaller P:E ratio such as the ones in PEV-70 cost substantially less per kWh and have greater potential for cost reduction than batteries with higher P:E ratios.

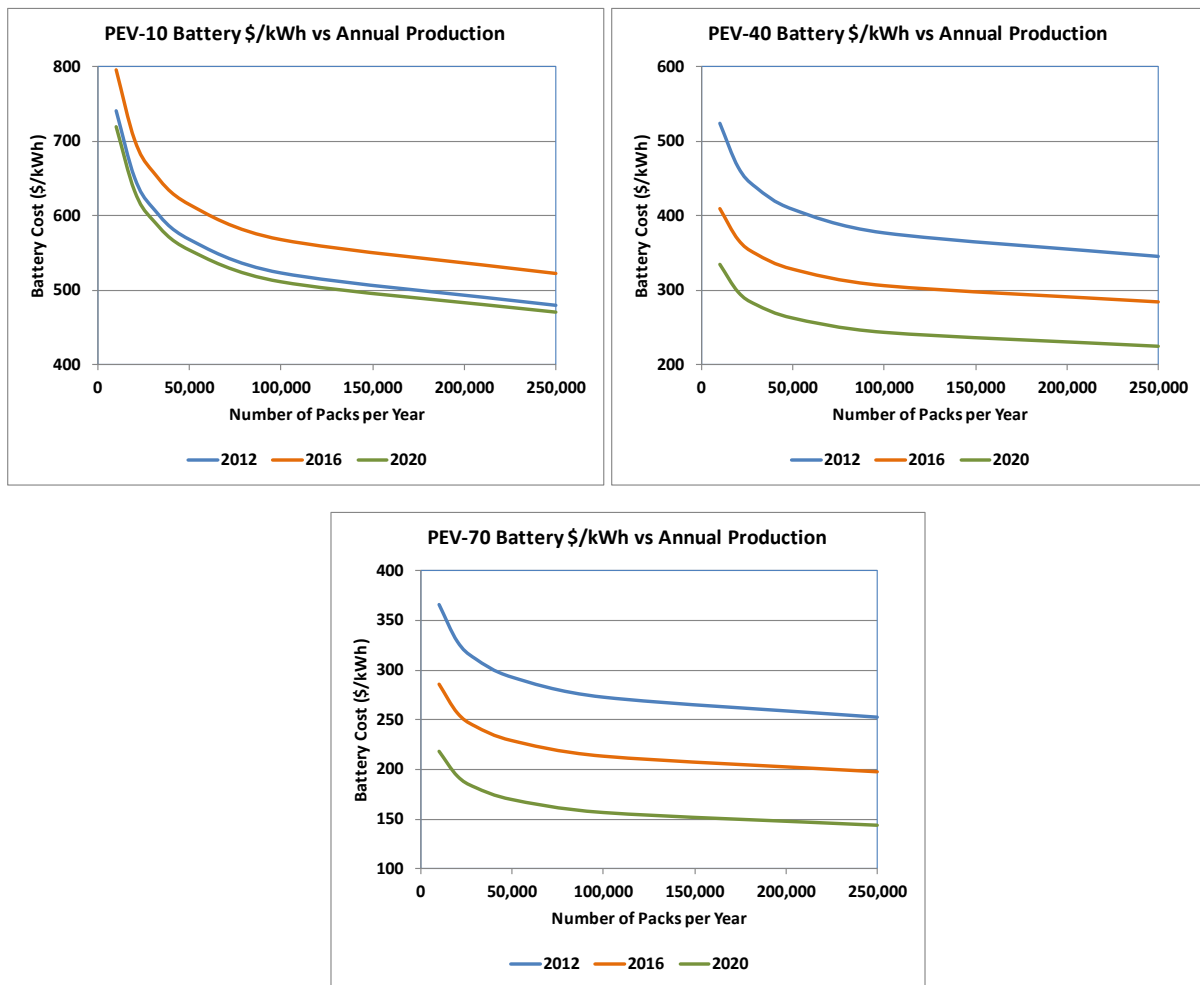


Figure 3-3
Case 1: PEV-10/-40/-70 battery \$/kWh costs: 2012-2020

Table 3-5
Case 1: PEV-10/-40/-70 battery \$/kWh costs (2012 -2020)

PEV-10	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$741	\$652	\$611	\$568	\$523	\$480
2016	\$796	\$702	\$660	\$615	\$568	\$523
2020	\$719	\$633	\$594	\$553	\$511	\$470

PEV-40	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$525	\$466	\$438	\$409	\$377	\$345
2016	\$409	\$368	\$348	\$328	\$306	\$284
2020	\$334	\$297	\$280	\$262	\$243	\$224

PEV-70	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$366	\$329	\$311	\$293	\$273	\$253
2016	\$285	\$257	\$243	\$229	\$214	\$198
2020	\$219	\$193	\$182	\$170	\$157	\$144

Likely Battery Costs

The battery specific cost projections in Fig. 3-3 assume production rates far above today's that may or may not materialize by 2020, much less by 2016. A more realistic approach to projecting battery cost evolution over the nearer term is to assume that battery production rates increase over the years, for example from 10,000 packs in 2012 to 50,000 in 2016 and 100,000 packs in 2020. The learning curves of Fig. 3-3 permit estimates to be made for these evolving production volumes, with the caveat that the validity of such cost learning curves becomes increasingly uncertain at production rates below approximately 50,000 packs per year. Under these more realistic assumptions, specific costs still decline substantially over the years, as summarized below and illustrated in Figure 3-4:

- PEV-10 costs are around \$740/kWh today and decrease to \$511/kWh by 2020.
- PEV-40 costs are around \$525/kWh today and decrease to \$243/kWh by 2020.
- PEV-70 costs are around \$366/kWh today and decrease to \$157/kWh by 2020.

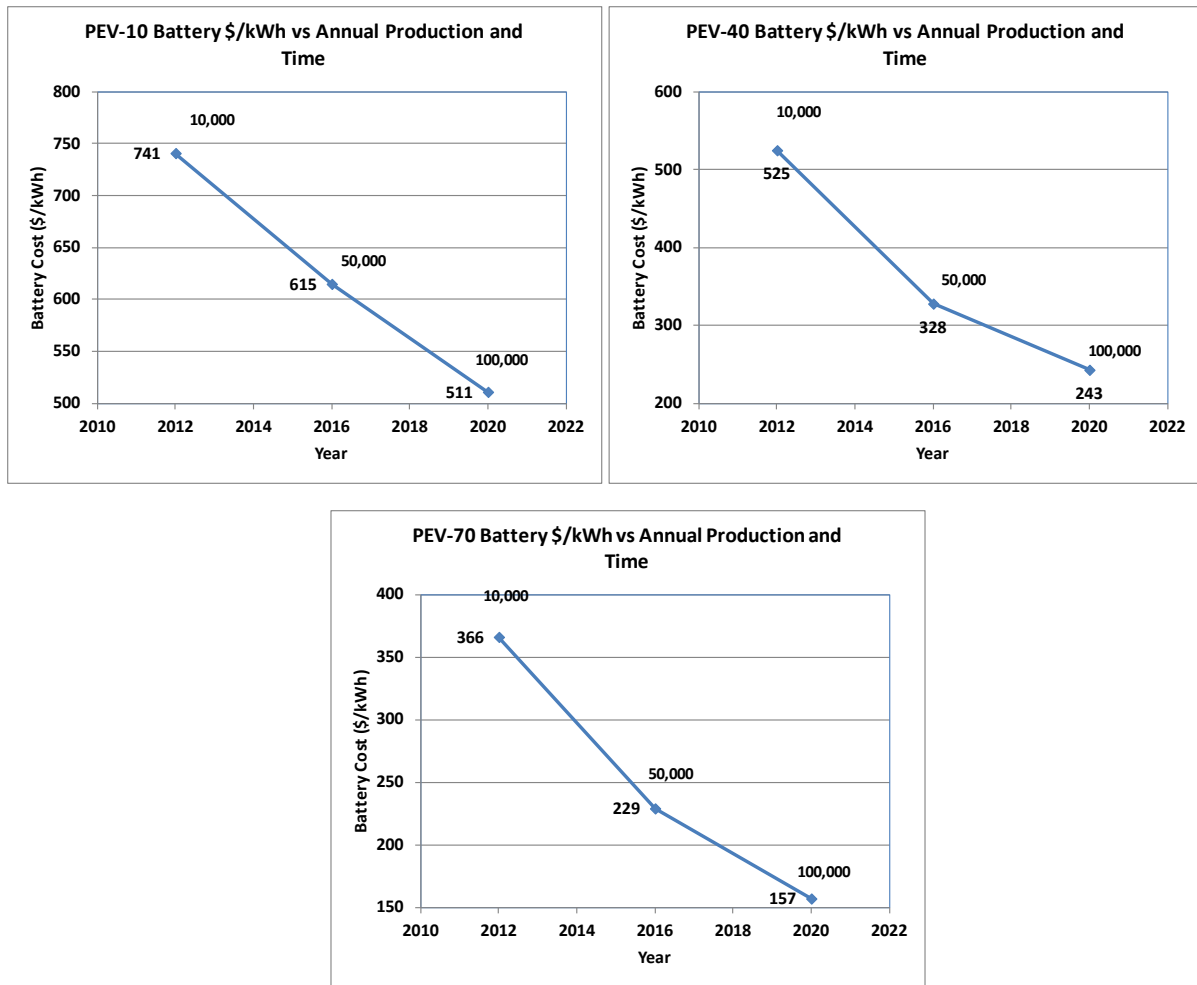


Figure 3-4
Case 1: PEV-10/-40/-70 expected battery costs: 2012-2020

Battery Weight and Volume

Projected battery weights and volumes are other primary outputs of the model. Figure 3-5 shows a reduction in battery weight and volume for all the three PEV cases. The percentage decrease in weight and volume from 2012 to 2020 is shown in Table

Table 3-6
Case 1: Percentage decrease in weight and volume from 2012 to 2020

	% reduction	
PEV	Weight	Volume
PEV-10	32	32
PEV-40	43	50
PEV-70	58	58

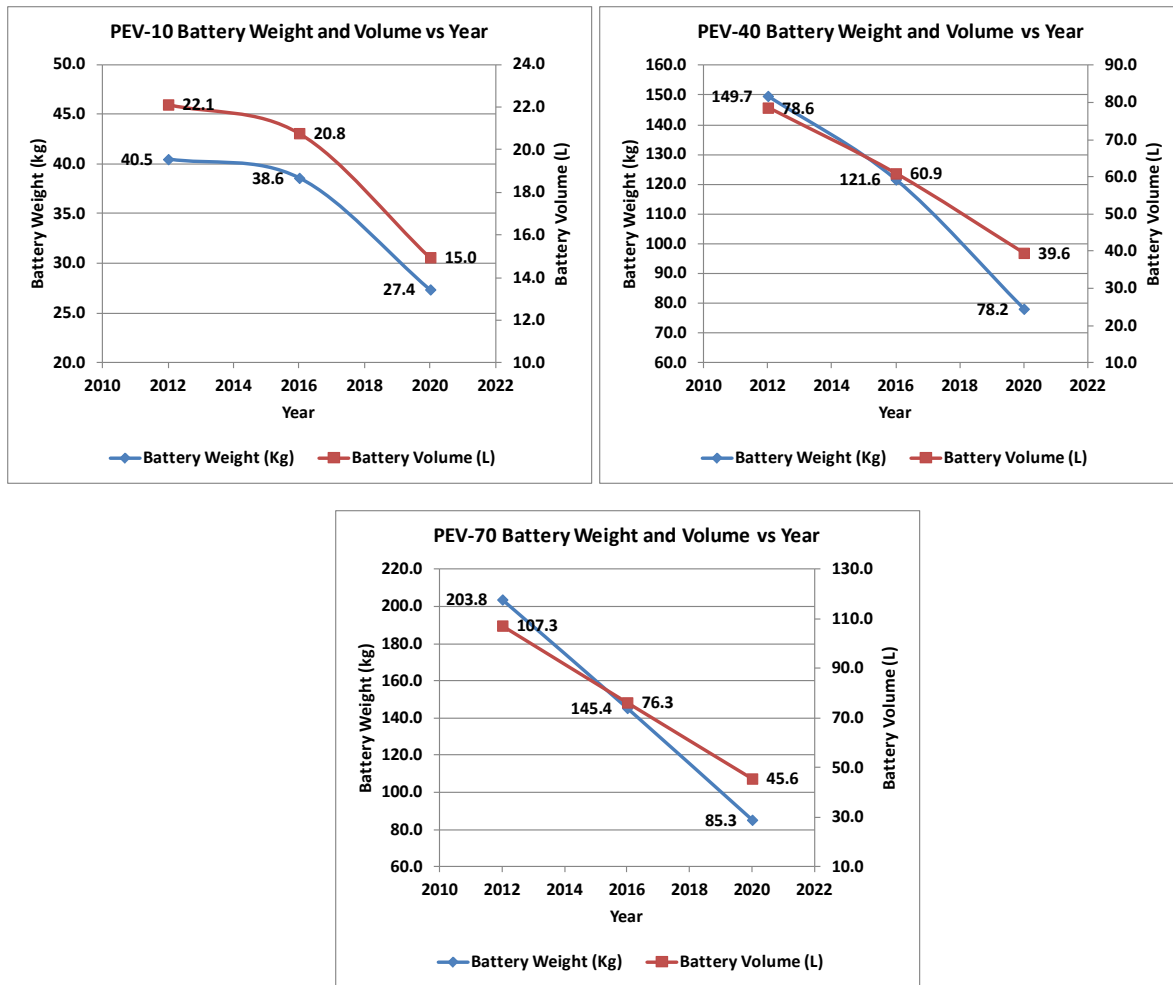


Figure 3-5
Case 1: PEV-10/-40/-70 battery weight and volume: 2012-2020

Specific Energy and Energy Density vs Year

As battery materials continue to improve and weight and volume decrease accordingly, the specific energies and energy densities of lithium ion batteries are projected to significantly improve in the nearer and longer term. This trend is shown in Figure 3-5. By 2020, the PEV-10 energy density and specific energy increase due to improved chemistry. PEV-40 batteries are projected to experience increases in specific energy and energy densities of as much as 90% compared with today's technology. Even more impressive, PEV-70 batteries may see increases of specific energies and energy densities of as much as 140% compared to today.

