The UC Davis Emerging Lithium Battery Test Project

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Abstract

This report is concerned with the testing and evaluation of various battery chemistries for use in PHEVs. Test data are presented for lithium-ion cells and modules utilizing nickel cobalt, iron phosphate, and lithium titanate oxide in the electrodes. Cells with $NiCoO_2$ (nickelate) in the positive electrode have the highest energy density being in the range of 100-170 Wh/kg. Cells using iron phosphate in the positive have energy density between 80-110 Wh/kg and those using lithium titanate oxide in the negative electrode have energy density between 60-70 Wh/kg. The power densities can vary over a wide range even for a given chemistry. In general, it is possible to design high power batteries (500-1000 W/kg at 90% efficiency) for all the chemistries if one is willing to sacrifice energy density and likely also cycle life. The data indicate that high power iron phosphate cells can be designed without a significant sacrifice in energy density. When power densities greater than 2000 W/kg for lithium-ion batteries are claimed, it is for low efficiency pulses. For example, for an efficiency of 65%, the 15Ah EIG iron phosphate battery has a pulse power of 2330 W/kg rather than the 919 value for a 90% efficient pulse.

Cycle life data were not taken as part of the present study. However, cell cycle life data reported by Altairnano for their cells using lithium titanate oxide in the negative electrode indicate cycle life in excess of 5000 cycles for charge and discharge rates of 2C and greater. It seems likely that the cycle life of both titanate oxide and iron phosphate lithium batteries will be satisfactory for vehicle applications.

The cost of lithium batteries remains high ($500-1000 /kWh) when purchased in relative small quantities, but detailed cost modeling of batteries done at Argonne National Laboratory for the various chemistries indicate that in high production volume (greater than 100,000 packs per year), the costs to the OEMs of all chemistries can be in the range of $250-400/kWh depending on the battery size (kWh energy stored). The lithium titanate chemistry is projected to have the highest cost, but it also will have the longest cycle life.

R&D is continuing to increase the energy density of lithium-ion batteries. Proto-type cells presently being developed have energy densities in the range of 250-300 Wh/kg using layered metal oxides/spinels in the positive electrodes. Higher energy densities appear to be likely combining these electrodes with negative electrodes using composites of silicon oxides and carbon. R&D on electrically rechargeable Zinc-air cells is presently in progress. Energy densities in the range of 300-400 Wh/kg, 700-1000 Wh/L appear to be possible using the Zn-air chemistry. The power capability of the advanced batteries is uncertain at the present time.

1. Introduction

This project has been performed in collaboration with EPRI under contract with the California Air Resources Board. It was started in the Spring of 2007 with the objective to evaluate emerging lithium battery technologies for plug-in hybrid vehicles. By emerging lithium battery chemistries were meant iron phosphate and titanate oxide which were being developed because there were safety concerns relative to the better known $NiCoO_2$ and $NiCoAlO_2$ chemistries. During the course of the project, numerous cells and modules using the emerging chemistries were obtained from different battery developers worldwide and tested to determine their performance characteristics. Unfortunately batteries were not obtained from the larger developers (for example, Saft/Johnson Controls, LG Chem, A123, Enerdel) who are working with DOE and the auto companies in the United States. However, it is felt that the performance of the batteries that were obtained are representative or even more advanced than of those being developed on the USABC/DOE programs.

This report is intended to summarize the findings of the testing done to date on the EPRI/CARB contract and to compare the performance of the various lithium chemistries for plug-in hybrid vehicle applications. The report will also indicated areas in which the testing has not been completed and in which additional testing can be undertaken with available modules and test facilities. Finally, some projections will be made of future improvements in lithium battery performance that seem likely based on progress that has occurred in the last several years.

2. Batteries obtained for testing

As noted previously, this program was concerned with the testing of emerging lithium battery chemistries – namely, iron phosphate in the positive electrode and lithium titanate oxide in the negative electrode. The general characteristics of batteries with the various lithium chemistries are shown in Table 1. The relative advantages of the different chemistries are evident in the table.

Table 1: Characteristics of lithium-ion batteries using various chemistries

Chemistry Anode/cathode	Cell voltage Max/nom.	Ah/gm Anode/cathode	Energy density Wh/kg	Cycle life (deep)	Thermal stability
Graphite/ $NiCoMnO_2$	4.2/3.6	.36/.18	100-170	2000-3000	fairly stable
Graphite/ Mn spinel	4.0/3.6	.36/.11	100-120	1000	fairly stable
Graphite/ $NiCoAlO_2$	4.2/3.6	.36/.18	100-150	2000-3000	least stable
Graphite/ iron phosphate	3.65/ 3.25	.36/.16	90-115	>3000	stable
Lithium titanate/ Mn spinel	2.8/2.4	.18/.11	60-75	>5000	most stable

The cells and modules obtained from the various battery developers are given in Table 2. Batteries were obtained for testing of a wide range of cell capacities (Ah) and forms (cylindrical spiral wound and laminated prismatic). Single cells as well as modules assembled from the cells were obtained and tested. Several of the modules were equipped with battery management units.

3. The UC Davis Battery Laboratory and facilities

The battery test facilities at UC Davis were significantly enhanced during the course of the present contract with the installation of an ABC-150 and the purchase of a Test Equity 4ft^3 temperature chamber. The facilities now available for testing batteries (see Table 3) permit the testing of modules and packs up to voltages of 400V and currents of 500A and cells and modules at temperatures between -35 deg C and >100 deg C. Most of the testing on the present contract was done using the Bitrode at voltages up to 50V and currents up to 400A at ambient temperatures. Future testing can be done at higher voltages and over a range of temperatures.

Table 3: Summary of the test equipment in the Battery Test Laboratory at UC Davis

1. Arbin tester 2 channels, 5A, 20V 4 channels, 20A, 20V
2. Bitrode tester 1 channel, 400A, 50V
3. ABC-150 2 channels, 500A, 400V
4. Test Equity Temperature Chamber (4 ft^3) -35 degC to 150 degC

4. Test procedures

The various cells and modules were tested using a consistent set of test procedures intended to determine their performance characteristics for vehicle applications. The test procedures are summarized in Table 4. The testing included constant current and constant power tests over the maximum ranges for which the cells/modules functioned satisfactorily within manufacturer specified voltage limits. Normal charging algorithms from the battery developers were used for most of the testing, but some fast charging tests were made for a small number of the cells. Pulse testing of the cells/modules was done to determine their open-circuit voltage and resistance as a function of state-of-charge. As discussed later in this section, these results were then used to calculate their pulse power characteristics. No life cycle testing was done as part of the present contract.

