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Journal of Power Sources 54 (1995) 155–162

JOURNAL OF POWER SOURCES

Lithium-ion battery for electronic applications

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Abstract

Lithium-ion (rocking-chair) batteries with lithiated metal oxide cathodes and carbon anodes are finding use in many emerging electronic applications with current drains ranging from a few microamperes (e.g., memory backup, real-time clock, bridge function) to many milliamperes (e.g., laptop computers, phones, etc.). The majority of these applications (e.g., coin, cylindrical, prismatic cell configuration) require a steady low current with periodic high drain pulses. We have found that lithium-ion systems based on lithiated nickel oxide cathodes ($LiNiO_2$) and carbon anodes can be tailored for high capacity moderate rate or moderate capacity high rate applications. In the first instance, a graphitic carbon anode and ethylene carbonate-based electrolyte (e.g., ethylene carbonate–dimethyl carbonate (EC–DMC)) has proven effective while in the second case a petroleum coke anode and propylene carbonate-based electrolyte (e.g., propylene carbonate–dimethoxyethane (PC–DME)) look best. An unoptimized, experimental $LiNiO_2/LiPF_6$, EC–DMC/graphitic carbon, AA-cell has delivered 620 mAh at 0.1 mA cm^{-2} but the capacity then dropped to 535 mAh at 1 mA cm^{-2} and 375 mAh at 3 mA cm^{-2}. Efforts are under way to improve the rate capabilities of cells incorporating graphitic carbon anodes. Initial results indicate that microfiber graphite, special electrolytes and in-house prepared $LiM_xNi_{1-x}O_2$ compounds will achieve the desired performance levels.

Keywords: Lithium-ion batteries; Rechargeable lithium batteries

1. Introduction

Nagaura and Tozawa (Sony Corporation) [1] introduced the first lithium-ion rechargeable battery in portable telephones in June 1991, using a lithiated cobalt oxide cathode and a non-graphitic carbon anode ($LiCoO_2$/carbon). Since then, many announcements have been made of improvements to the system's energy density and rate capability. Table 1 shows a comparison of lithium-ion technologies being developed by various companies. This list is not inclusive of all companies in the field but, rather, summarizes those who have published information in the open literature. Among the transition metal oxides, $LiNiO_2$, $LiMn_2O_4$ and $LiCoO_2$ are the most promising. Criteria for cathode material selection include: (i) electrochemical compatibility with the electrolyte solution over the required charge/discharge potential range; (ii) facile electrode kinetics; (iii) a high degree of reversibility, and (iv) air stability in the fully lithiated state. Although $LiNiO_2$ has the lowest operating voltage of the three materials listed, it offers many advantages as a lithium-ion cathode material. These include: (i) good high temperature stability; (ii) low self-discharge rate; (iii) high specific capacity; (iv) compatibility with many electrolyte solutions; (v) environmentally friendly, and (vi) moderately low in cost.

Criteria for anode material selection include: (i) high reversible discharge capacity (e.g., $\geqslant 372$ mAh g^{-1}); (ii) low surface area for improved safety (e.g., <10 m^2 g^{-1}); (iii) high true density (e.g., >2.0 g cm^{-3}); (iv) compatibility with electrolyte solutions and binders; (v) dimensionally and mechanically stable; (vi) available, and (vii) reasonably priced. Among the many carbons reported in the literature [2–4], graphitic and pyrolytic carbons offer the most promise even though various cokes are presently used in commercial batteries.

Criteria for electrolyte selection include: (i) good conductivity (e.g., 3×10^{-3} to 2×10^{-2} mS cm^{-1}) over a wide range of temperature; (ii) liquid range between at least -40 and 70 °C; (iii) thermal stability up to at least 85 °C; (iv) electrochemical window between 0 and 5.0 V versus lithium; (v) compatibility with cell components; (vi) availability, and (vii) low cost. Among the various salts, lithium hexafluorophosphate ($LiPF_6$), lithium hexafluoroarsenate ($LiAsF_6$), lithium bis(trifluoromethylsulfonyl)imide ($LiN(CF_3SO_2)_2$) and lithium tris(trifluoromethylsulfonyl)methide ($LiC(CF_3SO_2)_3$) are the most promising. Among the various solvents, ethylene carbonate (EC), 1,2 dimethoxyethane (DME),