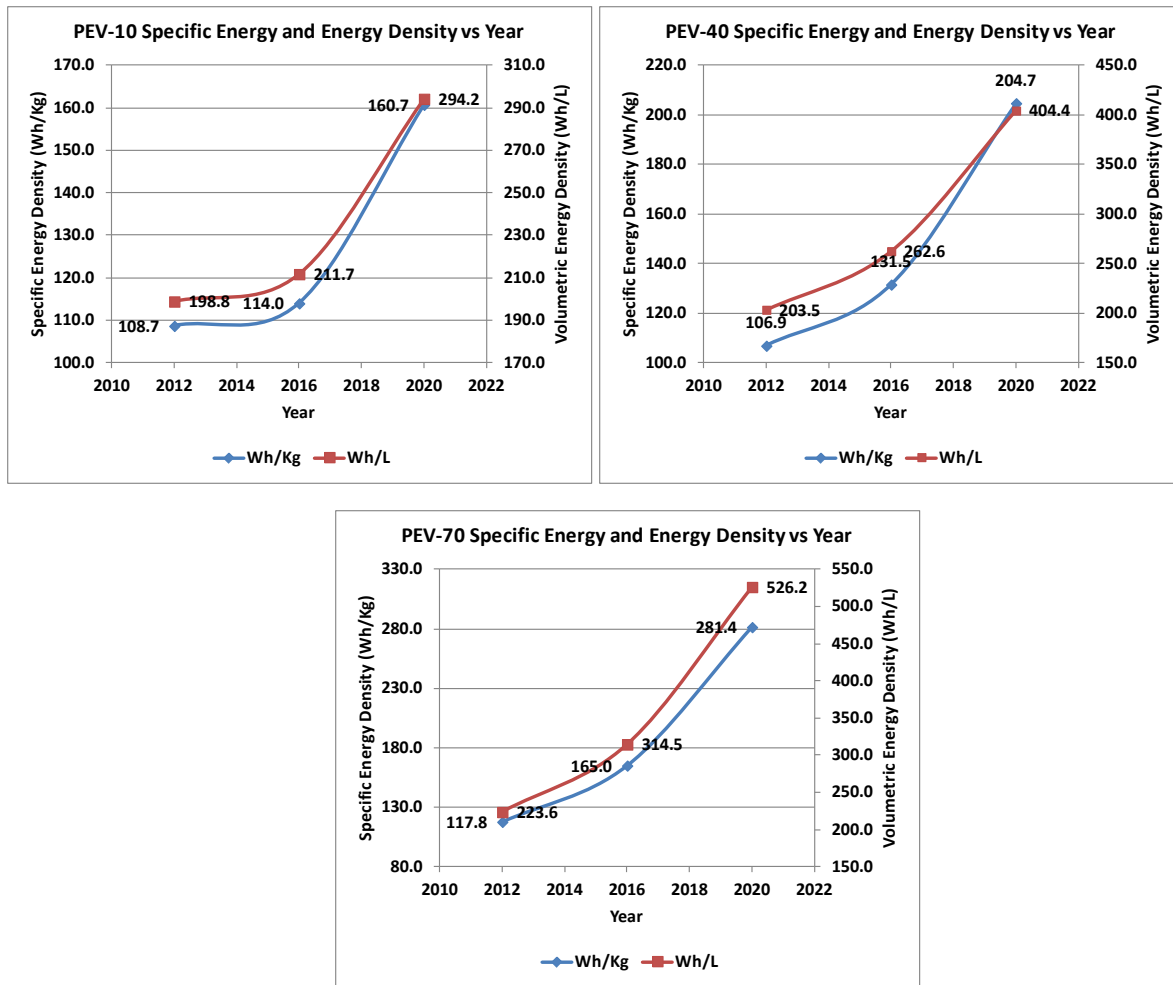


Figure 3-6
Case 1: PEV-10/-40/-70 specific energy and energy density: 2012-2020

Case 2: Decreasing Battery Capacities Through 2020

This case assumes that battery capacities will decrease in the future due to various improvements in vehicle efficiencies. For the purpose of this analysis, it has been assumed that packs will migrate to a single string configuration as explained under scenario 2 in the last chapter. The pack voltage is assumed to remain the same over the years for each vehicle type. Pack structure and voltage assumptions were listed in Table 2-8 above.

The pack kWh and cell Ah capacities assumed for Case 2 are shown in Tables 3-6 and 3-7. The P:E ratios of the three packs are shown in Table 3-8. All other assumptions are as detailed in chapter 2.

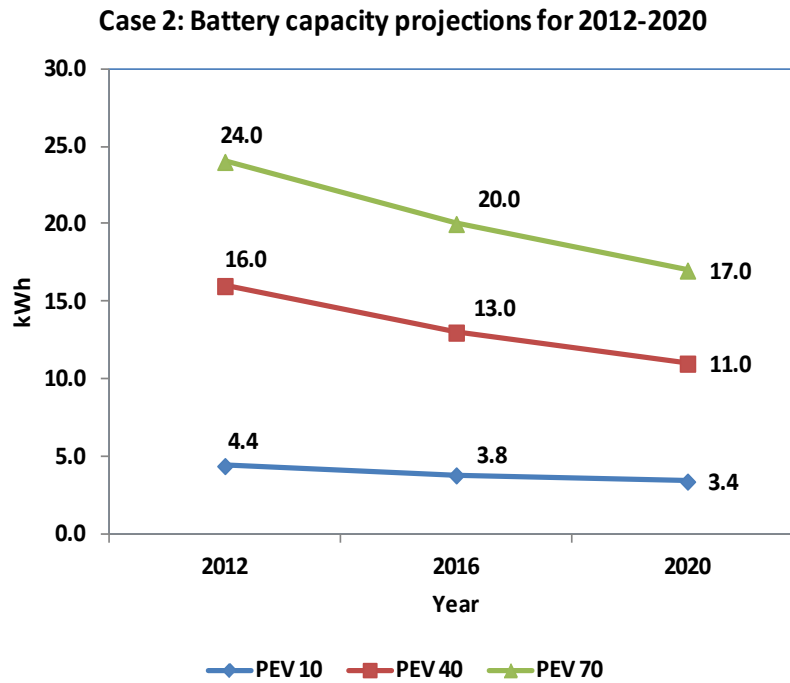


Figure 3-7
Case 2: Battery capacity projections for 2012-2020

Table 3-7
Case 2: Battery kWh capacity assumptions (2012 -2020)

	Battery Size (kWh)		
Vehicle	2012	2016	2020
PEV-10	4.4	3.8	3.4
PEV-40	16	13	11
PEV-70	24	20	17

Table 3-8
Case 2: Cell Ah capacity (2012 -2020)

	Cell Ah		
Vehicle	2012	2016	2020
PEV-10	21	18	16
PEV-40	44 (3 x 15)	35	30
PEV-70	67 (2 x 33)	55	47

Table 3-9
Case 2: Battery P:E ratios (2012 -2020)

Vehicle	P:E ratio		
	2012	2016	2020
PEV-10	11.4	13.2	14.7
PEV-40	9.4	11.5	13.6
PEV-70	4.6	5.5	6.5

Battery Pack Costs

Figure 3-8 shows the cost curves over volume for the three vehicles, and cost numbers are given in Table 3-6. As in Case 1, the cost reductions for the PEV-10 are incremental only compared to the reductions projected for PEV-40 and PEV-70.

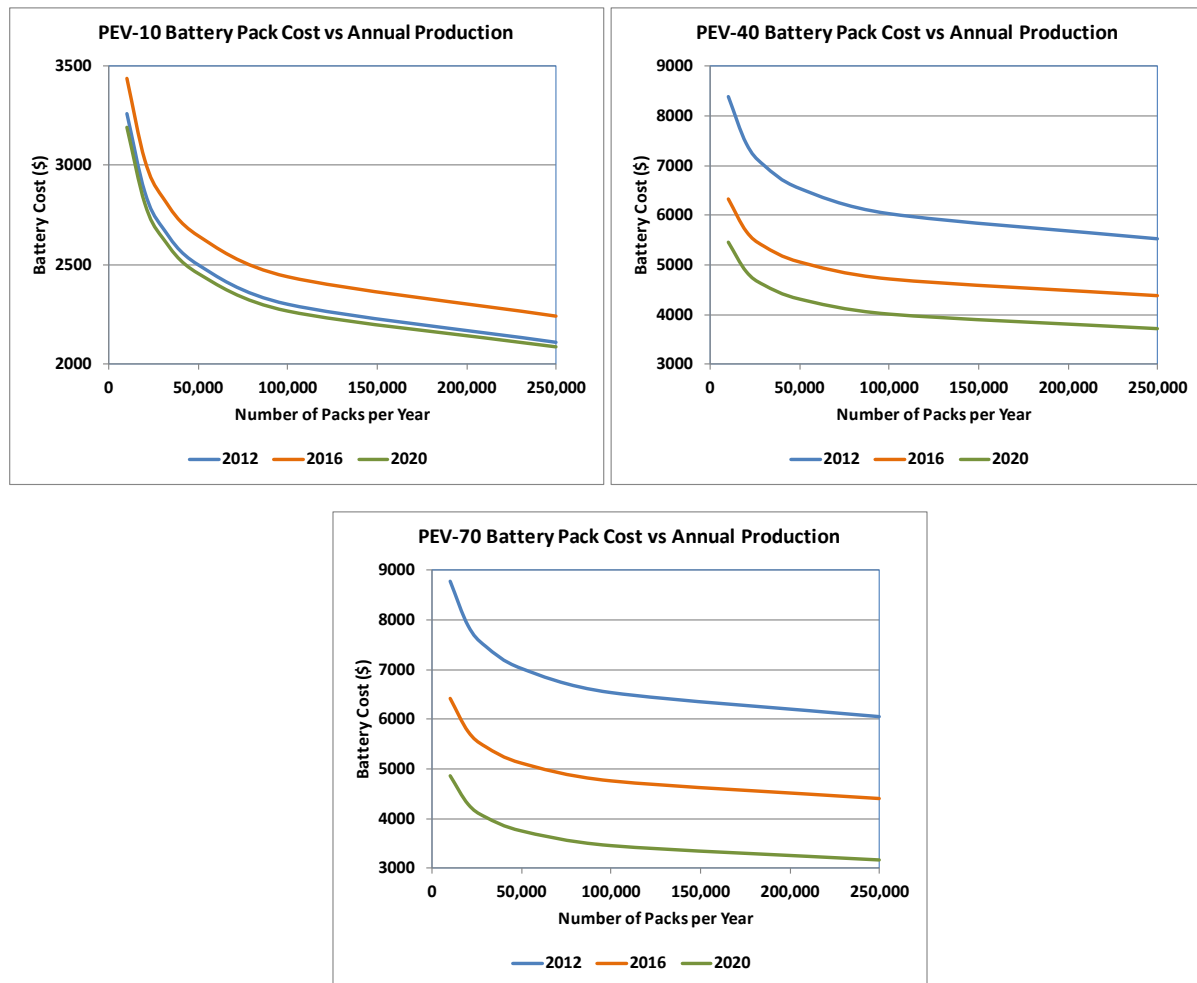


Figure 3-8
Case 2: PEV-10/-40/-70 battery pack costs: 2012-2020

Table 3-10
Case 2: PEV-10/-40/-70 battery pack costs (2012 -2020)

PEV-10	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$3,260	\$2,867	\$2,687	\$2,500	\$2,302	\$2,111
2016	\$3,435	\$3,026	\$2,839	\$2,646	\$2,441	\$2,244
2020	\$3,192	\$2,809	\$2,635	\$2,456	\$2,267	\$2,087

PEV-40	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$8,397	\$7,452	\$7,009	\$6,541	\$6,033	\$5,526
2016	\$6,322	\$5,670	\$5,367	\$5,050	\$4,709	\$4,372
2020	\$5,448	\$4,859	\$4,588	\$4,306	\$4,005	\$3,714

PEV-70	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$8,777	\$7,886	\$7,469	\$7,027	\$6,545	\$6,063
2016	\$6,410	\$5,747	\$5,437	\$5,110	\$4,756	\$4,402
2020	\$4,851	\$4,281	\$4,018	\$3,743	\$3,449	\$3,161

Battery Specific Costs (\$/kWh)

Battery specific costs are shown in Figure 3-9 and Table 3-10. There are several interesting observations here:

- The \$/kWh costs for a PEV-10 actually increase into 2020. This is attributed to the fact that the P:E ratios increase into 2020 with the battery power increasing and the battery size decreasing into 2020.
- The \$/kWh costs for a PEV-40 show an incremental increase from 2012 to 2020.
- The \$/kWh costs for the PEV-70 on the other hand decreases considerable over time.