Table 4: Test Procedures for Lithium-ion batteries

1. Constant current tests: C/3 to 3C
2. Constant power tests: 50 W/kg to 1000 W/kg
3. Pulse tests (5-10 sec): 3C to 10C in charge and discharge
4. PSFUDS cycles: max power steps 500 W/kg to 1500 W/kg

Table 2: Batteries tested -manufacturers, technology, and characteristics

Manufacturer	Technology type	Ah	Voltage range	Cell configuration
K2	Iron phosphate	2.4	3.65-2.0	cylindrical
EIG	Iron phosphate	10.5 15.7	3.65-2.0	laminated prismatic
A123	Iron phosphate	2.1	3.6-2.5	cylindrical
Lishen	Iron Phosphate	10.2	3.65-2.0	cylindrical
EIG	Graphite/ Ni CoMnO2	18	4.2-3.0	laminated prismatic
GAIA	Graphite/ LiNiCoO2	42	4.1-3.0	cylindrical
Quallion	Graphite/ Mn spinel	1.8 2.3	4.2-3.0	cylindrical
Altairnano	Lithium Titanate	11 52	2.8-1.5	laminated prismatic
EIG	Lithium Titanate	12.0	2.7-1.5	laminated prismatic

Lithium-ion battery modules available for testing

Chemistry Anode/cathode	Developer	Voltage	Ah	Resistance mOhm	Weight kg pack.fact.	Volume L Pack.fact.
Nickel Cobalt	EIG	72	20	60	13.4 .67	11.3 .41
Iron Phosphate	EIG	74	14	55	13.6 .69	11.3 .34
Lithium titanate	Altairnano	16V	11	2	16.3 ----	11.4 ----
Lithium titanate	Altairnano	24V	50	10	21.4 .75	12.6

For vehicle applications, the primary performance characteristics of interest are the energy density (Wh/kg and Wh/L) and useable power density (W/kg and W/L) of the cells. For lithium batteries for which the energy density is weakly rate dependent (Wh/kg essentially independent of W/kg for constant power discharges), interpretation of energy density data is straightforward and not controversial. There is currently considerable controversy, however, concerning the interpretation of the power density data and what is the usable power density of lithium batteries. The USABC battery test manual (Reference 1) specifies the Hybrid Pulse Power Characterization (HPPC) test for determining the power density of a battery for hybrid vehicles. The USABC manual also describes an energy efficiency test (EET) which involves a sequence of discharge and charge pulses at high power. The intent of the HPPC test is to determine the maximum power at which the battery can provide the same power for charge and discharge within the limits of a specified minimum voltage V_{min} and maximum voltage $V_{max.}$ The intent of the EET is to determine whether the battery can meet specified power pulses with a round-trip efficiency of at least 90%. In the present program at UC Davis, the pulse power characteristics of a cell/battery are calculated using the following relationship:

$P = EF\ (1-EF)\ V_{oc}^{\ 2}/R$

where $EF = V_{pulse}/V_{oc}$ is the efficiency of the pulse and R is the resistance of the cell

Hence when the open-circuit voltage of the cell and its resistance are known, its pulse power characteristics can be calculated. Note that the power capability is dependent on the pulse efficiency and that if a roundtrip efficiency of 90% is required, a pulse efficiency of 95% is required for both the charge and discharge pulses.

It is of interest to compare the cell power characteristics determined by the USABC and UC Davis approaches. This is done as follows.

USABC method

$P_{ABC} = V_{min}\,(V_{nom.OC} - V_{min})/R$ discharge

$P_{ABC} = V_{max}\,(V_{max} - V_{nom.OC})/R$ charge

V_{nomOC} is the open-circuit voltage at a mid-range SOC

V_{min} is the minimum voltage at which the battery is to be operated in discharge

V_{max} is the maximum voltage at which the battery is to be operated in charge (regen)

R is the effective pulse resistance of the battery

Pulse efficiency method

$P_{EF} = EF(1-EF)\ V^{\ 2}_{nomOC}/R$ both charge and discharge pulses

Ratios of the maximum peak power predicted by the two methods

discharge

$P_{EF}/P_{ABC} = EF(1-EF)/\ [(V_{mim}/V_{nomOC})(1-V_{min}/V_{nomOC})]$

charge

$P_{EF}/P_{ABC} = [(V_{nomOC}/V_{max,ch})^2/(1-V_{nomOC}/V_{max,ch})]\ EF(1-EF)$

Example: Iron Phosphate

$V_{nomOC} = 3.2$, $V_{min} = 2$, $V_{max} = 4.0$

Efficiency	EF(1-EF)	Discharge P_{EF}/ P_{ABC}	charge P_{EF}/ P_{ABC}
.95	.0475	.20	.15
.90	.09	.38	.29
.85	.1275	.54	.41
.80	.16	.68	.51
.75	.1875	.80	.60
.70	.21	.90	.67

Example: Nickel Cobalt

$V_{nomOC} = 3.7$, $V_{min} = 2.5$, $V_{max} = 4.3$

Efficiency	EF(1-EF)	Discharge P_{EF}/ P_{ABC}	charge P_{EF}/ P_{ABC}
.95	.0475	.22	.25
.90	.09	.41	.48
.85	.1275	.58	.68
.80	.16	.73	.85
.75	.1875	.86	1.0
.70	.21	.96	.1.0

Example: Lithium Titanate Oxide

$V_{nomOC} = 2.3$, $V_{min} = 1.5$, $V_{max} = 3.2$

Efficiency	EF(1-EF)	Discharge P_{EF}/ P_{ABC}	charge P_{EF}/ P_{ABC}
.95	.0475	.21	.09
.90	.09	.40	.17
.85	.1275	.56	.23
.80	.16	.71	.29
.75	.1875	.83	.35
.70	.21	.93	.39

For efficiencies of 90-95%, the USABC method predicts for all the battery chemistries a power density for a given cell of a factor of 2.5-5 greater than the UC Davis method. The USABC energy test seems to indicate the desire to achieve a round-trip efficiency of at least 90% which is inconsistent with the HPPC approach which corresponds to pulse efficiency of less than 75%. Hence it is argued that the power densities (W/kg) at 90-95% efficiency presented in this report are consistent with the intent of the USABC and properly represent the power capability of the batteries tested for hybrid vehicle applications.

5. Battery performance data summaries

Detailed data were taken for all the cells listed in Table 2. Selected data for some of the cells are shown in Tables 5- 10 as illustrations of the performance of the iron phosphate and lithium titanate oxide cells. More complete data can be found in References 2, 3.