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SSDI 0378-7753(94)02059-C

Table 1
Comparison of lithium-ion technologies being developed by various companies[a]

Manufacturer	Anode material	Cathode material	Nominal operational voltage (V)	Cell types	Cell sizes	Status
Sony	Petroleum coke	$LiCoO_2$	3.6	Cylindrical	14500, 20500, 18650, 16630, 26XXX	Full production
				Square	48 mm×40 mm×8 mm 48 mm×34 mm×8 mm	
Panasonic	Graphite	$LiCoO_2$	3.6	Cylindrical	17500, 18650	Sampling
				Square	40488	
Sanyo	Graphite	$LiCoO_2$	3.8	Cylindrical	18650	Sampling
Toshiba	Linear graphite hybrid	V_2O_5 $LiCoO_2$	3.0 3.6	Coin	2025, 2430	Full production
				Cylindrical	18506, 18650, 18835	Full production
VARTA	Graphite	$LiCoO_2$	3.6	Unknown	Unknown	Pilot line
Rayovac	Petroleum coke	$LiNiO_2$	3.3	Coin	1225, 2335	Pilot line
				Cylindrical	AA, D	Experimental
Bellcore	Petroleum coke	$LiMn_2O_4$	3.6	Experimental cells only	4.2 cm×7.6 cm×0.6 cm	Experimental
SAFT	Petroleum coke	$LiNiO_2$	3.3	Cylindrical	D	Pilot line

[a] Above information obtained from open literature and personal communications.

propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) or a combination thereof, are the most promising [5,6].

In this paper, we will review the best available data on commercial coin and cylindrical lithium-ion cells for electronic applications and compare these data with in-house work on the $LiNiO_2$/carbon technology using coin, AA, and prismatic test cells.

2. Experimental

Cathode and anode evaluations were done in coin cell hardware 12 mm×2.5 mm, either as half-cells (using metallic lithium counter electrodes) or as full lithium-ion cells with petroleum coke anodes. The construction of electrodes for spirally-wound AA cells was accomplished via a coating process. $LiNiO_2$ was synthesized in-house from LiOH and $Ni(OH)_2$ at 625 °C under an oxygen atmosphere [7]. Cycling of cells and half-cells was done using a Maccor cycler.

3. Results and discussion

3.1. Coin cells/half-cells

Coin cells and half-cells have been used to evaluate various carbons, binders, electrolyte formulations and cathode materials. Table 2 summarizes capacity, voltage profile and rate capability results obtained from coke, graphite and pryolytic carbon. Maximum capacity was reported from pyrolytic carbon at low drain rates (e.g., 0.53 mA cm^{-2}). Most graphites will deliver a reversible capacity higher than petroleum coke but will lose such capacity at high drains. Thus, graphites are ideally suited for low drain applications (e.g., memory backup, real-time clocks) but not high drain applications (e.g., cameras, telephones, etc.).

Development of the poly(vinylidene fluoride) (PVDF) binder system for lithium-ion electrodes has resulted in excellent cycle-life capabilities. For example, Sony 20500 cells retained 77% of their capacity after 1200 cycles [8]. Significantly, no swelling or separation from the current collector was observed in these cells after prolonged cycling. Similar results have been obtained with coin cells using calendered electrodes. Fig. 1 shows the cycle-life performance of coin cells with calendered electrodes (polytetrafluoroethylene (PTFE) binder versus those with pressed electrodes using an ethylene/propylene/diene polymer (EPDM) binder. Up to 1200 cycles were obtained from the 1225 coin cells incorporating the calendered electrodes at 2.0 mA cm^{-2} discharge with little fade in capacity. The pressed electrodes, on the other hand, exhibited a much greater degree of capacity fade. It is interesting to note that

Table 2
Performance and property comparison of coke, graphite and pyrolytic carbon anode materials