The above observations are directly attributable to the differences in the P:E ratios of the batteries. The P:E ratios for the PEV-10 batteries are large and as such the associated battery costs are more dependent on the power than is the case for a PEV-70 battery that is more of an energy device.

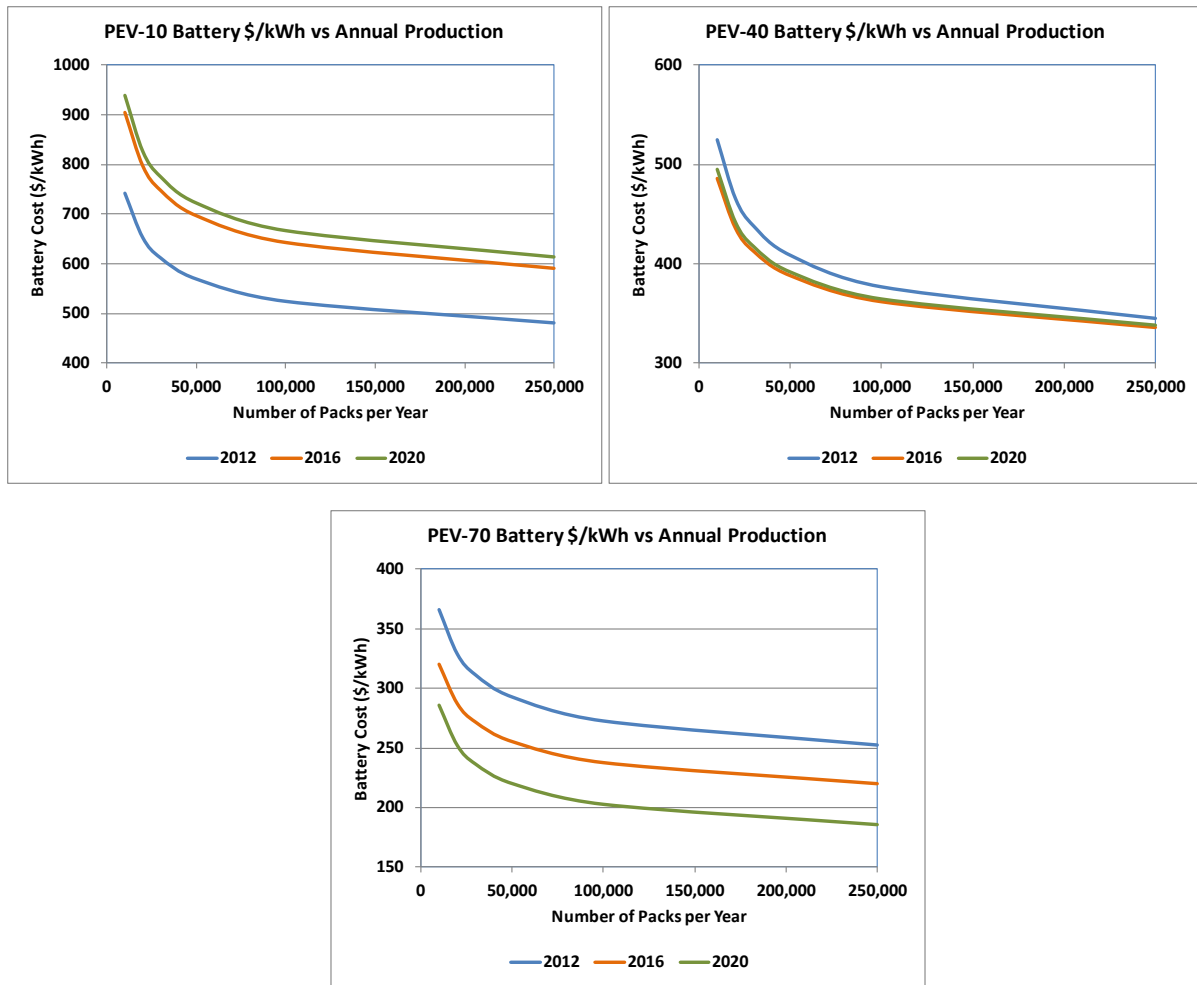


Figure 3-9
Case 2: PEV-10/-40/-70 battery \$/kWh costs: 2012-2020

Table 3-11
Case 2: PEV-10/-40/-70 battery \$/kWh costs (2012 -2020)

PEV-10	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$741	\$652	\$611	\$568	\$523	\$480
2016	\$904	\$796	\$747	\$696	\$642	\$591
2020	\$939	\$826	\$775	\$722	\$667	\$614

PEV-40	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$525	\$466	\$438	\$409	\$377	\$345
2016	\$486	\$436	\$413	\$388	\$362	\$336
2020	\$495	\$442	\$417	\$391	\$364	\$338

PEV-70	10,000	20,000	30,000	50,000	100,000	250,000
2012	\$366	\$329	\$311	\$293	\$273	\$253
2016	\$320	\$287	\$272	\$256	\$238	\$220
2020	\$285	\$252	\$236	\$220	\$203	\$186

Likely Battery Costs

As for Case 1 a more realistic approach to projecting nearer term battery specific costs is to assume that battery production rates increase over the years, from 10,000 packs in 2012 to 50,000 in 2016 and 100,000 packs in 2020. Under these more realistic assumptions costs still decline substantially over the years, as summarized below and illustrated in Figure 3-10: PEV-10 costs are around \$740/kWh today and decrease to \$667/kWh by 2020.

- PEV-40 costs are around \$525/kWh today and decrease to \$364/kWh by 2020.
- PEV-70 costs are around \$366/kWh today and decrease to \$203/kWh by 2020.

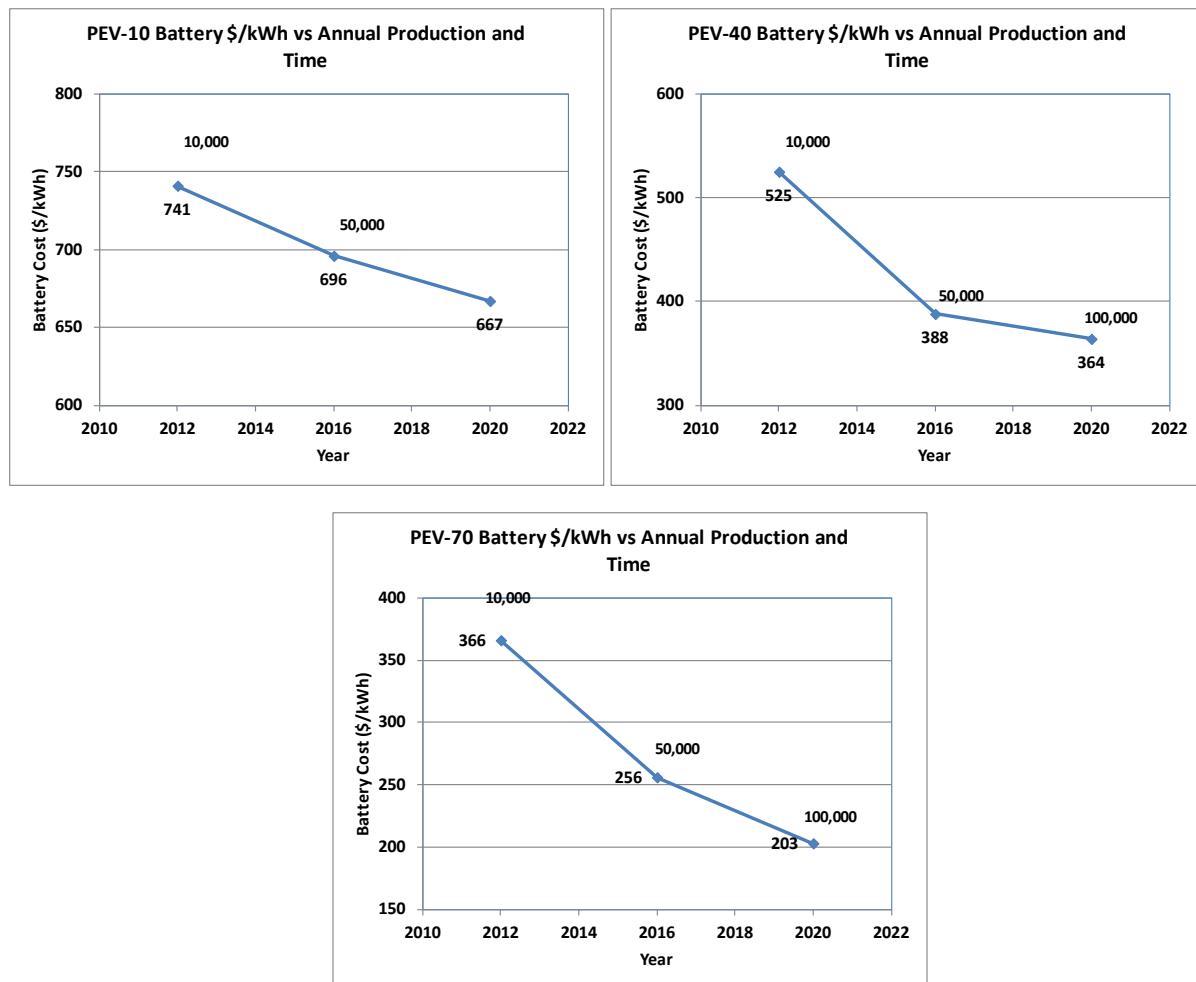


Figure 3-10
Case 2: PEV-10/-40/-70 expected battery costs: 2012-2020

Battery Weight and Volume

For the same reasons as in Case 1 battery weights and volumes also decrease significantly over time in Case 2 as illustrated in Fig. 3-12. This trend is caused by the combination of reduced battery capacities and to increased specific energies and energy densities as well as a reduction in battery capacities going forward into the future. Figure 3-5 shows a reduction in battery weight and volume for all the three PEV cases. The percentage decrease in weight and volume from 2012 to 2020 is shown in Table 3-12; they are slightly larger than in Case 1.