Table 5: Test data for the 15 Ah EIG iron phosphate cell

<u>Iron Phosphate</u>				
FO 15A	**Weight .424kg**	**3.65-2.0V**		
Power (W)	**W/kg**	**Time (sec)**	**Wh**	**Wh/kg**
62	**142**	**2854**	**49.5**	**117**
102	**240**	**1694**	**48.0**	**113**
202	**476**	**803**	**45.1**	**106**
302	**712**	**519**	**43.5**	**103**
401	**945**	**374**	**41.7**	**98**
Current (A)	**Time (sec)**	**Ah**	**Crate**	**Resistance mOhm**
15	**3776**	**15.7**	**.95**	
30	**1847**	**15.4**	**1.95**	**2.5**
100	**548**	**15.2**	**6.6**	
200	**272**	**15.1**	**13.2**	
300	**177**	**14.8**	**20.3**	

Table 6: Test data for the Altairnano 11Ah lithium titanate oxide cell

Constant current test data (2.8-1.5V)

I(A)	**nC**	**Time (sec)**	**Ah**	**Resistance mOhm**
10	.8	4244	11.8	--
20	1.7	2133	11.9	--
50	4.5	806	11.2	2.2
100	9.2	393	10.9	2.1
150	15.3	235	9.8	--
200	---	116	6.4	--

Resistance based on 5 sec pulse tests

Constant power test data (2.8-1.5V)

Power W	**W/kg**	**Time sec**	**nC**	**Wh**	**Wh/kg**
30	88	2904	1.2	24.2	71.2
50	147	1730	2.1	24.0	70.7
70	206	1243	2.9	24.2	71.0
100	294	853	4.2	23.7	69.7

150	441	521	6.9	21.7	63.8
170	500	457	7.9	21.6	63.5
260	764	255	14	18.4	54.2
340	1000	103	35.0	9.7	28.6

Cell weight: .34 kg

Table 7: Test data for the Altairnano 50Ah lithium titanate oxide cell

Constant current discharges (2.8-1.5V)

Current A	nC	Time sec	Ah	Resistance mOhm
50	.96	3773	52.4	
100	1.95	1847	51.3	1.0
200	4.0	904	50.2	.95
300	6.1	588	49.0	1.0

Constant power discharge (2.8-1.5V)

Power W	W/kg	Time sec	nC	Wh	Wh/kg
100	62	3977	.9	111	69
200	125	1943	1.85	108	67
300	188	1244	2.9	102	64
400	250	849	4.2	94	59
500	313	636	5.66	88	55
600	375	516	7.0	86	54

Cell weight: 1.6 kg

The resistance of the cells was determined from pulse tests performed at various states-of-charge. Pulse data for the EIG iron phosphate and NiCo cells are shown in Tables 8 and 9. Comparisons of the pulse power characteristics of the NiCo, iron phosphate, and titanate oxide cells are given in Table 10. Power densities are shown for pulse efficiencies of 80%, 90% and 95%.

Table 8: Pulse characteristics of the EIG 20Ah NiCo cell at various states-of-charge

Voc	DOD %	$V_{2\ sec}$	Effic. %	R mOhm	Power W	W/kg
4.12/250A	**0**	**3.33**	**80.8**	**3.16**	**833**	**1850**
3.98/250A	**10**	**3.24**	**81.4**	**2.96**	**810**	**1800**
3.88/250A	**20**	**3.14**	**80.9**	**2.96**	**785**	**1744**
3.78/250A	**30**	**3.06**	**81.0**	**2.88**	**765**	**1700**
3.72/250A	**40**	**2.98**	**80.1**	**2.96**	**745**	**1655**
3.67/250A	**50**	**2.90**	**79.0**	**3.08**	**725**	**1611**

3.63/250A	**60**	**2.84**	**78.2**	**3.16**	**710**	**1578**
3.59/250A	**70**	**2.74**	**76.3**	**3.4**	**685**	**1522**
3.54/100A	**80**	**3.18**	**89.8**	**3.6**	**318**	**706**
3.48/100A	**90**	**2.96**	**85.1**	**5.2**	**296**	**658**

Table 9: Pulse characteristics of the EIG 15Ah Iron phosphate cell at various states-of-charge

Voc	DOD %	$V_{2\ sec}$	Effic. %	R mOhm	Power W	W/kg
3.45/75A	**0**	**3.08**	**89**	**4.9**	**231**	**711**
3.3/75A	**10**	**3.02**	**91.5**	**3.73**	**227**	**698**
3.28/75A	**20**	**3.0**	**91.5**	**3.73**	**225**	**692**
3.26/75A	**30**	**2.98**	**91.4**	**3.73**	**224**	**689**
3.25/75A	**40**	**2.96**	**91.0**	**3.87**	**222**	**683**
3.25/75A	**50**	**2.94**	**90.5**	**4.13**	**220**	**679**
3.24/75A	**60**	**2.91**	**89.8**	**4.4**	**218**	**672**
3.21/75A	**70**	**2.85**	**88.8**	**4.8**	**214**	**658**
3.17/75A	**80**	**2.74**	**86.4**	**5.7**	**206**	**632**
2.58/75A	**90**	**2.06**	**79.8**	**6.9**	**155**	**475**

Table 10: Comparisons of the power characteristics of NiCo, Iron phosphate and Titanate oxide cells

		95% effic.		90% effic.		80% effic.	
Cell	Wh/kg at C/1	30% DOD	80% DOD	30% DOD	80% DOD	30% DOD	80% DOD
NiCo 20Ah	**140**	**524 W/kg**	**367 W/kg**	**993 W/kg**	**696 W/kg**	**1762 W/kg**	**1237 W/kg**
Iron phosphate 15 Ah	**115**	**318 W/kg**	**198 W/kg**	**604 W/kg**	**375 W/kg**	**1075 W/kg**	**667 W/kg**
Titanate oxide 11 Ah	**71**	**388 W/kg**	**229 W/kg**	**738 W/kg**	**432 W/kg**	**1312 W/kg**	**768 W/kg**

The performance advantages of the Ni Co chemistry compared to the emerging chemistries are shown clearly in Table 10.

Test data for a 16V module of the Altairnano 11Ah cells are shown in Table 11. The characteristics of the module follow directly from the characteristics of the 11Ah cells.