Item	Coke	Graphite					Pyrolytic carbon
Type	Petroleum coke	Synthetic (KS-15)	Synthetic (KS-44)	Isotropic (EC-110)	Whisker	Natural (IBA)	Pyrolytic carbon
Structure	Disordered structure	← Ordered layer structure →					Disordered structure
Capacity (mAh/g)							
Irreversible (I)	43.55	125.59	74.82	75.98	75.00	129.00	120.00
Reversible (R)	197.07	355.43	347.72	333.48	362.50	380.00	470
Ratio (I/R%)	22.10	35.33	21.51	22.78	20.69	33.94	25.53
Electrolyte	$LiPF_6$/PC–DME	$LiPF_6$/EC–DMC	$LiPF_6$/EC–DEC	$LiPF_6$/EC–DEC	$LiClO_4$/EC–DEC	$LiPF_6$/EC–DEC	$LiClO_4$/EC–DEC
Voltage profile	Sloping	Flat	Flat	Flat	Flat	Flat	Sloping
Rate capabilities							
Max. rate (mA cm^{-2})	3.0	1.5	1.5	1.5	1.5	1.5	1.0
Structure parameters							
$d(002)$ (Å)	~3.46	3.34	3.34	3.34	3.36	3.34	3.80
L_c (Å)	46	900	> 1000	> 1000	761	> 2000	12.0
Diffusion coefficient (cm^2 s^{-1})	$\sim 10^{-7.6}$	$> 10^{-6.8}$	$> 10^{-6.8}$	$> 10^{-6.8}$	$> 10^{-5.8}$	$10^{-6.8}$	
Density (g cm^{-3})	2.14	> 2.20	2.25		> 2.20		1.60
Surface area (m^2 g^{-1})	4.00	14.00	10.00	9.50	6.00–8.00		4.00

Table 3
Summary of specific capacities obtained during the first intercalation/de-intercalation cycle for Lonza KS-44 synthetic graphite with various electrolyte solutions

Solution	Intercalation capacity (mAh g^{-1})	De-intercalation capacity (mAh g^{-1})	Irreversible capacity (mAh g^{-1})	Percent of theoretical capacity (%)
1.0 M $LiN(CF_3SO_2)_2$/PC–EC (50:50)	1335	248	1087	67
1.0 M $LiN(CF_3SO_2)_2$/PC–DME (50:50)	441	98	343	26
1.0 M $LiN(CF_3SO_2)_2$/EC–DME (50:50)	590	194	396	52
1.0 M $LiN(CF_3SO_2)_2$/EC–DEC (50:50)	458	350	108	94

Note: The tests were conducted by cycling between the voltage limits of 0.1 and 2.0 V vs. lithium at a current density of 0.1 mA cm^{-2}.

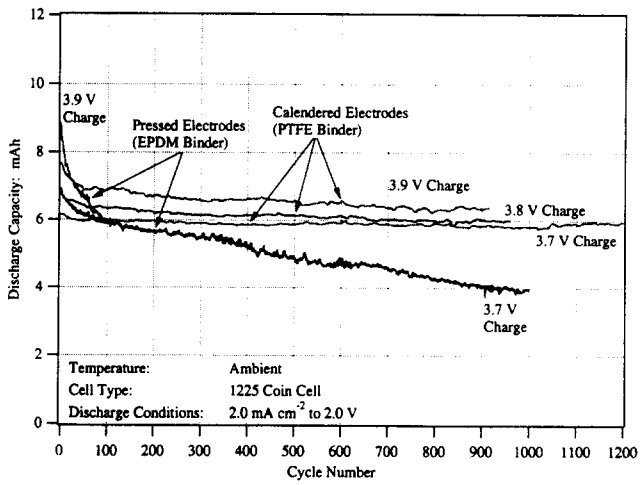

Fig. 1. Cycle-life performance of 1225 coin cells with calendered electrodes vs. pressed electrodes.

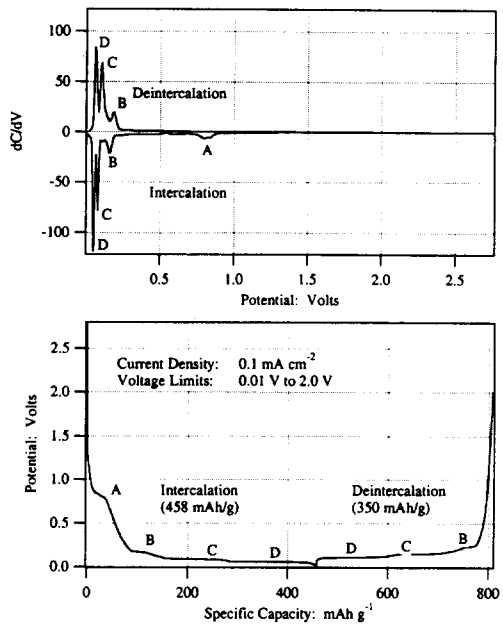

Fig. 2. Voltage profile and derivative plot for the first cycle intercalation/de-intercalation of Lonza KS-44 graphite using a 1.0 M $LiN(CF_3SO_2)_2$/EC–DEC(50:50) electrolyte solution. The phase assignments were taken from Ref. [9]. (A) exfoliation of graphite (irreversible); (B) lithium intercalation: 1′+4 two-phase region; (C) lithium intercalation: 2L+2 two-phase region, and (D) lithium intercalation: 2+1 two-phase region.