Table 3-12
Case 2: Percentage decrease in weight and volume from 2012 to 2020

	% reduction	
PEV	Weight	Volume
PEV-10	29	30
PEV-40	49	52
PEV-70	66	65

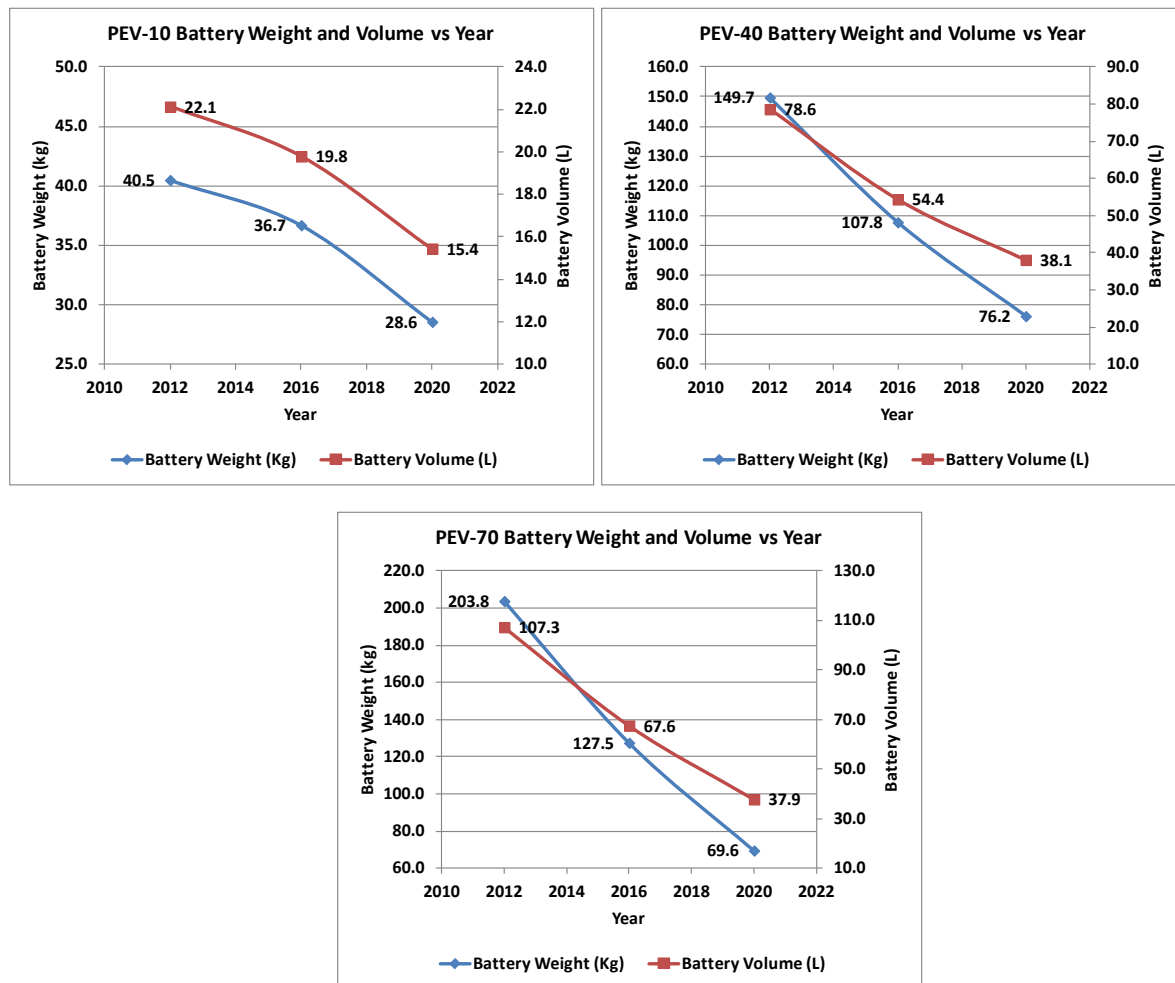


Figure 3-11
Case 2: PEV-10/-40/-70 battery weight and volume: 2012-2020

Specific Energy and Energy Density vs Year

Again as in Case 1, improvements in battery materials coupled with reductions in weight and volume, result in decreases in the specific energies and energy densities of the battery into 2020. This is shown in Figure 3-11. The PEV-40 battery is projected to have an increase of specific energy and energy density of as much as 36% compared to batteries available today. Similarly, the PEV-70 battery is expected to have an increase of specific energy and energy density of more than 100% compared to today's numbers.

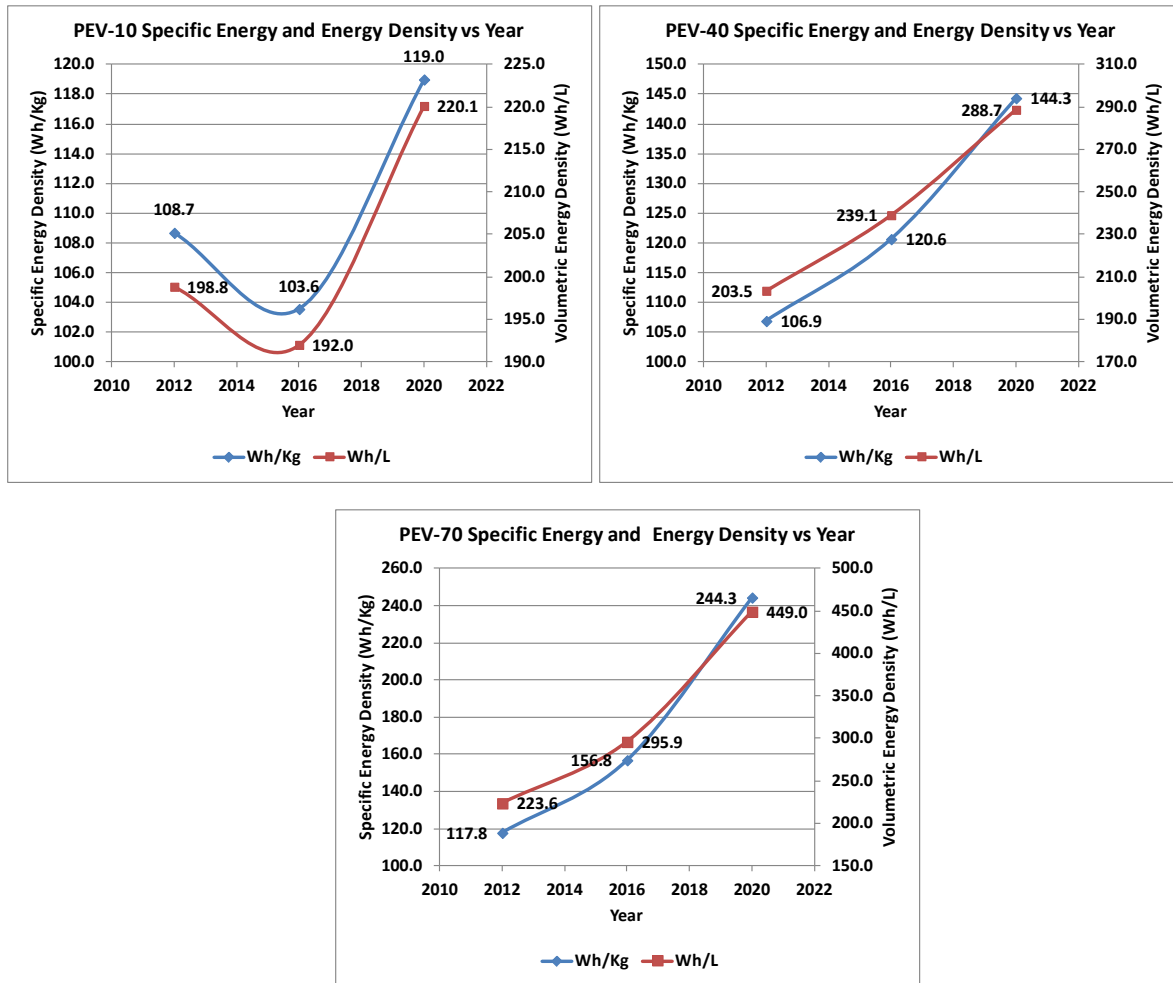


Figure 3-12
Case 2: PEV-10/-40/-70 specific energy and energy density: 2012-2020

Sensitivity of Battery Cost to Power

The analysis of chapter 3 makes clear that battery costs depend strongly on battery power. To determine this sensitivity quantitatively, additional simulations were carried out in which battery power was varied. Figure 3-13 shows the battery total cost curves for a PEV-40 and a PEV-70

for two battery power levels each: 150 kW and 110 kW for the PEV-40 battery, and 110 kW and 100 kW for the PEV-70 battery. The PEV-40 battery cost exhibits significant dependence on power; the impact is not as significant for a PEV-70.

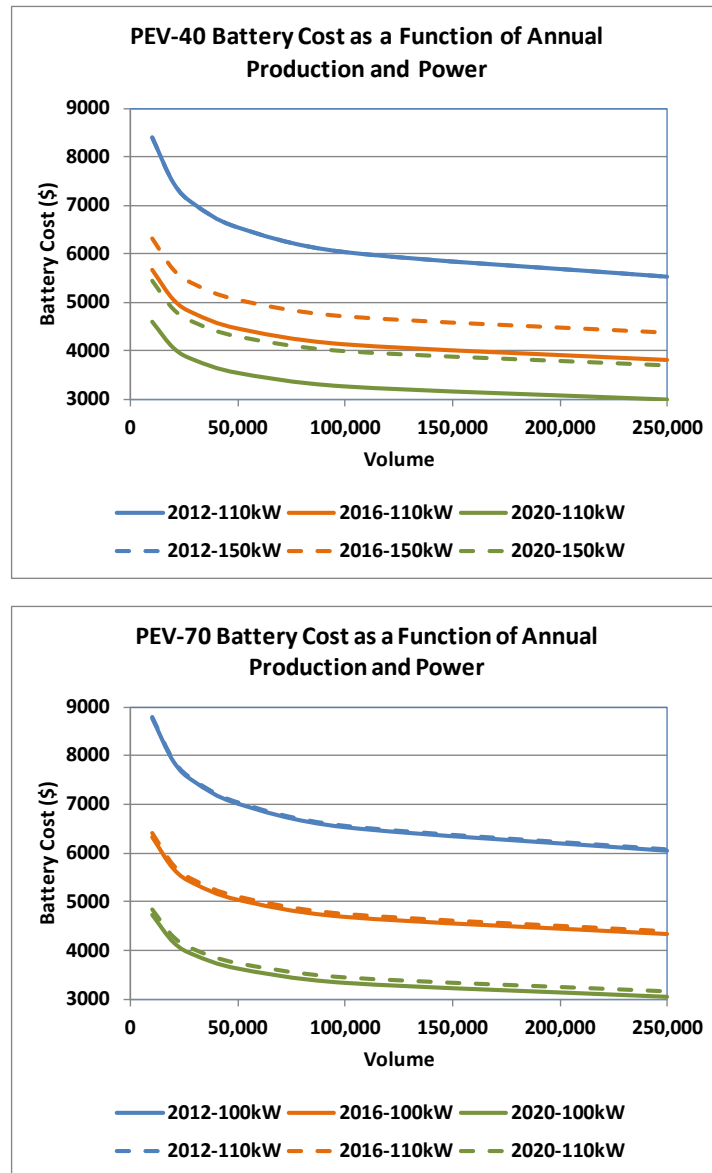


Figure 3-13
PEV-40 and -70 battery pack costs as a function of battery power: 2012-2020

In part the PEV-70 battery costs do not increase much with power because of the smaller difference in between the two power levels considered. More importantly, in contrast to the situation with the PEV-40, the larger PEV-70 battery is able to deliver higher power levels with little or no increase of the battery's total electrode area, a primary cost driver. In explanation, as power levels of a battery of given capacity (i.e. the P:E ratio) increase, electrode coating thickness usually needs to be decreased to limit ohmic and efficiency losses. As a result, the same battery capacity (which is proportional to the electrode active mass) now requires more battery area, a major cost driver.

Figures 3-14 and 3-15 show this effect graphically: The electrode coating thickness must decrease significantly with increasing battery power for both a PEV-40 and a PEV-70 which, in turn, increases battery active surface area and cost. The figure also shows that coating thickness needs to be thinner for PEV-40 with its larger P:E ratio. This is part of the explanation for the higher battery specific cost (\$/kWh) levels of PEV-40 compared to PEV-70 and PEV-10 compared to PEV-40. It also explains why battery specific costs do not decline as much as total costs over the time frame of the study's projections: the higher specific power of the smaller-capacity future batteries increases specific cost, thus offsetting the advantages provided by advanced chemistries with higher specific energy. Most important, however, total battery costs decline substantially over time, and battery weight and volume decrease very substantially