Table 11: Test data for the Altairnano 16V module)

Constant current discharge (8 cells in parallel, 6 in series)

I(A)	Time (sec)	nC	Ah	Resistance mOhm
50	6908	.52	95.9	
100	3419	1.05	95.0	
200	1704	2.11	94.7	1.95
300	1113	3.23	92.8	2.0
400	833	4.32	92.6	2.0

Cell mass: 16.3 kg, resistance based on 5 sec pulses of the module
90% efficiency pulse: 9.0 kW, 553 W/kg

Constant power discharges

Power (W)	(W/kg) cells	Time (sec)	kWh	(Wh/kg)cells
1000	61	4576	1.27	77.9
1500	92	2975	1.24	76.1
2000	122	2217	1.23	75.5
2500	250	1756	1.22	75.0
3000	184	1459	1.22	75.0
3500	215	1221	1.19	73.0
3600	221	1222	1.22	75.0

Charge at 88A to 16.3V, discharge from 16.3 to 9V

6. Fast charging characteristics of lithium-ion batteries

There is presently considerable interest in fast charging of batteries in both battery-powered and plug-in hybrid vehicles. It has been claimed that both the lithium titanate oxide and iron phosphate chemistries can be fast charged in about ten minutes. A series of tests have been performed using the 11Ah titanate oxide cell and the 15Ah iron phosphate cell whose characteristics were discussed previously. Tests were performed for charging rates between 1C and 8C. The cell temperature was tracked with a thermocouple mounted on the output terminal. The cells were charged to a maximum (clamp) voltage and then the current was tapered to 1/10 the initial charge current. For all the tests, the cells were discharged at the 1C rate (1hr.) to determine the effect of charging rate on cell Ah capacity. The test results, which are summarized in Table 12, indicate that both battery chemistries can be fast charged. However, the fast charge capability of the titanate oxide chemistry appears to be superior to that of the iron phosphate chemistry both with respect to temperature rise during charging and the Ah capacity retention for charging up to the maximum voltage without taper. For example, in the case of the lithium titanate oxide cell charged at 66A in 620 sec, the 1C capacity was 11.2 Ah compared to 12.0 Ah for a 1C (1 hr) charge.

Both cells were also fast charged for five repeated cycles to investigate the effect on the temperature rise and Ah capacity. In these tests, the cells were not actively cooled. The results for the lithium titanate oxide cell are shown in Table 13 and in Figure 1. The charge time to the maximum voltage (cut-off of charge) was 614 sec with a temperature rise during charging of 4.5 deg C. However, the temperature decreased back to ambient during the discharge so that the temperature remained stable during the five cycles. The capacity of the cell was 11.2Ah for each cycle.

These tests indicate that fast charging of the lithium batteries should be possible without great difficulty if high power charging stations are available. Recent life cycle data (see Figure 2) taken by Altairnano indicate that the 11 Ah cells have long cycle life under fast charge (6 C) conditions so the effect of fast charging on cycle life should not be a concern for the lithium titanate oxide batteries.

Table 12: Fast charge test data for lithium-ion chemistries

EIG iron phosphate 15 Ah cell

						Temp Rise During Cha	
Charge Current (Amps)	Time to Cutoff (secs)	Taper Time (secs)	Charge to Cutoff (Amp-hrs)	Total Charge (Amp-hrs)	Discharge (Amp-hrs)	Initial Temp (C)	Temp Change (C)
15	3630	210	15.2	15.4	15.50	22.5	0
30	1770	210	14.7	15.4	15.45	22.5	1.5
45	1140	199	14.2	15.4	15.38	22.5	3
60	840	172	13.9	15.3	15.30	23.5	4.5
75	630	184	13.1	15.3	15.29	25.5	5.5
90	480	219	11.9	15.2	15.17	23	7
120	240	316	7.9	15.2	15.16	25	9
No Taper							
60	780.4		12.9		12.99		
90	464.8		11.6		11.60		

Altairnano titanate oxide 11 Ah cell

						Temp Rise During Cha	
Charge Current (Amps)	Time to Cutoff (secs)	Taper Time (secs)		Charge (Amp-hrs)	Discharge (Amp-hrs)	Initial Temp (C)	Temp Change (C)
11	3920	81	11.9	12.0	12.00	22.5	0
22	1950	68.5	11.9	12.0	12.00	22	0.5
33	1300	57.7	11.9	12.0	12.00	22.5	1.5
44	970	59.2	11.8	12.0	12.01	23	2.5
55	760	74.8	11.6	12.0	11.97	21.5	4
66	620	83	11.3	12.0	11.97	22.5	4.5
88	440	103.1	10.7	12.0	11.97	24	6.5

Table 13: Repeated fast charging cycles for the 11Ah lithium Titanate oxide cell

66 Amps charge to 2.8V 12A discharge to 1.5V no active cooling

Cycle	Charge or Discharge	Time to Cutoff (secs)	charge Amp-hrs	Discharge Amp-hrs	Initial Temp (C)	Highest Temp (C)
1	Chg	614.4	11.26		21.5	26
2	Dischg			11.19	24	22
2	Chg	614.7	11.27		21.5	26.5
3	Dischg			11.18	24	22
3	Chg	614.5	11.27		21.5	26
4	Dishcg			11.18	24	22
4	Chg	614.1	11.26		21.5	26
5	Dischg			11.17	23.5	22
5	Chg	614.1	11.26		21.5	26