the electrode thickness in the coin cell is about 0.040 versus 0.010 in or less thickness in cylindrical cells.

An obvious way to boost the capacity of lithium-ion batteries is to replace the petroleum coke anode with a graphitic carbon. This, however, has been hindered by the low reversible capacity and poor cycle life of graphitic carbons in many electrolyte solutions. These problems are believed to be the result of extensive exfoliation caused by solvent co-intercalation. The effect of electrolyte solution in the first intercalation/de-intercalation of Lonza KS-44 synthetic graphite is presented in Table 3. As can be seen, PC- or DME-based electrolytes exhibited large irreversible capacities combined with de-intercalation capacities well below the theoretical value of 372 mAh g^{-1}. Only the solutions containing EC–DMC and EC–DEC solvent mixtures performed well, (e.g., useful capacity of 328 to 350 mAh g^{-1}). Such solutions are now being widely used with graphitic carbons. Fig. 2 shows the voltage profile and derivative plot for KS-44 graphite using a $LiN(CF_3SO_2)_2$/EC–DEC (50:50) solution. Referring to the derivative plot, the peak observed at approximately 0.8 V is believed to be due to exfoliation of the graphite and is completely irreversible. The three sharp peaks appearing between about 0.2 and 0.0 V represent two-phase regions that are formed during the lithium intercalation/de-intercalation processes [9]. These processes are highly reversible.

Lithium coin half-cells have also been used to evaluate various cathode materials. Fig. 3 shows the first cycle discharge profile and the specific capacity of the most promising cathode materials for lithium-ion batteries. It is interesting to note that $LiNiO_2$ has the highest capacity compared with the other materials. However, utilizing the maximum available capacity in $LiNiO_2$ would result in significant penalties in the areas of safety, charge retention, and cycle life. As will be discussed in the next section, specific discharge ca-

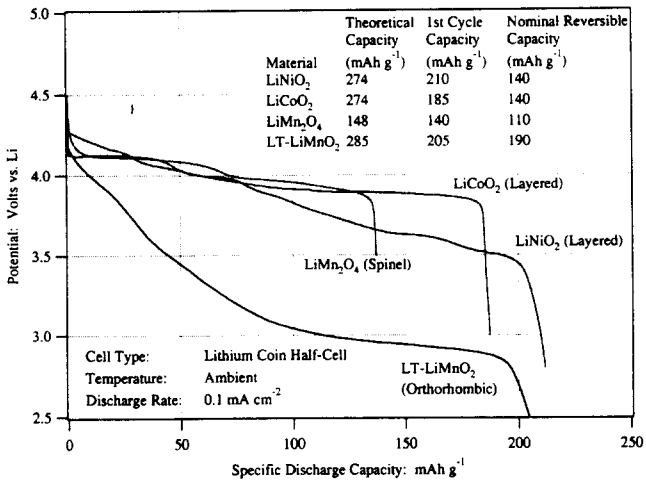

Fig. 3. First cycle discharge voltage profiles for various lithium-ion cathode materials.

pacities for $LiNiO_2$ are generally limited ot about 140 mAh g^{-1} in practical cells.

Comparative performance of $LiNiO_2$/carbon coin cells (1225 size) with other rechargeable coin cells is presented in Table 4. Lithium-ion cells have higher voltage, rate, cycle life, energy density and cumulative capacity than comparable sizes with metallic Li or LiAl anodes. Fig. 4 illustrates the enormous advantage in cycle life that lithium-ion cells can offer in comparison with cells utilizing metallic lithium anodes.

Because of the above advantages, lithium-ion coin cells will be used as replacement for metallic lithium and nickel–cadmium batteries for electronic applications (e.g., memory backup, real-time clock and bridge function). Tables 4 and 5 summarize these advantages.