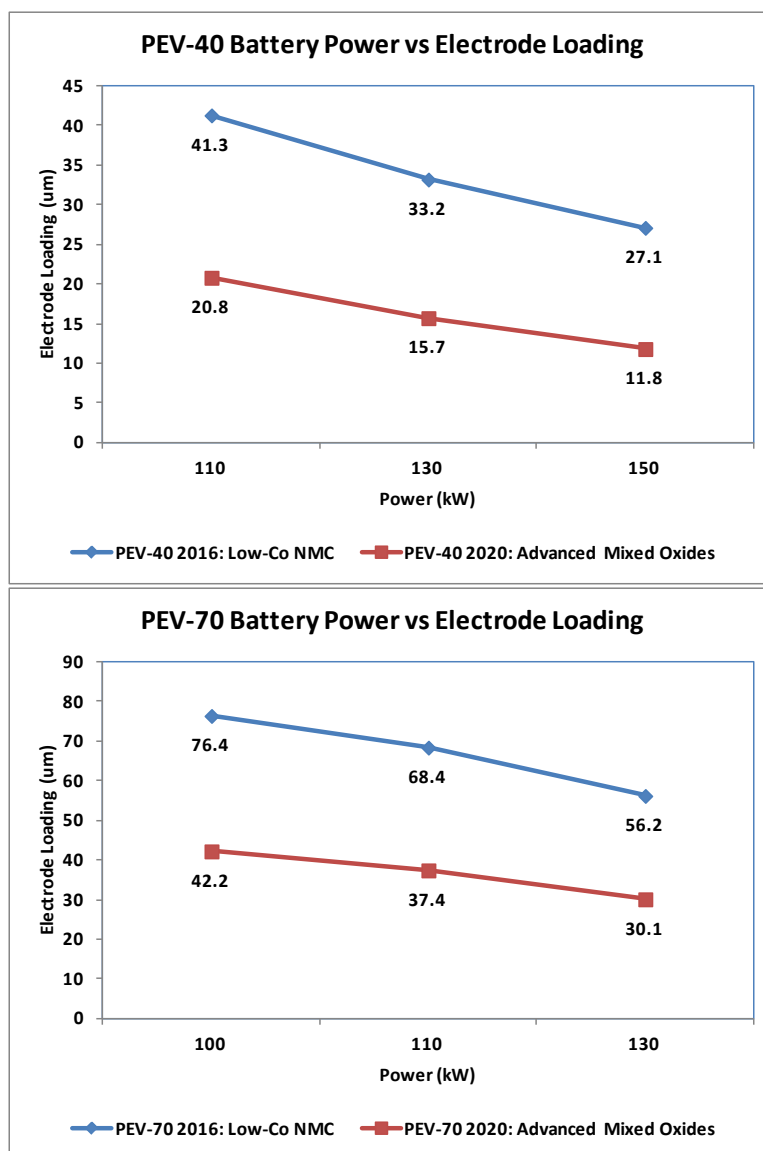


Figure 3-14
PEV-40 and -70 electrode loading vs battery power: 2012-2020

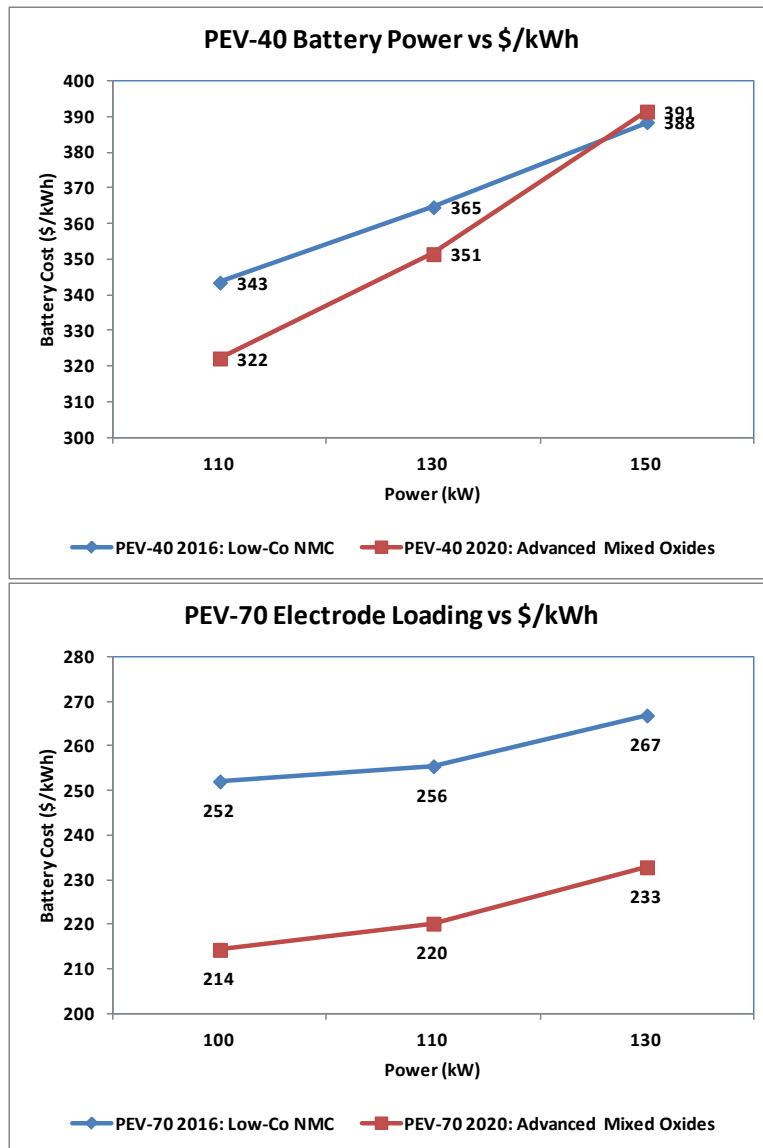


Figure 3-15
PEV-40 and -70 electrode loading vs \$/kWh: 2012-2020

Summary

Improving vehicle efficiencies and battery technology are likely to result in smaller batteries for the same given range. These changes, coupled with decreasing material costs will result in smaller, lower cost packs in the future. By 2020 PEV-10 battery packs are expected to decrease from 4.4 kWh today to 3.4 kWh (a decrease of 23%); PEV-40 battery packs will decrease from 16 kWh today to 11 kWh and PEV-70 battery costs will decrease from 24 kWh today to about 17 kWh, both decrease of around 30%. Even larger increases in specific energy and energy density are projected for each vehicle type.

A cost sensitivity study and forecast was done using the ANL BatPac 1.1 model with material type, material cost, vehicle efficiency, useable SOC, and battery size as key variables. The time frame for the analysis was from 2012 to 2020 with 2016 as an intermediate point. Two scenarios were analyzed –the first one assuming unchanged battery capacities for each vehicle type till 2020, and the other assuming decreasing battery capacities through 2020. The latter assumption is supported by the expected lower Wh/miles specific consumption of the vehicles in the future along with the likely availability of advanced battery materials and designs that will permit deeper depths of discharge compared to today's batteries. Battery power is assumed to be unchanged through 2020 for each vehicle.

Cost simulations show that in the case of decreasing battery capacity, PEV-10 battery specific costs will decline from today's \$740/kWh to \$667/kWh by 2020; PEV-40 battery specific costs will decline from today's \$525/kWh today to \$364/kWh by 2020; and PEV-70 battery specific costs will decline from today's \$366/kWh to \$203/kWh by 2020. The specific cost reductions are more significant when the battery size is held constant (and therefore the P:E ratio as all the analysis assumes constant power), but the reductions in total battery costs are greater if battery capacities are assumed to decline over time.

Battery specific (\$/kWh) costs strongly depend on battery specific power and the P:E ratio. As a result, the PEV-40 battery costs more than the PEV-70 of 50% larger capacity. The need for higher specific power for the PEV-40 battery requires a reduction of electrode loadings and increases the battery total cell area needed for a given battery capacity which, in turn, increases battery cost. Because this important cost factor depends on battery cell design, the impact of cell designs must be considered explicitly when projecting future battery costs. This aspect will be a key topic of study in 2013.

4

LITHIUM-SULFUR BATTERIES: STATUS, ISSUES AND PROSPECTS

Introduction

The lithium-sulfur (Li-S) electrochemical system in principle offers the high specific energy and low active materials costs needed for batteries that meet the requirements for mass-market electric vehicles: at approximately 2500Wh/kg the theoretical specific energy of Li-S is at least 5 times higher than that of Li Ion, and Li-S active materials costs are much lower. Investigations over more than 30 years have shown the fundamental feasibility of lithium-sulfur as a battery electrochemistry but also revealed several major problems for the realization of practical Li-S batteries.

Driven by the rapidly growing commitments to electric vehicle development and commercialization, efforts to overcome the problems surrounding the Li-S battery have expanded significantly in the last few years. As discussed below, important progress is being achieved in understanding and tackling the most important technical issues, and first attempts are now being made to base Li-S cell technologies on this progress. However, it is not yet clear whether the most serious problem – substantial, irreversible loss of sulfur electrode and cell capacities with cycling – can be overcome with the currently pursued approaches. Moreover, it is not obvious that these approaches even if successful will also result in the desired major increases in battery energy storage performance over that of Li Ion batteries.

This report is a first attempt to assess recently reported R&D advances for their potential to become the basis of Li-S technologies that can meet the requirements for EV propulsion. The emphasis is on the potential of Li-S for achievement of high energy storage performance and extended deep cycling, but the prospects for achievement of adequate battery discharge rates are also discussed. As part of the analysis several possible directions for resolving limiting technical problems are identified.

Background

Past investigations of the Li-S electrochemical couple as a possible basis for high energy batteries have established the couple's most important characteristics several of which continue to cause serious problems for battery development:

- Sulfur has sufficient electrochemical reactivity to serve as a positive electrode (“cathode”) in a number of non-aqueous electrolytes (Refs. 1-4). Sulfur is partially soluble in these electrolytes, and dissolved sulfur can be discharged with practical rates (Ref.5). However, it is not clear whether dissolved or solid sulfur – or possibly both – are the predominantly involved species in the discharge of sulfur.
- Sulfur is electrically insulating in all forms. To permit its discharge sulfur has to be in intimate contact with a conducting material, typically carbon in a variety of forms.

- Li-S cells with properly designed sulfur cathodes (and lithium anodes of sufficient capacity) can deliver close to the theoretical maximum capacity, approximately 1670mAh per gram of sulfur when discharged for the first time (Refs. 6, 7). At increasing charge and discharge rates progressively less cathode capacity is electrochemically available (Refs. 7, 8, 9).
- Sulfur cathode capacity declines irreversibly after the first discharge-charge cycle, first rapidly and then more slowly with continued cycling. The observed capacity loss patterns and rates depend strongly on the method used to prepare the cathode (Refs. 6, 8, 9, 10).
- The discharge of sulfur cathodes in the presence of Li^+ ions proceeds through a series of polysulfides (general formula: Li_2S_n) with decreasing sulfur content, starting with Li_2S_8 and ending with lithium sulfide (Li_2S) (Ref. 1, 5, 11). In the electrolytes of interest polysulfides with $n \geq 4$ are readily soluble as polysulfide anions $\text{Li}_2\text{S}_n^{2-}$ but polysulfide discharge products with $n < 4$ precipitate as solids. The ultimate discharge product Li_2S is insoluble and tends to block (“passivate”) part of the cathode. (Ref. 5).
- Dissolved polysulfides increase the viscosity of electrolytes contained in the sulfur electrode and the separator and thus cause substantial increases of the cell resistance (Ref. 12).
- Soluble polysulfides can migrate through the electrolyte and react with the Li anode to form lower polysulfides in a cell self-discharge reaction. Higher and lower polysulfides together act as redox shuttles between anode and cathode that accelerate self-discharge (Ref. 13). The self-discharge process results in formation of an insoluble layer (largely Li_2S) on the Li anode which constitutes an irreversible loss of sulfur cathode and Li-S cell capacity. As the Li anode surface layer is growing it increasingly protects Li from further attack, similar to – but apparently less effectively than – the solid-electrolyte interface (SEI) layer that protects Li anodes in Li Ion cells.
- Addition of lithium nitrate to the electrolyte of Li-S cells results in a “passivating” surface film on Li that tends to protect anodes from attack by dissolved polysulfides (Refs. 6, 14).
- Nearly all Li-S cell investigations report high reversibility (low overpotential) of the cathode charge reaction.
- When Li-S cells are recharged, mossy deposits of lithium tend to form on partially discharged anode surfaces which can lead to anode capacity loss. However, formation of dendritic Li deposits and cell shorting does not seem to be a problem with Li-S cells because polysulfides in the electrolyte react preferentially with Li dendrites.

The key problems of Li-S cells – self-discharge, and capacity loss with cycling, both caused by dissolved polysulfides – are being addressed since several years with partial success. Broadly speaking one can distinguish two technical strategies that differ with respect to cathode and cell design: (1) retaining polysulfide discharge products within the cathode structure throughout their stepwise discharge to Li_2S , or/and (2) preventing dissolved polysulfides from reaching the lithium anode by interposing a barrier impermeable to polysulfides between cathode and anode. In the next sections the cycling capabilities of Li-S cells that use these strategies are reviewed, the upper limits of the volume- and weight-based energy densities likely to be achieved with such cells are estimated, and the prospects for practical cell discharge rates are examined.

Cycle Life, Energy Storage and Discharge Rate Potential of Li-S

Fig. 4-1 shows the cross section of two lithium-sulfur cells with their functional components. The conceptually simplest cell design (Fig. 4-1a) has been used almost exclusively in investigations up to now.