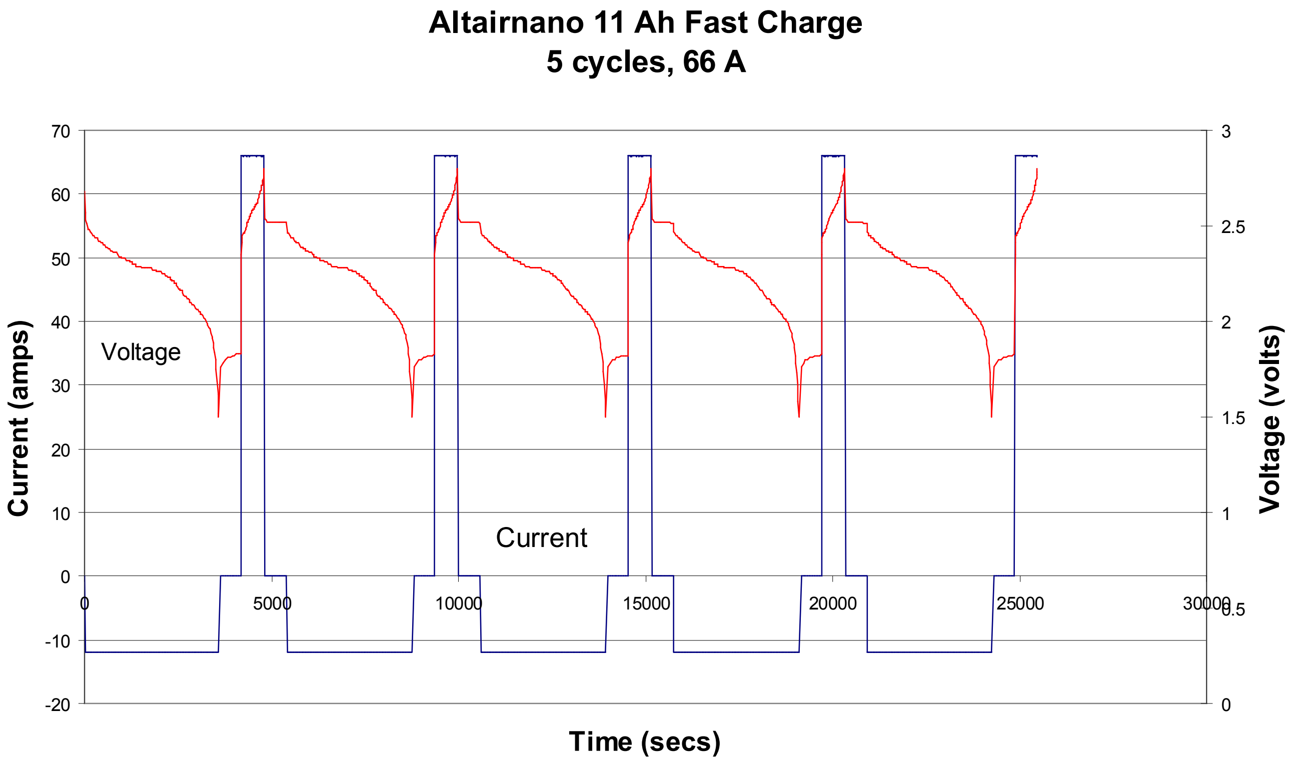
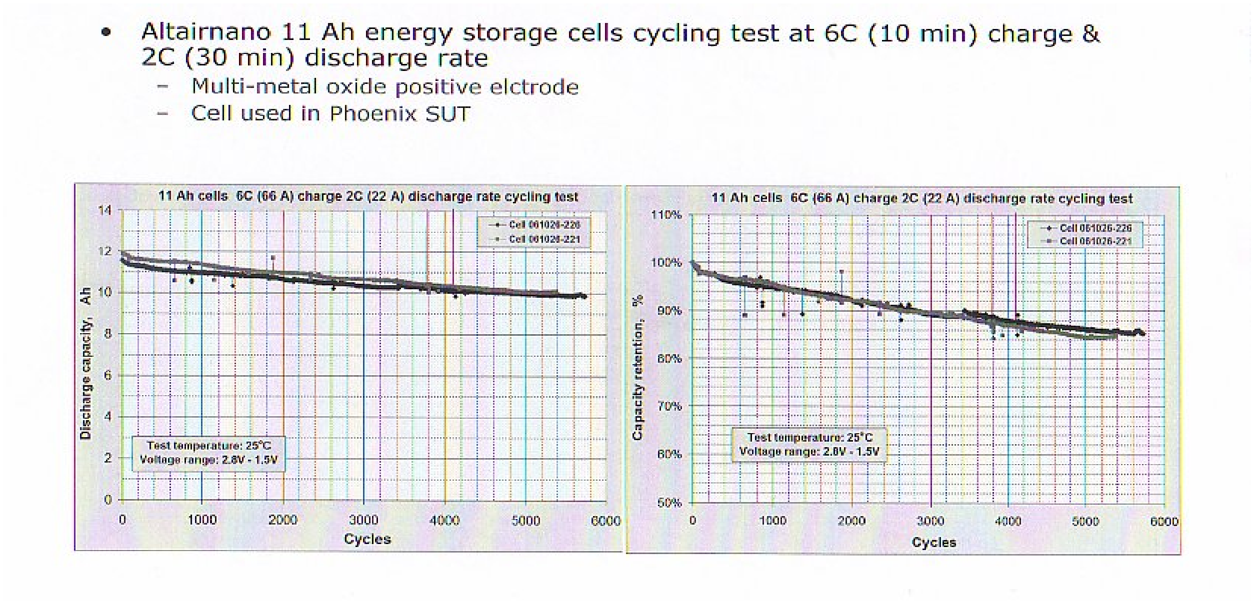


Figure 2: Five fast charge cycles for the Altairnano 11Ah lithium titanate cell



- Altairnano 11 Ah energy storage cells cycling test at 6C (10 min) charge & 2C (30 min) discharge rate
  - Multi-metal oxide positive elctrode
  - Cell used in Phoenix SUT

Figure 3: Life cycle data from Altairnano for the 11 Ah cell under fast charging (6C) conditions

7. Battery testing uncompleted

Due to a contractually set end date for the contract and the limited funds available, all testing on the batteries available was not able to be completed. In addition, the installation of the ABC-150 and work to become familiar with its operation took longer than was anticipated. Hence considerably more testing of the cells and modules that were obtained during the course of the program could be done. This is especially true of the modules obtained from EIG and Altairnano. The EIG modules came equipped with battery management units and associated software to track cell voltages and temperatures. The voltages of the EIG modules were 70-80V which required operation of the ABC-150 to test them. It is anticipated in the future that the ABC-150 will be used to test both modules and high voltage battery and ultracapacitor packs.

Testing with the temperature chamber was not undertaken during the contract period. The effects of low temperature on cell resistance and power capability and on charge acceptance and high temperature on cycle life are of special interest. There are many tests that could be undertaken with the batteries presently available using the temperature chamber, but time did not permit that in light of the contractual end date for the contract.

8. Survey of emerging battery technologies

Energy and power performance

A summary of the data for the different chemistries is shown in Table 14. It is clear from the table that both the energy density and power capability of the cells vary over a wide range and that there are significant trade-offs between energy and power with all the chemistries. Energy density and power capability are discussed separately the following sections.

Energy density

It is clear from Table 14 that the energy density of cells using NiCo (nickelate) in the positive electrode have the highest energy density being in the range of 100-170 Wh/kg. Cells using iron phosphate in the positive have energy density between 80-115 Wh/kg and those using lithium titanate oxide in the negative electrode can have energy density between 60-70 Wh/kg. Hence in terms of energy density, the rankings of the different chemistries are clear and the differences are significant: 1. NiCo, 2. iron phosphate, 3. lithium titanate oxide. The question of what fraction of the energy density is useable in a specific vehicle application could decrease the relative advantage of the different chemistries.