3.2. Cylindrical cells

Lithium-ion batteries made with multiples of cylindrical cells are finding more and more applications in electronic portable devices (e.g., laptop computers, cellular phones, camcorders, etc.) because of their higher energy density, lower weight and longer cycle life as compared with traditional nickel–cadmium or the newly developed nickel–metal hydride cells. Table 1 shows some of the recently developed lithium-ion cylindrical sizes.

For the lithium-ion system to be commercially viable, it should have capacity and energy density advantages over nickel–metal hydride at reasonably low cost to the user. Among the lithiated oxide cathodes, $LiNiO_2$ is the most competitive with the metal hydride system at a moderate cost (e.g., higher capacity than $LiMn_2O_4$ but lower cost than $LiCoO_2$). To increase the capacity of lithium-ion batteries, higher specific energy cathode and anode materials must be used. This means $LiNiO_2$ and graphitic carbon.

Table 4
Comparative performance of $LiNiO_2$/carbon coin cells with other rechargeable coin cells

Performance parameter	Li/V_2O_5	$LiAl/MnO_2$	$Li–C/V_2O_5$	$LiNiO_2$/carbon	$LiNiO_2$/carbon advantages
Nominal voltage (V)	3.0	3.0	3.0	3.3	
Operating voltage range (V)	3.3–2.0	3.3–2.0	3.3–2.0	4.0–2.0	Higher voltage
Calculated or rated capacity, 1225 size (mAh)	9.0	11.2	5.3	11.0	
Standard discharge rate (μA)	90	90	90	1000	Better rate capability
Standard charge					
Voltage (V)	3.5	3.6	3.5	4.0	Faster and higher
Current (mA)	1.0	1.0	2.0	2.0	rate of charge
Cycle life					
50% DOD	100	125		2000–4000	More cycles
100% DOD	60	50	500	1000–2000	
Lifetime energy at 100% DOD (mAh)	540	560	2650	12000	Longest lifetime energy
Specific energy (Wh kg^{-1})	27	34	26	35	Higher energy density
Energy density (Wh l^{-1})	95	118	91	115	
Self discharge at room temperature (%/month)	1	1	10	5	
Environmental concerns	Vanadium	None	Vanadium	Nickel	
Residential metallic lithium at disposal	Yes	Yes	Yes	No	

Table 5
Lithium-ion coin cells for memory backup, real-time clock and bridge applications

Item	Requirement		Existing battery capability		Lithium-ion 2335	Lithium-ion advantages
	Memory/RTC	Bridge	Memory/RTC	Bridge		
a) Electrical						
Cell size			ML2016	N120TA	2335	
Capacity (mAh)	45	20	20	120	60	Higher capacity
Operational voltage (V)	3.00	7.20	3.00	1.20	3.0	Wattage will meet bridge requirements
Rate						
Maximum continuous	10 μA	20 mA/5 min	100 μA	50 mA/5 min	5 mA continuous 50 mA/5 min	180 vs. 100 days
Maximum pulse	None	200 mA/1 min	None	200 mA/1 min	100 mA/1 min	One cell may perform both functions
Cycling						
Charge times	4–5 days	16 h	1–5 days	16 h	3 h to 8 days	Flexibility of charge regime
No. of Cycles	1000 shallow 4–6 deep	500	1000 shallow 4–6 deep	300	> 1000	More cycle life
b) Others						
Operational temperature (°C)	10 to 50	10 to 40	10 to 50	10 to 40	−10 to 55	High temperature stability
Storage temperature (°C)	0 to 70	0 to 50	−20 to 70	0 to 50	−20 to 60	High temperature stability
Self-discharge (%/year)	5	10	3	100	10	

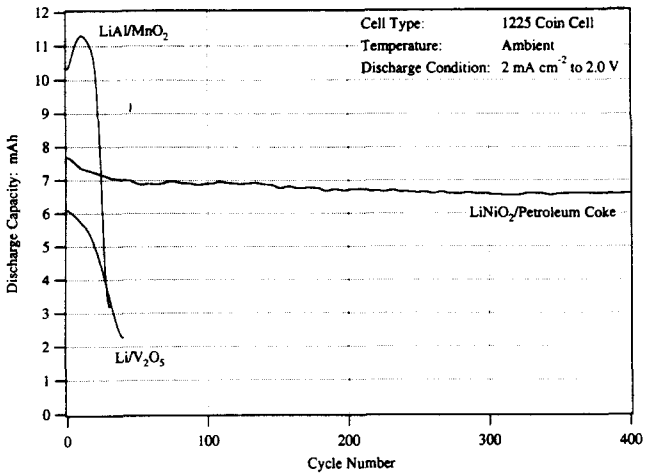

Fig. 4. Cycle-life performance of 1225 coin cells with carbon vs. metallic lithium anodes.