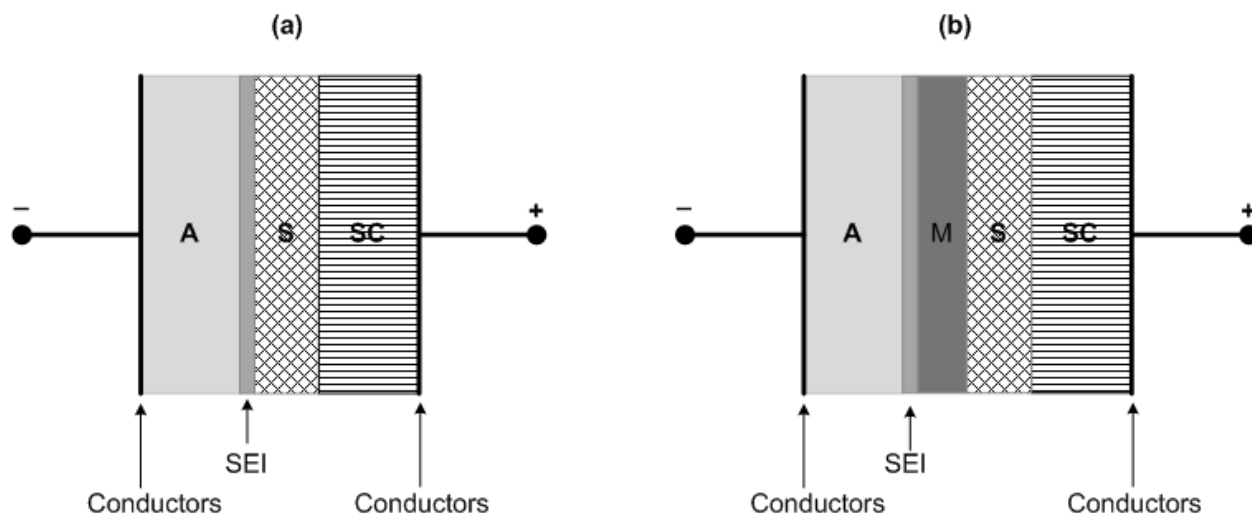


Figure 4-1
Cross Sections of Lithium-Sulfur Cells (Conceptual)

The cell consists of a solid lithium anode (A) separated from a sulfur cathode (SC) by a porous polymer separator (S). Once such a cell is assembled, polysulfide products of self discharge and/or electrochemical discharge reach, and react with, the Li anode to form a solid-electrolyte-interface film (SEI) on the anode that provides partial protection from polysulfide attack. In the design shown in Fig 4-1b, a solid membrane (M) barrier is inserted between anode and cathode to prevent polysulfides from reaching the anode. The characteristics and battery prospects of barrier-less Li-S cells are discussed first, those of barrier-type cells further below.

Cells without Dedicated Polysulfide Barriers

Cycle Life

High rates of self-discharge and capacity loss in cycling are reported in earlier work that used cathodes made from intimate mixtures of sulfur, conducting carbon and binder powders. Cathode and cell capacity loss rates are reduced very substantially if sulfur is contained in cathode structures with pores that are sufficiently small to minimize polysulfide out-diffusion while still providing adequate electrolyte access and pore conductance.

In Table 4-1, the most promising sulfur cathode capacity and capacity retention data reported in the last few years for such structures (lines 2 and 3) are compared with data for a conventional cathode made from a sulfur-carbon-binder mixture (line 1):

Table 4-1
Capacities and Capacity Retention of Sulfur Cathodes

Literature Reference	Cathode construction [S content in weight %] Special features	Cathode Thickness in μm (10^{-4}cm)	Specific Capacity when new (mAh/g of S)	Specific Capacity after [] cycles (mAh/g of S)	Initial Discharge Capacity ¹ (mAh/cm ²)
10	Mixture of sulfur, porous carbon and binder ([70])	25-30	up to 1,100	≈ 250 [50]	1
8	S-infiltrated mesoporous carbon microspheres [42]	40	$\approx 1,300$	≈ 600 [50]	1.6
9	S-infiltrated carbon nanotubes [54]	~ 120	≈ 900	> 800 [100]	11
6	S-carbon mix [47]; LiNO_3 addition; cell compression	?	up to 1,500	≈ 800 [300]	7

¹calculated from experimental cathode data

Compared with the use of a conventional cathode mix (Table 1, Ref. 10), approaches to contain sulfur and discharge products (Ref. 8 and 9) are able to preserve much higher fractions of the initial capacity, at least up to 50-100 cycles. In particular, a sulfur cathode consisting of oriented carbon nanotubes (Ref. 9) initially delivered around 900 mAh/g, more than 50% of the sulfur theoretical capacity (1670 mAh/g) and retained nearly 90% of the initial capacity for at least 100 deep discharge-charge cycles. Furthermore, the nanotube structure could be deposited as a relatively thick coating that delivered a cathode discharge capacity of more than 10 mAh/cm². In combination with the encouraging cycling performance this is a major improvement over previously achieved sulfur cathode and Li-S cell performance.

Whether any of these approaches has the potential to eventually achieve the 1,000+ deep cycles needed for competitive EV applications is unclear at this time. However, it is considered promising that cells with apparently conventional mixed cathodes are able to deliver at least 300 deep cycles (Table 1, Ref. 6) with reasonable capacity retention if Li anodes are protected through the addition of LiNO_3 to the electrolyte and maintained under compression to combat the formation of mossy lithium deposits with cycling. It may be speculated that addition of LiNO_3 (or perhaps other film-forming chemical agents) to the electrolyte of cells with retained-sulfur cathodes will further reduce capacity loss rates and extend deep cycle life: the rate of polysulfide loss due to diffusion to the anode, already low in such cells because of the low electrolyte concentration of polysulfide, should be reduced even more by the film formed on the Li anode.

Energy Storage Performance

The following analysis is largely based on the sulfur cathode specific and discharge capacities reported by Hagen et al. (Ref. 9) but the data in Table 4-1 indicate that similar initial specific and discharge capacities can be achieved with other approaches.

Assumptions:

cathode specific capacity:	900 mAh/g of S (typical for well-performing sulfur cathodes)
cathode thickness:	200 $\mu\text{m} = 20 \times 10^{-3} \text{ cm}$
sulfur content in cathode:	54% by weight
average density of cathode:	1 g/cm^3 (representative for porous sulfur-carbon structures)
cathode loading with S:	11 $\times 10^{-3} \text{ g/cm}^2$ (calculated from above data)
cathode discharge capacity:	approx. 10 mAh/ cm^2 (calculated from above)
separator (electrolyte-filled):	thickness = $2.5 \times 10^{-3} \text{ cm}$ (polymer porosity 50%, density 1 g/cm^3)
Li anode loading:	$2.6 \times 10^{-3} \text{ g/cm}^2$ (stoichiometric for 10mAh/ cm^2 discharge capacity)
Li anode thickness:	approx. $5 \times 10^{-3} \text{ cm}$

Accordingly, a Li-sulfur cell with 10mAh/ cm^2 discharge capacity will have components (see Fig. 1) of the following thickness:

Li anode (A):	$6 \times 10^{-3} \text{ cm}$ (allowing for a typical 20% excess of Li)
separator (S):	$2.5 \times 10^{-3} \text{ cm}$
sulfur cathode (SC):	$20 \times 10^{-3} \text{ cm}$
anode conductor:	$1.2 \times 10^{-3} \text{ cm}$ (Cu sheet, typical for Li Ion cells of similar area capacity)
cathode conductor:	<u>$2 \times 10^{-3} \text{ cm}$ (Al sheet, typical for Li Ion cells)</u>
Cell section thickness and volume:	$31.7 \times 10^{-3} \text{ cm}$ and 0.0317 cm^3

The maximum energy that can be delivered by a 1 cm^2 (0.0317 cm^3) section of a Li-S cell with a typical average discharge voltage of 2.15V is 10mAh x 2.15V = 21.5mWh. Accordingly the energy density of the cell section is $ED_{\text{Li-S}} = 21.5 \text{ mWh}/0.0317 \text{ cm}^3$ or approximately 680Wh/L. Adding an enclosure (for example, a 0.25 mm coated aluminum sheet to contain a 10 cell-layer stack of cells) reduces the energy density upper limit to 586Wh/L; for a “pouch” type enclosure (e.g. a 5 mil plastic sheet) the upper limit would be around 630Wh/L.

The maximum specific energy of a 1 cm^2 section of a Li-S cell of 10mAh/ cm^2 discharge capacity can be estimated from the component weights as follows:

Li anode (A):	$3 \times 10^{-3} \text{ g/cm}^2$ (allowing for a typical 20% excess of Li)
separator (S):	$2.5 \times 10^{-3} \text{ g/cm}^2$ (separator and electrolyte density $\approx 1 \text{ g/cm}^3$)
cathode (SC):	$20 \times 10^{-3} \text{ g/cm}^2$ (sulfur in CNT, average density $\approx 1 \text{ g/cm}^3$)
anode conductor:	$10.7 \times 10^{-3} \text{ g/cm}^2$ (Cu sheet)
cathode conductor:	<u>$5.4 \times 10^{-3} \text{ g/cm}^2$ (Al sheet)</u>
Cell section weight:	$41.6 \times 10^{-3} \text{ g/cm}^2$

The maximum specific energy of the 1 cm^2 ($41.6 \times 10^{-3} \text{ g}$) cell section accordingly is $SE_{\text{Li-S}} = 21.5 \text{ mWh}/41.2 \times 10^{-3} \text{ g}$, or approximately 517Wh/kg. Allowing for the necessary enclosure (e.g. for a 10-layer stack) reduces this value to around 395Wh/kg (prismatic aluminum case), respectively 465Wh/kg (plastic pouch enclosure).

It is instructive to compare the energy density and specific energy values for Li-S with those for Li Ion technology. Listed below are the component measures (thickness and weight) for a 1cm² section of a Li Ion cell, calculated by the author for a charge capacity of 10mAh/cm² from data for a 5mAh/cm² state-of-the-art PHEV-design cell (Ref. 15):

Cell discharge voltage (average):	3.6V	
Cell discharge capacity:	10mAh/cm ²	
Negative electrode (graphite):	28.510 ⁻³ cm	[30x10 ⁻³ g/cm ²]
Separator:	2x10 ⁻³ cm	[2x10 ⁻³ g/cm ²]
positive electrode (e.g. NCA):	25x10 ⁻³ cm	[67x10 ⁻³ g/cm ²]
Cu negative conductor:	1.2x10 ⁻³ cm	[10.7x10 ⁻³ g/cm ²]
<u>Al positive conductor:</u>	<u>2x10⁻³ cm</u>	<u>[5.4x10⁻³ g/cm²]</u>
Cell section thickness [weight]	0.059 cm	[0.115g/cm ³]

The energy density and specific energy of this Li Ion cell section can now be estimated:

$$ED_{Li\ Ion} = 10mAh \times 3.6V / 0.059\ cm^3 = 610mWh/cm^3\ or\ 610Wh/L, and$$

$$SE_{Li\ Ion} = 10mAh \times 3.6V / 0.115\ g = 313Wh/kg.$$

Allowing for the thickness and weights of 10-cell stack enclosures results in:

$$ED_{Li\ Ion} = 565Wh/L\ (aluminum\ case)\ and\ ED_{Li\ Ion} = 590Wh/kL\ (plastic\ pouch), and$$

$$SE_{Li\ Ion} = 280Wh/kg\ (aluminum\ case)\ and\ SE_{Li\ Ion} = 305Wh/kg\ (plastic\ pouch).$$

The comparison of these values with those estimated above for Li-S cell sections shows that Li-S has the potential to exceed the specific energy of state-of-the-art Li Ion cells by around 40% if aluminum cases are used, and about 50% for pouch-enclosed cells. On the other hand, the energy density of Li-S cells is unlikely to exceed that of Li Ion cells by more than 5% to 7%.

Because the energy densities of Li-S and Li Ion cells are comparable, it seems reasonable to estimate the upper limits of the energy storage performance of complete Li-S batteries from Li-S cell section data and the cell section-to-battery scaling factor for the energy density and specific energy typical for Li Ion technology. For a complete 32.4 kWh Li Ion EV battery (using aluminum cell cases) the Argonne National Lab's battery model predicts (Ref. 15) an energy density of $ED_{Li\ Ion}^B = 324Wh/L$ and a specific energy of $SE_{Li\ Ion}^B = 173Wh/kg$. Thus, the scaling factors for going from a 1cm² cell section to a complete Li Ion battery are $ED_{Li\ Ion}^B / ED_{Li\ Ion} = 324/565 \approx 0.575$ for energy density, and $SE_{Li\ Ion}^B / SE_{Li\ Ion} = 173/280 \approx 0.62$ for specific energy. Applying these factors to Li-S cell section data results in the following upper limits for complete Li-S batteries:

$ED_{Li-S}^B = 0.575 \times 590 \approx 340Wh/L$, and $SE_{Li-S}^B = 0.62 \times 395 \approx 245Wh/kg$ (for aluminum cell cases), increases of 5% (energy density) and 40% (specific energy) over Li Ion. Rough estimates for complete batteries with pouch cells are 375Wh/L for energy density (16% increase over Li Ion with prismatic aluminum cell cases) and 288Wh/kg for specific energy (66% increase).