Table 14: Summary of the performance characteristics of lithium-ion cells of different chemistries from various battery developers

Manufacturer	Technology type	Ah	Voltage range	Wh/kg at 300 W/kg	$(W/kg)_{90\%eff.}$ 50% SOC
K2	Iron phosphate	2.4	3.65-2.0	86	667
EIG	Iron phosphate	10.5 15.7	3.65-2.0	83 113	595 895
A123	Iron phosphate	2.1	3.6-2.5	88	1146
Lishen	Iron Phosphate	10.2	3.65-2.0	82	161
EIG	Graphite/ Ni CoMnO2	18	4.2-3.0	140	895
GAIA	Graphite/ LiNiCoO2	42	4.1-3.0	94	1742 at 70%SOC
Quallion	Graphite/ Mn spinel	1.8	4.2-3.0	144	491 at 60%SOC
		2.3	4.2-3.0	170	379 at 60%SOC
Altairnano	Lithium Titanate	3.8 11 52	2.8-1.5	35 70 57	1710 654 340
EIG	Lithium Titanate	12.0	2.7-1.5	43	584

Power capability

The situation regarding the power capability (W/kg) of the different chemistries is not as clear as was the case for energy density because of the energy density/power capability trade-offs inherent in battery design. Further the question of the maximum useable power density is also application specific. In order to have a well-defined basis for comparing the different chemistries and cells, the power density (W/kg) for a 90% efficient pulse at 50% SOC is shown in Table 14 for most of the cells. The power densities can vary over a wide range even for a given chemistry. This is particularly true for the graphite/NiCoMn chemistry. In general, it seems possible to design high power batteries (500-1000 W/kg at 90% efficiency) for all the chemistries if one is willing to sacrifice energy density and likely also cycle life. The data in Table 14 indicate that high power, iron phosphate cells can be designed without a significant sacrifice in energy density. When power densities greater than 2000 W/kg for lithium-ion batteries are claimed, it is for low efficiency pulses. For example, for an efficiency of 65%, the 15Ah EIG iron phosphate battery has a pulse power of 2330 W/kg rather than the 919 value for a 90% efficient pulse.

General considerations for battery selection

The selection of the battery for plug-in hybrid vehicles is a complicated process and depends on many factors. In simplest terms, the battery must meet the energy storage (kWh) and peak power (kW) requirements of the vehicle and fit into the space available. In addition, the battery must satisfy the cycle life requirements both for deep discharge cycles in the charge depleting mode and shallow cycling in the charge sustaining mode of operation. Further the battery unit must be designed to meet the thermal management, cell-to-cell monitoring, and safety requirements. The final considerations are concerned with the initial and life cycle costs of the battery.

As indicated earlier in the report, a primary reason for the present development of lithium-ion batteries of various chemistries is related to safety issues with the batteries using NiCo and other metal oxides in the positive electrode. There have been some instances in which those cells/batteries have experienced thermal runaway events and as a result, the NiCo based battery systems are treated with considerable caution. They incorporate extensive cell monitoring circuitry as protection against possible destructive thermal events.

Cells using iron phosphate in the positive electrode are thought to be much less prone to thermal runaway both because they are less energetic (significantly lower energy density) and do not produce oxygen on overcharge which can react exothermically with the graphite in the negative electrode. Cells using lithium titanate oxide (LTO) in the negative are even less energetic (lower energy density) than cells using iron phosphate and in addition the LTO replaces the graphite in the negative electrode removing a combustible substance in the cell. Hence both the iron phosphate and lithium titanate chemistries are inherently safer than the NiCo chemistry.

Life cycle considerations

Another important issue in evaluating lithium-ion battery chemistries is cycle life and calendar life. In a plug-in hybrid vehicle, a battery life of at least ten years is thought to be necessary. This means that the battery must be able to sustain about 3000 deep discharge cycles in the charge depleting mode and several hundred thousand shallow cycles at low states-of-charge in the charge sustaining mode. Hence a PHEV battery must have the life cycle characteristics of an EV battery and a HEV battery. Whether any of the lithium battery chemistries can meet these life cycle requirements has not yet been determined.

It is expected that both the iron phosphate and lithium titanate chemistries will have significantly longer cycle life than the NiCo chemistry. This is especially true of the lithium titanate chemistry. Life cycle testing of cells done by Altairnano (References 4-6) as part of their development program have indicated a cycle life of greater than 5000 cycles even for fast charge and discharge rates (see Figure 3 and Figure 4).

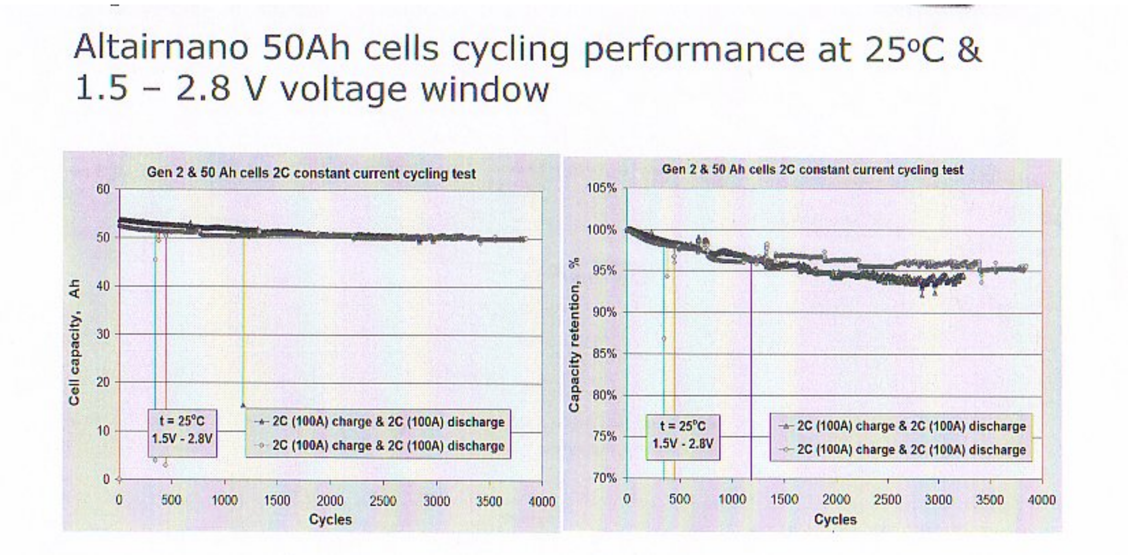


Figure 4: Life cycle data for the Altairnano 50Ah cell (Altairnano data)

Battery cost considerations

It is of interest to investigate the relative cost ($/kWh) of lithium-ion batteries of the different chemistries. None of the chemistries is presently available in large quantities so the cost of batteries available for purchase is high – often more than $1000/kWh. Large format iron phosphate cells from China are lower in cost being in the range of $400-500/kWh.