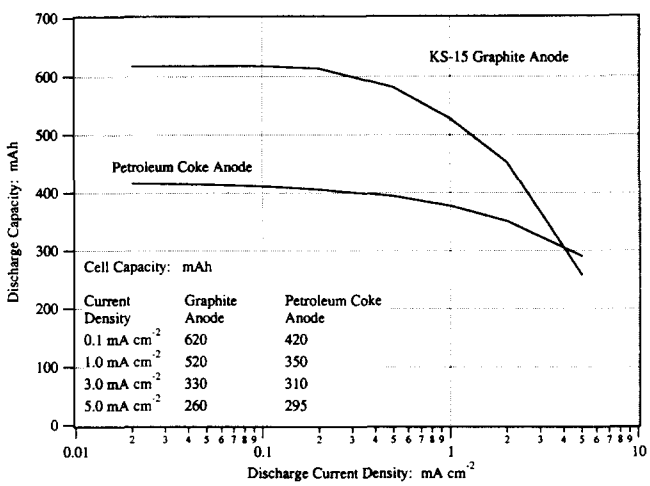

Fig. 5. AA-cell capacity as a function of current density for cells with anodes of either graphite of petroleum coke.

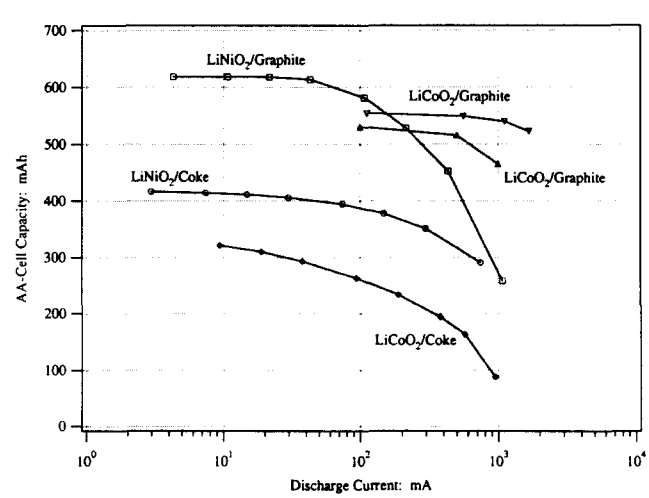

Fig. 6. Comparative performance of various lithium-ion technologies normalized to the AA-size cell.

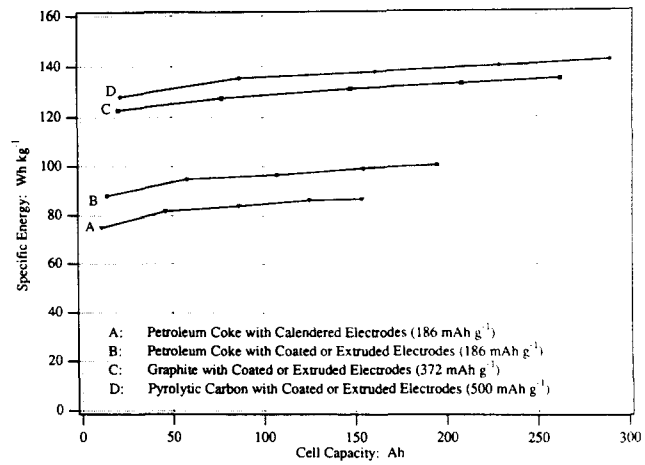

Fig. 7. Energy density projections of $LiNiO_2$/carbon prismatic cells.

Another way of increasing cell capacity is by charging $LiNiO_2$/carbon cells at 4.5 V and adjusting the cell balance accordingly. As discussed earlier, $LiNiO_2$ will yield a first charge capacity of 264 mAh g^{-1} (0.96 F mol^{-1}) to 4.5 V and a discharge capacity of 210 mAh g^{-1} (0.77 F mol^{-1}). Under these conditions, projected AA-cell capacities would be 475 mAh for petroleum coke anodes and 720 mAh for a graphite anode. However, safety, charge retention and cycle life would be compromised by this approach.