In principle two avenues exist for increasing the energy storage performance of Li-S cells and batteries beyond these limits: (1) improving the utilization of sulfur above 900mAh/g (54% of theoretical), and (2) increasing the cell discharge capacity above 10mAh/cm². For the purpose of establishing the uppermost limits for Li-S energy storage performance the author estimated the energy density and specific energy for a cell based on a cathode with 100% sulfur utilization (1670mAh/g) and a discharge capacity of 10mAh/cm² x 1670/900 = 18.5mAh/cm². These estimates (for cells in a prismatic aluminum case) are:

$$ED_{\max} = 930\text{Wh/L (+58\% over 900 mAh/g, 10 mAh/cm}^2\text{ cell)} \text{ and } SE_{\max} = 565\text{Wh/kg (+43\%)}$$

In addition, two intermediate but still highly optimistic cases were estimated, a) 100% utilization of sulfur (1670mAh/g) with the cell discharge capacity kept at 10mAh/cm², and b) 900mAh/g sulfur capacity and 18.5mAh/cm² cell discharge capacity. With these assumptions the upper limits (aluminum cell case) become:

$$ED_a = 837\text{Wh/L (42\% over 900mAh/g, 10mAh/cm}^2\text{ cell)}, \text{ and } SE_a = 480\text{Wh/kg (+22\%)}, \text{ and } ED_b = 666\text{Wh/L (13\% over 900mAh/g, 10mAh/cm}^2\text{ cell)}, \text{ and } SE_b = 455\text{Wh/kg (+15\%)}$$

To arrive at the upper limits of energy storage performance for complete Li-S batteries these cell section estimates need to be multiplied by approximately 0.6, to result in:

$$ED^B \approx 560\text{Wh/L and } SE^B \approx 340\text{Wh/kg (battery with 1670mAh/g of sulfur, 18.5mAh/cm}^2\text{)}$$

$$ED^B \approx 500\text{Wh/L and } SE^B \approx 290\text{Wh/kg (battery with 1670mAh/g of sulfur, 10mAh/cm}^2\text{)}$$

$$ED^B \approx 400\text{Wh/L and } SE^B \approx 273\text{Wh/kg (battery with 900mAh/g of sulfur, 18.5mAh/cm}^2\text{)}$$

None of these estimates is considered realistic at the present state of knowledge: past efforts have failed to stabilize sulfur cathode capacities above approximately 1000mAh/g for more than a few cycles, and discharge capacities substantially higher than 10mAh/cm², already a high value for non-aqueous battery cells, are unlikely to permit battery discharges at EV-type rates, see also next section. Reasonably realistic upper limits for Li-S battery energy storage performance are, therefore:

$$ED^B_{\text{Li-S}} \approx 340\text{Wh/L and } SE^B_{\text{Li-S}} \approx 245\text{Wh/kg (900mAh/g, 10mAh/cm}^2\text{ ; aluminum cell cases)}$$

$$ED^B_{\text{Li-S}} \approx 375\text{Wh/L and } SE^B_{\text{Li-S}} \approx 290\text{Wh/kg (900mAh/g, 10mAh/cm}^2\text{ ; pouch enclosures)}$$

Discharge Rate Capability

The battery of a full size electric typically needs to store 30-40 kWh energy for adequate range and deliver a peak power of about 100-120 kW, for a (peak) power-to-energy capacity (P:E) ratio of at least 3:1 and preferably 4:1. The inverse of the P:E ratio is the time (in hours) in which the battery would be fully discharged at peak power if that power level were sustainable; P:E ratios of 3:1 and 4:1 thus correspond to discharge rates that would fully discharge the battery in 1/3 and 1/4 hours, respectively. These rates also are termed “3C” and “4C” rates where C is the battery capacity; a P:E ratio of 3:1 thus means that the battery has a peak discharge rate capability of 3C. The minimum sustainable discharge rates required for an EV battery are substantially lower than the peak rate, for example C/3.

In the analysis above literature data were invoked to show that Li-S cells (and batteries) could have discharge capacities of 10mAh/cm² or possibly more. Discharging this capacity at EV-type (C/3 to 3C) rates requires a minimum sustainable current density of 1/3x10 mA/cm² $\approx$ 3.3mA/cm² and a minimum peak (pulse) current density of 3x10mA/cm² = 30mA/cm². The feasibility of attaining these current densities will now be examined on the basis of available experimental data and some reasonable extrapolations from them.

The highest Li-S cell discharge rates reported in the literature are summarized in Table 4-2:

Table 4-2
Discharge Capability of Sulfur Cathodes

Literature Reference	Cathode Construction; Sulfur Content [%]	Cathode Thickness in μm (10^{-4}cm)	Initial Specific Capacity (mAh/g)	Initial Discharge Capacity (mAh/cm ²)	Specific Capacity (mAh/g of sulfur) at various rates ¹ : [mA/cm ² ; C-rate]
6	mix of S, porous carbon, binder [47]	?	up to 1,560	6	$\approx 1400^2$ [2; C/3] $\approx 1250^2$ [13; 2.15 C]
16	mix of S, porous carbon, binder [?]	?	up to 1,560	2.5	? [15; 6C]
8	S-infiltrated mesoporous carbon microspheres [42]	40	$\approx 1,300$	1.6	$\approx 1300^3$ [1.25; C/1.3] $\approx 600^4$ [1.25; C/1.3] $\approx 600^5$; [2.5; 1.6 C]
9	S-infiltrated carbon nanotubes [54]	≈ 120	≈ 900	11	900^6 [1.28; C/8.6] 700^7 [2.56; C/4.3] $\approx 600^8$ [3.84; C/2.86]
10	mix of S, carbon, binder [70]	25-30	up to 1,100	1	1100^9 [0.05; C/20] 250^{10} [0.05; C/20]

¹ all discharge current densities and C-rates calculated or estimated from experimental data

² initial capacity

³ initial capacity; ⁴ after 100 cycles; ⁵ after 25 cycles;

⁶ initial and after 100 cycles; ⁷ after 100 cycles; ⁸ after 70 cycles

⁹ initial capacity; ¹⁰ after 50 cycles

Among the data in Table 4-2 the combination of high discharge capacity and promising cell discharge rate reported by Mikhaylik et al. (Ref. 6, line 1) stands out. However, the high capacities and discharge rates appear to refer to new cells, and capacity dropped nearly 50% in 40 cycles. A higher-power design 2.5Ah cell of similar composition but smaller 2.5mAh/cm² discharge capacity reportedly could be discharged continuously with up to 15A (6C rate, or 15mA/cm²) which would be more than sufficient for EV applications. However, no sulfur specific capacity data was available for this cell, and its 2.5mAh discharge capacity yields substantially lower specific energy and energy density estimates for 1cm² cell sections:

$SE_{2.5\text{ Ah}} \approx 360\text{Wh/kg}$ and $ED_{2.5\text{ Ah}} \approx 450\text{ Wh/L}$, assuming 50% thinner conductors than for 10mAh/cm² discharge capacity cells (see previous section) and a pouch enclosure for 10 cells.

This specific energy is quite close to the 350 Wh/kg specified in a Sion Power product sheet for a rechargeable 2.5Ah Li-S cell (Ref. 17), but its energy density (320Wh/L) is substantially lower than the estimates, reflecting either lower packing efficiency as the cell section model, or perhaps addition of extra electrolyte to prevent anode dry-out (Refs.6, 16).

It remains to be seen whether the Li-S cell described in Ref. 6 can be developed to deliver 1000+ deep cycles at $\geq 50\%$ sulfur utilization while fully utilizing a 7-10 mAh/cm² area capacity in a sustained C/3 (2.2-3.3 mAh/cm²) discharge at ≥ 2 V, and whether it can deliver a 3C pulse for 10 sec at ≥ 1 V. Attaining 1000+ cycles will be the key obstacle, and Sion seems to believe (Ref. 6) that a polysulfide barrier beyond the SEI is needed for success.

Li-S cells constructed with sulfur-retaining cathode structures to minimize polysulfide and capacity loss (and thus more promising cycle life prospects) seem to be limited to less than 5mA/cm² (see Table 2, Ref. 8 and 9). Even at less than 4mA/cm² the available cathode capacity is only 2/3 of 900mAh/g, the basis for the promising energy density and specific energy estimates in the previous section. A linear extrapolation of the capacity vs. current density data in the last column of Table 2 (line 3) shows that the available capacity would have dropped to zero at around 9 mA/cm² – substantially less than the 3C (30 mA/cm²) peak discharge rate capability required for EV applications.

Evidently the cathode structures developed up to now lose a large part of their active inner surfaces as current densities increase toward the levels of interest to EV applications. This effect is caused by the resistance of pores providing electrolyte access to cathode active surfaces, and it is enhanced by an up to 4-fold increase of electrolyte resistivity as polysulfide concentrations in the electrolyte build to high levels during cell discharge (Ref.12). To permit near-complete utilization of cathode inner surfaces electrolyte conductivities probably would have to be increased from typical current levels of $1-2 \times 10^{-3}$ S/cm (Ref.18) by nearly one order of magnitude while retaining electrolyte chemical and electrochemical stability. To date no such electrolyte has been identified in Li-S R&D.

This analysis suggests that Li-S cells with sulfur-containment cathodes, although reasonably effective in retaining sulfur discharge products and thus an important step toward the required cycle life, are unlikely to permit EV-level discharge rates for cells with discharge capacities ≥ 10 mAh/cm² unless a major advance is achieved in electrolyte conductivity. The data of Ref. 9 suggest that a carbon nanotube cathode structure of 2.5mAh/cm² discharge capacity would be able to deliver 900 mAh/g at the C/3 rate and probably sustain a 3C pulse rate, sufficient for EV applications. However, with the same assumptions as for the Sion 2.5Ah cell (see preceding page) such a cell would yield only SE ≈ 360 Wh/kg and ED ≈ 450 Wh/L, approximately 40% respectively 30% lower than the values for a Li-S cell with 10mAh/cm². In fact, the specific energy would likely be only around 20% higher than that of a state-of-the-art Li Ion cell, and the energy density would actually be 30% lower.

The Li-S cell described in Ref. 6 comes closer to delivering the needed combination of high discharge capacity and discharge rate capability: a 3-x improvement of electrolyte conductivity might be sufficient to allow discharge pulses of 30mA/cm² (5C for a 6mAh/cm² area capacity, see Table 2, line 1). However it appears that, to meet the 1000+ cycle requirement, the approach will need to include polysulfide loss control measures beyond the addition of LiNO₃ to the

electrolyte. One obvious measure is to interpose a barrier impermeable to dissolved polysulfides and other chemical species (such as electrolytes) but permeable to Li^+ ions between the sulfur cathode and lithium anode. Such a barrier would not only prevent polysulfide loss but protect the Li anode from attack by the electrolyte.

Solid membrane permeable only to Li^+ ions already are being investigated in efforts to develop lithium-air and lithium-water batteries (Refs. 19, 20) and are beginning to be used in Li-S cell R&D. The energy storage performance and likely limitations of Li-S cells with membrane barriers are discussed in the following section.

Cells with Dedicated Polysulfide Barriers

Fig. 1b is a schematic representation of a barrier-type cell. Possible choices for the lithium ion permselective barrier membrane (M) include Li^+ -conducting polymer membranes made, for example, from polyethylene oxide (Refs. 21, 22). Because polysulfides are somewhat soluble in PEO and similar polymers, a thin film (SEI) is likely to form at the Li anode surface during cell operation, but its growth will be slow since limited by slow polysulfide diffusion through the polymer membrane.

Alternatively, certain glasses conduct Li^+ ions sufficiently (Ref. 23) to be considered as membranes that almost certainly would be impermeable to polysulfides. However, known Li^+ -conducting glasses react with Li metal and thus need to be protected by another barrier that does not react with lithium metal but is permeable to Li^+ ions. Thus in Fig. 1(b) M is intended to also stand for a glass membrane and SEI for a glass-protecting, Li^+ -conducting layer.

All of these layers add to the volume, weight and resistance of a Li-S cell without barrier membranes. In the following the impacts of these increases on energy density, specific weight and discharge rate capability of Li-S cells and batteries are estimated. Because barrier membrane materials and cell characteristics are different for the polymer and glass electrolyte alternatives, their impacts are discussed separately in the following.