Projection of the cost of batteries requires inputs on the material costs as well as the cost of manufacturing equipment and processes. It is difficult to get good information on the costs of the various materials used in the electrodes of batteries. When such information is available, it is straightforward to estimate the differences in the electrode material costs for the different chemistries assuming ideal use of the materials in the electrodes. In terms of $/Wh, the following equation can be used:

$$(\$/\text{Wh})_{\text{materials}} = \{[((\$/\text{gm}) + (\$/\text{cm}^3)_{\text{electrolyte}}/\rho/\varepsilon)/\text{Ah/gm}]_{\text{anode}} + [((\$/\text{gm}) + (\$/\text{cm}^3)_{\text{electrolyte}}/\rho/\varepsilon)/\text{Ah/gm}]_{\text{cathode}}\}/\text{Vnom}.$$

The values for the Ah/gm and Voc are given in Table 1. Calculated values for the electrode material costs ($/kWh) are shown in Table 11 for assumed unit costs of the various materials. The material unit costs used in the calculations are based on those used in a recent Argonne Lab study (References 7-8). The results shown in Table 15 indicate that there is not a large difference in the electrode material costs of the various chemistries and also that electrode material costs should not dominate the total battery cost. Note that in general the higher cost lithium battery chemistries have the potential for longer cycle life which on a life cycle cost basis can compensate for the higher initial cost of those chemistries. This is especially true of the lithium titanate chemistry.

Table 15: Relative electrode material costs for various lithium battery chemistries

Chemistry Anode/cathode	Cell voltage Max/nom.	Electrode material $/kg Anode/cathode*	Electrode material cost $/kWh	Cycle life (deep)
Graphite/ $NiCoMnO_2$	4.2/3.6	19/19	44	2000-3000
Graphite/ Mn spinel	4.0/3.6	19/8	35	1000
Graphite/ $NiCoAlO_2$	4.2/3.6	19/19	44	2000-3000
Graphite/ iron phosphate	3.65/ 3.25	19/16	47	>3000
Lithium titanate/ Mn spinel	2.8/2.4	12/8	58	>5000

*** T**he contribution of the electrolyte ($16/L) to the material costs was small partly because the porosity of the electrodes was only about 30%.

Researchers at Argonne National Laboratory (ANL) have developed a detailed lithium battery cost model that is applicable to the various electrode chemistries. The model and results obtained at ANL are discussed in detail in References 7-8. Results obtained at UC Davis with the model for plug-in hybrid vehicle applications are summarized in Table 16 for the three electrode chemistries. The results given in the table are consistent with the test data presented in previous sections of the report. For example, the energy densities of the three chemistries are very close to those of the cells tested (see Table 14). As discussed in Reference 7, the peak power corresponds to a pulse voltage of 80% of V_{oc}, which is an efficiency of 80%. The power densities (W/kg) given in Table 16 for the modeled batteries are consistent with those shown in Table 10 based on the test data.

Table 16: Summary of battery performance and cost projections for various lithium battery chemistries using the Argonne National Laboratory cost model

NiCoAl	kWh	kW	kg	Wh/kg	W/kg	$ cell Mat.	$ battery	$/kWh Cell mat.	$/kWh battery
available	5.1	50	44	116	1136	716	1890	140	371
energy	10.1	50	74	136	676	1156	2820	114	279
60%	20.2	76	143	141	531	2163	4143	107	205
LiFePhos.	**kWh**	**kW**	**kg**	**Wh/kg**	**W/kg**	**$ cell Mat.**	**$ battery**	**$/kWh Cell mat.**	**$/kWh battery**
available	4.8	50	47	102	1064	742	1943	155	405
energy	9.4	50	80	118	625	1148	2838	122	302
65%	18.7	76	149	126	510	2132	4147	114	222
LiTitanate	**kWh**	**kW**	**kg**	**Wh/kg**	**W/kg**	**$ cell Mat.**	**$ battery**	**$/kWh Cell mat.**	**$/kWh battery**
available	3.6	50	55	65	909	668	1855	186	515
energy	7.2	50	103	70	485	1196	2901	166	403
85%	14.4	76	201	72	378	2352	4458	163	310

Another aspect of the battery cost model that should be noted is that it accounts for the differences in the fraction of the stored energy expected to be available using the three chemistries – 60% from NiCoAl, 65% from LiFe phosphate, and 85% from Li titanate oxide. This is the reason that the stored energy (kWh) is different for the three chemistries. This is also the reason that the battery costs for the different batteries are nearly the same even though the energy densities are quite different. Note also that on a $/kWh basis, the Li titanate batteries are significantly more expensive than the other two chemistries, but a significant part of the unit cost difference is negated by its higher energy use fraction. The battery costs ($/kWh) are sensitive to the unit material costs ($/kg), but it seems unlikely that the relative costs of the three chemistries will be much different than that shown in Table 16.

The cost projections obtained using the ANL model indicate that in large scale production (at least 100,000 packs/year), battery costs to the OEM auto companies can be in the $300-400/ kWh range for plug-in hybrids of an all-electric range of 20-40 miles. On a cost basis, the emerging technologies – iron phosphate and lithium titanate oxide do not appear to be at a significant cost disadvantage compared to NiCoAl. The emerging chemistries do have significant advantages in the areas of safety and cycle life as discussed previously.

9. Prospects for higher energy density batteries

There are two general approaches to increase the energy density of batteries beyond that of presently available lithium-ion batteries. One approach is to incorporate into the lithium batteries electrode materials with higher specific charge (mAh/gm) and/or to increase the voltage of the cells to values higher than 4V. A second approach is to develop batteries using a completely different chemistry than used in the present lithium batteries. One of the new chemistries being pursued is Zn-air. This chemistry has been pursued in the past with limited success mostly using mechanical recharging by replacing the Zn electrode. The new work on Zn-air is to develop electrically rechargeable cells which require a bi-functional air electrode. The two approaches will be discussed separately.

Higher energy density lithium-ion batteries

Considerable research (References 9-14) is being done to increase the energy density of lithium batteries beyond the present values of about 170 Wh/kg. It is not the intent of this section of the report to review in detail that research, but rather to indicate its direction and objectives. Much of the research is being done for DOE at the various national laboratories (Reference 9). This work seems to be concentrated on the development of higher specific charge (mAh/gm) cathode materials which are thermally stable. Additional research (References 12-14) especially on silicon composites and nanotubes/nanowires for the anode is being done at start-up, private companies.