A more conservative design approach is to limit the charge capacity of $LiNiO_2$ to well below its theoretical value to achieve better cathode stability and reversibility. We have found that 4.0 V is the maximum practical charge potential that should be used with $LiNiO_2$/carbon cells to ensure safe operation and long cycle life. Under these conditions, $LiNiO_2$ would be limited to a maximum first charge capacity of 170 mAh g^{-1} (0.62 F mol^{-1}) and a discharge capacity of 142 mAh g^{-1} (0.52 F mol^{-1}).

Fig. 5 shows a plot of capacity versus current density obtained from a stepwise discharge test of prototype AA cells containing graphite and petroleum coke anodes following a charge at 4.0 V. With the graphite anode, the low rate capacity was substantially greater than with the petroleum coke anode (e.g., 620 versus 420 mAh at 0.1 mA cm^{-2}). At a higher current density of 4 mA cm^{-2}, however, the capacity advantages disappeared. The reduced rate capabilities with the graphite anode can be at least partly attributed to electrolyte solution properties. For example, in this work, an EC-based electrolyte (e.g., 1 M $LiPF_6$/EC–DMC (50:50)) was used with the graphite anode while a DME-based solution (e.g., 1 M $LiPF_6$/PC–DME (50:50)) was used with the petroleum coke anode. The first electrolyte is less conductive and more viscous than the second electrolyte thus yielding poorer capacity at high current densities.

Fig. 6 shows the continuous improvement in the capacity and current density of AA cells since the introduction of the first cell in 1990, (e.g., $LiCoO_2$/coke). More improvements are projected with microfiber graphite, special electrolytes and an in-house prepared $LiM_xNi_{1-x}O_2$ where M is a selective elemental additive(s).

3.3. Prismatic cells

Small prismatic cells of the aqueous electrolyte type (e.g., nickel–cadmium and nickel–metal hydride) are commercially available for electronic applications. The use of small prismatic lithium-ion cells is emerging. Large prismatic cells have also been considered for electric vehicles and military applications such as NSWC-DATPS (Naval Surface Warfare Center-Diver Active Thermal Protection System).

Traditionally, prismatic cells have been preferred in applications with moderate current density requirements (e.g., less than 1.0 mA cm^{-2}). In these applications the prismatic form factor will result in 15 to 30% capacity advantage over the cylindrical form factor. In the development of prismatic cells, electrode processing, integrity and cost assume major importance. With lithium-ion cells, several electrode manufacturing techniques can be used such as slurry coating, calendering or extrusion. The success of these processes will depend on the availability of a good binder to adhere the electrode materials to the current collector. We have found that PVDF binder at the 5–10% level is an effective binder for coated electrodes while PTFE is also an effective binder when fibrillated by a calendering process. By increasing the amount of PTFE in the electrode mix, a continuous extrusion process of such electrodes may become feasible.

Many factors will affect the energy density and capacity of prismatic cells (e.g., electrode thickness, density, formulation, etc.). Fig. 7 shows the effect of carbon-type and electrode processing method on the projected energy density of prismatic cells. In this work, coated and extruded electrodes have yielded higher values than calendered electrodes due to their higher densities. By increasing the anode carbon specific capacity, (e.g., pyrolytic carbon), future prismatic cells are expected to exceed 130 Wh kg^{-1} in large cell sizes.

4. Conclusions

Half-cells and coin cells have proven to be very effective tools for evaluating and selecting materials to be used in lithium-ion batteries. From this work, coin cells have been developed that are suitable for electronic applications (e.g., memory backup, real-time clock and bridge function) followed by prototype cylindrical cells (e.g., AA-size) having improved carbon and $LiNiO_2$ materials. A maximum capacity of 620 mAh for the AA cell was obtained at low current density, representing the highest value reported to date in the literature. Further improvements in cathode/anode capacity, processing techniques and components are forthcoming which will allow lithium-ion cells to compete favorably with nickel–cadmium and nickel–metal hydride cells for electronic applications.

Acknowledgements

The authors gratefully acknowledge the US Army Research Laboratory (ARL) and the Naval Surface Warfare Center (NSWC) for their support of portions of the work conducted at Rayovac.

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