Polymer Electrolyte Membrane Barriers

Insertion of a polymer electrolyte membrane adds volume and weight to in a Li-S (or any other) cell. To estimate the approximate impacts on specific energy and energy density it is assumed that the membrane is $25\mu\text{m}$ ($5 \times 10^{-3}\text{cm}$) thick and weighs $5 \times 10^{-3}\text{g/cm}^2$ (density 1g/cm^3). Because the membrane replaces a separator of the same thickness and weight, the specific energies and energy densities estimated for Li-S cells and batteries in the [Energy Storage Performance](#) section above remain unchanged. The main impact of the membrane barrier on cell performance thus is due to the fact that it adds three resistances to the cell: the resistance of the membrane itself, and the resistances of the membrane-electrolyte and membrane-lithium anode interfaces.

The best current choice of Li^+ -conducting polymer membrane material is polyethylene oxide intimately mixed with a lithium salt to provide conductance and Li^+ ion transport. However, even the highest conductivities reported for optimized composites do not exceed 10^{-4}S/cm at room temperature (Ref. 24). For a practical $25\mu\text{m}$ thick membrane this conductivity results in an area-specific membrane resistance $\text{ASR}_M = 2\text{ohm}\times\text{cm}^2$ which adds to the cell area-specific resistance and causes a voltage drop of 0.75V at the desired 30mA/cm^2 (3C) peak discharge rate. This drop may be acceptable as may be a 83mV drop at the C/3 (3.3mA/cm^2) continuous discharge rate. However, the two interface resistances are likely to be at least as high (Ref. 25) as the membrane

resistance itself and thus will contribute comparable or even higher voltage drops. The corresponding reductions of cell (and battery) charge and discharge efficiencies at the C/3 rate would be more than 10% of the cell discharge voltage just for the membrane and thus no longer acceptable. Adding liquid gelling agents when fabricating PEO-based membranes can increase conductivity up to 10-fold (Ref. 26) which mitigates the membrane resistance problem but this re-introduces an avenue for polysulfide transport through the gel phase of the membrane.

Especially the interface of the membrane with the solid Li anode is problematic because of morphological changes of the Li anode surface with cycling, and rather complex solid membrane materials and/or structures will be required to achieve a low anode interface resistance and maintain it for many cycles. It must be concluded that even the currently best-conducting polymer membrane materials and structures are unlikely to provide the combination of good conductance and polysulfide barrier effectiveness required for Li-S cells meeting the discharge capacity, C-rate and cycle life requirements for EV applications.

Recently several investigators reported (Refs. 21, 22) using mixed PEO-Li salt conducting polymers as a solid electrolyte in Li-S cells. In this approach, intimate mixtures of sulfur, conducting carbon and some conducting polymer serve as cathode that is pressed against a PEO-based membrane which, in turn, is pressed against a Li anode. This structure dispenses with the separator and minimizes the cathode-membrane interface resistance. However, at a conductivity of 10^{-4} S/cm the PEO electrolyte will cause a high cathode resistance. It is considered very unlikely that solid PEO electrolyte-based cell structures can be developed to have area-specific cell resistance values comparable with – much less below – those of Li-S cells with conventional liquid electrolytes. As a consequence, such cells are unlikely to meet EV-type discharge rate and capacity requirements, as is also suggested by their long discharge times (Ref. 21) and poor sulfur utilization (Ref. 22).

Glass Electrolyte Membrane Barriers

Insertion of a glass electrolyte membrane barrier adds volume and weight to a Li-S cell, first through the barrier itself. Second, because all currently known Li^+ ion conducting glasses appear to be unstable in contact with lithium, the glass membrane must be protected from direct contact with the Li anode through a thin layer of Li^+ ion conducting PEO-based polymer that also adds volume and weight. To estimate the approximate impacts on (i.e., decrease of) specific energy and energy density it is assumed that the protecting membrane has the same thickness and weight as the separator, and that the glass membrane is $20\mu\text{m}$ (2×10^{-3} cm) thick and weighs 5×10^{-3} g/cm² (density 2.5g/cm³). Adding this volume and weight in the estimates of the Energy Storage Performance section reduces the specific energy by 9% and the energy density by about 6% for the baseline Li-S cell (900mAh/g of sulfur; 10mAh/cm²) which is acceptable.

The main impact of the glass membrane barrier on Li-S cell performance is due to the fact that it adds four resistances to the cell: the resistance of the membrane itself, the resistances of its interfaces with the electrolyte and the protecting PEO film, and the PEO film-Li interface. Several current choices of Li^+ -conducting glasses exist (Refs. 23, 27), with conductivities up to 1.2×10^{-2} S/cm (Ref. 28), comparable to the highest-conductivity liquid organic electrolytes. A $20\mu\text{m}$ thick glass membrane of that conductivity would cause only a 5mV voltage drop even at the desired 3C (30mA/cm²) rate. However, a key issue with a glass barrier membrane is the collective resistance of the four interfaces it introduces.

In order to mitigate the interface resistance issue it is logical to consider using the glass also as the cell electrolyte. In contrast to the situation with PEO-based electrolytes, the potentially very good conductivity of some of the Li^+ conducting glasses should result in acceptably low resistances of the glass-containing cathode and its interface with the glass electrolyte membrane. Li-S cells using such structures have been described recently (Ref. 27, 29) but so far without key data for cathode specific capacity, charge capacity, or discharge rates. Also, no information on resistance and stability of the glass-protecting (PEO) film and film-anode interfaces has been reported.

A challenging problem for all-solid Li-S cells is the almost 100% volume increase when sulfur is discharged to lithium sulfide within a solid cathode structure. Accommodation for this increase (and the corresponding decrease during charging) needs to be made but no technical approaches have been reported as yet. Whether good contacts between sulfur, carbon conductor and the solid glass electrolyte phase can be maintained over many cathode discharge-charge cycles still looms as an open question. Finally, the long-term chemical and mechanical stability of the glass electrolyte in the cathode and the electrolyte membrane still need to be proven.

Summary: Prospects and Challenges for the Development of Li-S Batteries

Cycle Life

Relatively rapid, irreversible loss of capacity – compared, for example, to lithium ion cells and batteries – has been the largest barrier to the development of practical Li-S batteries. The problem arises primarily from the irreversible reaction of dissolved polysulfides, products of the sulfur cathode discharge, with the lithium anode. Two technical strategies are used in current R&D to mitigate the problem, (1) retaining polysulfide discharge products within the cathode structure throughout their stepwise discharge to lithium sulfide (Li_2S), or/and (2) preventing dissolved polysulfides from reaching the lithium anode by interposing some type of barrier impermeable to polysulfides between cathode and anode.

Both approaches have shown limited success. Carbon-based cathode structures (made e.g. from carbon nanotubes) designed to retain polysulfides within the pore volume of the structure have permitted >50% utilization of sulfur for at least hundred discharge-charge cycles with very good reversibility, at cathode discharge capacities of up to 10mAh/cm^2 but relatively low current densities. It can be speculated that modification of the SEI layer on the anode – achieved, for example, through addition of lithium nitrate to the electrolyte – might reduce polysulfide flux to the lithium surface further and extend cycle life toward the 1000+ cycle goal for EV applications.

A cycle life of around 300 cycles has been reported for cells with cathodes that, presumably, have a more open structure and thus higher current density capability. In such cells the addition of lithium nitrate appears to have created a surface film on the Li anode that is partially effective as a polysulfide barrier. However, to reach the 1000+ cycles with more open cathode structures probably will require more effective barriers between cathode and anode, such as polymeric or glass membranes that permit Li^+ ion passage but stop polysulfide species. No data are as yet available for Li-S cells with such membranes, but the experience with Li-water cells shows that barrier membranes and/or their interfaces with cathode and anode add significantly to total cell resistance and thus limit cell operation to low rates.

An interesting development direction to reduce the interface resistances in the cell yet retain a polysulfide barrier functionality is to replace the liquid electrolyte with high-conductivity lithium glass in the sulfur cathode and as a membrane-separator structure integrated with the cathode. This approach promises to reduce not only interface resistances but also the electrolyte solubility and mobility of polysulfides. Such cells might be able to combine low capacity loss (little or no polysulfide reaction with the Li anode) with reasonable energy storage performance and discharge rate capability due to the high Li^+ ion conductivity of the glass. However, successful use of solid lithium glass electrolytes in high performance Li-S cells will be contingent on resolution of two basic issues: glass stability against Li anodes (need for protective layer), and approximately 100% volume increase as the sulfur in the solid cathode is discharged to lithium sulfide (need for cathode structure that can accommodate cyclic volume changes). These issues present major development challenges that are barely tackled today.

Energy Storage Performance

Using the highest reported values for the combination of stable sulfur cathode utilization ($\sim 900\text{mAh/g}$) and discharge capacity ($\sim 11\text{mAh/cm}^2$) the author estimates specific energies of approximately 390Wh/kg and 490Wh/kg for 10-layer Li-S cell stacks encased in 0.25mm aluminum sheet and 5-mil plastic, respectively; the energy densities are 585Wh/L and 630Wh/L . Compared to the corresponding estimates for a 10mAh/cm^2 Li Ion 10-layer cell, the Li-S specific energies are higher by $\sim 40\%$ (aluminum case) and $\sim 60\%$ (plastic pouch). The corresponding battery-level specific energies for Li-S are estimated to be around 245Wh/kg and 290Wh/kg , respectively. On the other hand, the estimated energy densities for Li-S cells and batteries are only around 5% higher than for Li Ion which uses higher-density electrodes.

Yet higher values of specific energy ($+20\%$) and, especially valuable, of energy density ($+40\%$) could be attained if sulfur utilization in the cathode could be increased from $\sim 50\%$ to around 90% but all experimental work to date shows that utilization drops to 50% or below within a few cycles. At present it is not clear whether and how the desired combination of very high sulfur utilization, and long cycle life can be attained, and whether the resulting high discharge capacities can be discharged at EV-type C rates.

Discharge (and Charging) Rate Capability

The promising specific energy and energy density values estimated above for the “baseline” cell apply for relatively low discharge current densities, typically less than 1.5mA/cm^2 which is equivalent to the C/8 rate for the 10mAh/cm^2 cathode and cell discharge capacity. With increasing current densities and C rates the cathode capacities and energy storage performance delivered by experimental Li-S cells dropped progressively, primarily because less and less of the inner surface of the sulfur cathode was able to participate in the discharge process. This well known effect is caused by the resistance of the electrolyte in the pores of the cathode, likely exacerbated by a decrease of electrolyte conductivity as polysulfide discharge products are dissolving in the electrolyte. It appears that electrolytes with at least tenfold higher conductivities (e.g. $>10^{-2}\text{S/cm}$) are needed to enable high-capacity cathode structures highly effective in retaining polysulfide (and sulfur) to be discharged at EV-type peak rates, e.g. $>20\text{--}30\text{mA/cm}^2$.

It remains to be seen whether liquid electrolytes combining very high conductivities with good stability will become available, or whether glass electrolyte-based cells can be developed to deliver high capacities and discharge rates with sulfur cathode structures that overcome the issues mentioned above.

In summary, R&D on Li-sulfur cells has made important strides toward the goal of a new high energy battery technology that can meet the requirements for EV applications while delivering much higher energy storage performance than Li Ion batteries. An analysis of experimental data indicates good potential for Li-S specific energies exceeding those of Li Ion by about 50% although the energy density increases are likely to be small. Substantially larger increases, especially of specific energy, are possible in principle, but practical solutions to the required increases in sulfur cathode utilization and discharge capacity are not in sight and would seem extremely difficult to achieve.

The largest impediment facing the development of practical Li-S batteries for EV applications is inadequate cycle (and, also, calendar) life caused by the irreversible reaction of polysulfide discharge products with the lithium anode. The technical strategies used in current R&D to mitigate this problem – retaining polysulfide discharge products within the cathode structure, or/and using barriers in the cell to prevent polysulfides from reaching the lithium anode – have helped achieve stable cycling of Li-S cell for 100+ deep cycles at promising cathode capacities but only rather low current densities and C rates. Achieving the 1000+ cycles goal for EV applications will require further reductions of polysulfide flux to the Li anode surface. The morphological changes of the Li anode with cycling also will need attention inasmuch as they could become a limiting factor for cycle life.

Two obvious measures to achieve better polysulfide control are tighter cathode structures and/or dedicated polysulfide barrier membranes. However, tighter cathodes and dedicated polysulfide barriers will increase cell resistances and decrease the already inadequate discharge rates. The development of stable, high-conductivity liquid electrolytes or lithium ion-conducting glasses could become part of solution to the low-rate discharge limitation of Li-S cells (and batteries), in the case of glass electrolytes possibly in form of all-solid Li-S cells.

This study shows that a number of major, technically diverse advances are needed to realize the energy storage potential of lithium-sulfur batteries for electric vehicle applications, quantifies some of them and identifies promising research direction. Although no truly fundamental barriers to these advances appear to exist, the author believes that it will take more than a decade of intense R&D, engineering and innovative manufacturing development to overcome the current life and rate limitations and establish a successful high energy Li-S battery technology.

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