Although there is much discussion in the literature of increasing energy density by combining carbon and silicon oxides in the anode (negative electrode) in place of graphite and various layered composites of lithium metal oxides and lithium metal spinels in the cathode (positive electrode), there seems to be little quantitative discussion of the magnitude of the energy density increase that is likely to be achieved. However, discussions with a few companies presently involved with this type of technology indicate that large format cells with energy densities of 250-300 Wh/kg are under development. What is less clear is the power capability of those cells and whether the high energy density cells will have a P/E capability high enough for plug-in hybrid vehicle applications which require a P/E of at least 5. For a cell having an energy density of 275 Wh/kg, the power density should be at least 1375 W/kg for an efficiency of 90%.

New battery chemistry – Zn-Air

Toyota in a press release in July 2008 (Reference 15) indicated that they will be focusing on metal-air for the next- generation batteries beyond lithium-ion. This is not a new chemistry as there has been R&D on electrically rechargeable Zn-air batteries for electric vehicles starting in the late 1980s. As discussed in References (16, 17), large Zn-air batteries (80 kWh) were assembled for testing in passenger and vans. The energy density of that Zn-air battery was about 200 Wh/kg. In more recent years, work on Zn-air batteries focused on mechanically recharged systems mainly by Electric Fuel (References 18, 19) in Israel. There has been considerable in-vehicle testing of the Electric Fuel batteries in vans and buses (Reference 20). Primary Zn-air cells are presently mass marketed for use in small consumer devices like hearing aids.

Recently there has been a restart in R&D on electrically rechargeable Zn-air with the long- term goal of developing batteries for vehicles. However, the first cells are being developed of use in hearing aids and cell phones. One company involved with the new Zn-air development is Revolt Technology in Switzerland. A paper (Reference 21) available on their website (www.revolttechnology.com) explains their technology and includes some test data on small prototype cells. A recent visit to Revolt Technology in Staefa, Switerzerland confirmed the availability of cells (see a photo of a 10 Ah, 1.2V cell in Figure 5). The device shown has an energy density of about 450 Wh/kg and 1040 Wh/L. The power capability of the device is about 200 W/kg, which is much lower (about a factor of ten) than required to vehicle applications.

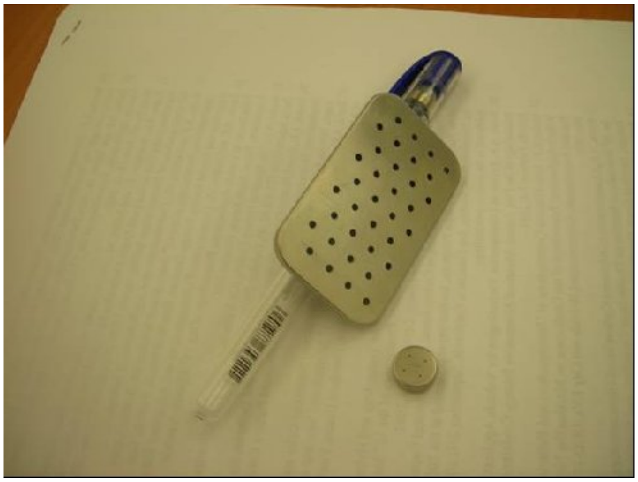


Figure 5: A 10Ah Zn-Air device being developed by Revolt Technology

It appears that significant progress is being made in developing advanced batteries with energy densities greater than the nickelate lithium-ion batteries presently available. Whether these advanced batteries will have the power capability and cycle life required for vehicle applications is not yet known.

10. Summary and conclusions

It is well recognized that the key issue in the design of a plug-in hybrid-electric vehicle is the selection of the battery. The consensus view is the battery will be of the lithium-ion type, but which of the lithium-ion chemistries to use is still a major question. The selection will depend on a number of factors: useable energy density, useable power density, cycle and calendar life, safety (thermal stability), and cost. This report is concerned with the testing and evaluation of various battery chemistries for use in PHEVs. Test data are presented for lithium-ion cells and modules utilizing nickel cobalt, iron phosphate, and lithium titanate oxide in the electrodes. Cells using $NiCoO_2$ (nickelate) in the positive electrode have the highest energy density being in the range of 100-170 Wh/kg. Cells using iron phosphate in the positive have energy density between 80-110 Wh/kg and those using lithium titanate oxide in the negative electrode have energy density between 60-70 Wh/kg. The situation regarding the power capability (W/kg) of the different chemistries is not as clear because of the energy density/power capability trade-offs inherent in battery design. The power densities can vary over a wide range even for a given chemistry. This is particularly true for the graphite/NiCoMn chemistry. In general, it is possible to design high power batteries (500-1000 W/kg at 90% efficiency) for all the chemistries if one is willing to sacrifice energy density and likely also cycle life. The data indicate that high power iron phosphate cells can be designed without a significant sacrifice in energy density. When power densities greater than 2000 W/kg for lithium-ion batteries are claimed, it is for low efficiency pulses. For example, for an efficiency of 65%, the 15Ah EIG iron phosphate battery has a pulse power of 2330 W/kg rather than the 919 value for a 90% efficient pulse.

Cycle life data were not taken as part of the present study. However, cell cycle life data reported by Altairnano for their cells using lithium titanate oxide in the negative electrode indicate cycle life in excess of 5000 cycles for charge and discharge rates of 2C and greater. It seems likely that the cycle life of both titanate oxide and iron phosphate lithium batteries will be satisfactory for vehicle applications.

The cost of lithium batteries remains high ($500-1000 /kWh) when purchased in relative small quantities, but detailed cost modeling of batteries done at Argonne National Laboratory for the various chemistries indicate that in high production volume (greater than 100,000 packs per year), the costs to the OEMs of all chemistries can be in the range of $250-400/kWh depending on the battery size (kWh energy stored). The lithium titanate chemistry is projected to have the highest cost, but it also will have the longest cycle life. The battery cost projections also indicate that material costs likely will not dominate the total costs so that as process and equipment costs are reduced in future years, the battery costs should decrease significantly with time.

R&D is continuing to increase the energy density of lithium-ion batteries. Proto-type cells presently being developed have energy densities in the range of 250-300 Wh/kg

using layered metal oxides/spinels in the positive electrodes. Higher energy densities appear to be likely combining these electrodes with negative electrodes using composites of silicon oxides and carbon. R&D on electrically rechargeable Zinc-air cells is presently in progress. Energy densities in the range of 300-400 Wh/kg, 700-1000 Wh/L appear to be possible using the Zn-air chemistry. The power capability of the advanced batteries is uncertain at the present time.

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