Panel Discussion
Future Prospects of Lithium Batteries

1. Introduction

1.1. B. Owens

Good afternoon, I should like to open the panel discussion session now. My name is Boone Owens and I will serve as co-chairman along with Professor Tetsuya Osaka. The panel discussion will address the future prospects for lithium batteries. Panel members are Dr R. Atanososki from 3M (USA), Professor J. Besenhard, University of Graz (Austria), Dr R. Ishikawa from LIBES (Japan), Dr S. Megahed from RBI (USA), Dr K. Nakajima from Sony (Japan), Dr A. Ohta from Matsushita Battery Industrial (Japan), Dr F. Gibbard from GRADCO (USA), (Dr Gibbard is currently chief executive officer of H Power Corporation in Belleville, NJ, USA), and Dr M. Broussely, from SAFT (France).

Professor Osaka has a few comments on the recent trends and future prospects for lithium and lithium-ion batteries.

1.2. T. Osaka

Fig. 1 shows the trend in battery revenues in Japan over the past 30 years. Lithium primary battery sales have increased continuously since the 1980s, and are still increasing. The total sales last year were about US$ 500 million. Recently, Ni-MH battery sales are increasing rapidly, but rechargeable Li-ion battery sales are increasing even faster, last year just reaching US$ 600 million. So, in the future, we assume such new batteries will become the main products. We are now projecting battery types and their energy densities as shown in Fig. 2. Today the Li-ion battery provides around 100 Wh kg⁻¹ but the technology improves, and we anticipate the Li metal secondary battery might appear at the start of the next century with 200 Wh kg⁻¹ or more.

1.3. B. Owens

Thank you Professor Osaka. The first topic, to be introduced by Dr Ohta, is the future of primary lithium batteries.

2. Future of primary lithium batteries — Dr A. Ohta

2.1. A. Ohta

Thank you, Dr Owens. Good to meet you ladies and gentlemen. I am in charge of providing topics of primary lithium batteries. I would like to present a brief overview of the current state of the affairs of primary Li batteries, not the future.

Honestly speaking, battery researchers and engineers including participants here, do not seem to have much interest in primary lithium batteries, at present. Consequently, there are few new topics of the R&D of these types of batteries. However, as Professor Osaka said, the production of lithium primary batteries is steadily increasing in Japan.

Only five primary lithium battery systems survive at present, CF, manganese oxide, thionyl chloride, iron disulfide and copper oxide. Unfortunately Li/copper oxide batteries will disappear soon since we cannot find any application in the markets.

First I would like to speak about CF batteries. This battery was developed 25 years ago, and it has been commercialized for 20 years. Performance and special features of this type of battery are well understood. The most important feature of this battery is that it has excellent high temperature characteristics. We confirmed that it can be stored for one year at 100 °C. In order to improve the thermal stability, new plastics were used for the separator and gasket. When this battery is stored at 150 °C for 500 h, there is almost no decrease in service life (Fig. 3).

Li-MnO₂ is the most popular type of lithium batteries, which accounts for sales of about 80% of the coin-type and about 20% of the cylindrical-type batteries. Various sizes are available and they are used for a variety of applications, for example, watches, computers, remote door locks, toys, memory back-up, etc. Cylindrical designs are mainly used for cameras.

Two Japanese companies are now producing lithium thionyl chloride batteries. 1.5 V Li–iron sulfide batteries are not produced in Japan. However, this type of battery is drawing attention as a popular commercial 1.5 V type battery to replace alkaline manganese batteries. The specific feature of
this battery seems to be high current discharge which exceeds that of alkaline manganese batteries. Cost is an important issue of this battery.

At present, I do not think we have any promising new alternative chemical system for primary batteries. Consequently, lithium primary batteries will remain one of the important primary batteries in the future too. We expect further improvement in the safety, temperature characteristics and cost reduction.

Thank you for your kind attention.

2.2. Question B. Owens

The first lithium primary battery that was used in a commercial product was a Li–iodine heart pacemaker battery in 1972. What are the future requirements for lithium primary batteries for implantable medical applications?

2.3. Answer E. Takeuchi, Wilson Greatbatch

The advancements in circuitry in electronic design over the past 20 years have been such that the battery is a very large portion of the total size of the medical device. So there is always a challenge to try to make the battery smaller while maintaining a service life of five ten 10 years. Present day pacemakers powered by Li–iodine batteries have a very good record of reliability and safety. Electronic improvements have enabled the pacemakers to provide more functions, so a battery with a lower resistance will probably be used soon for all pacemakers. The same issue is present for devices that require higher power such as the implantable cardiac defibrillator which also uses a primary cell. The challenge is to make the device smaller without sacrificing the longevity or performance of the device.

2.4. Question T. Takamura, Petoka

What are the future prospects for Li–air primary batteries?

2.5. Answer A. Ohta

Experimental Li–air batteries have been conceived, but practical designs remain difficult.

2.6. Question B. Owens

Dr Gibbard, do you have a comment on that?

Fig. 1. 25 year history of battery market in Japan.

Fig. 2. Evolution of the energy densities for rechargeable batteries from 1990 through 2000.

Fig. 3. High temperature (150 °C) storage of lithium carbon monofluoride primary batteries: a comparison of a new product to a conventional product.
2.7. Answer F. Gibbard

If you want to use an air electrode, you are probably going
to have to use an aqueous system, and that immediately raises
the possibility of incompatibility with lithium. However,
there was a significant effort in the USA more than ten years
ago directed towards realizing a lithium–air battery for large
military battery applications. That, as far as I know, did not
come to anything significant. The technical challenges are
formidable, even for a large system, and one in which the
battery is to be used up in a comparatively short period of
time. The challenges for making a battery that has a shelf life
of four or five years are much more formidable than that.

2.8. Answer K.M. Abraham, EIC

EIC has demonstrated a polymer electrolyte-based battery.
The results appeared as the first article in the January 1996
issue of the Journal of the Electrochemical Society. A poly-
mer electrolyte-based battery configuration will most proba-
bly make the Li/O2 system practically feasible. EIC has been
awarded US Patent No. 5 510 209 for this invention.

2.9. Question B. Owens (to S. Megahed)

Do you have another comment on primary batteries?

2.10. Answer S. Megahed

Yes, I just have a very brief comment on lithium–carbon
monofluoride, because I had the fortune to be working on it
for a good portion of my life. The best system as far as I know
for military and consumer use for high-temperature applica-
tions is carbon monofluoride, a primary cell. The major issues
for high temperatures were two technical problems. One of
them was finding the right separator, and the other problem
was finding the right gasket material that would withstand
very high temperatures. There are two materials that could
be used there. Glass separators could be used, but the most
important thing for gaskets is that it is very difficult to find
materials that will last at the high temperatures. We have
done work at 100 °C for one year, and even up to 220 °C for
less than minutes for surface-mount applications. The grom-
et material used for that is polyether ether ketone (PEEK).
It is a very difficult material to mold, and also highly expen-
sive. But what impressed me about this is that the weight loss
after one year at 85 °C is almost negligible. Nothing can go
through it, unlike polypropylene, for example. So, by having
carbon monofluoride as a very stable cathode material and
by selecting the right gasket material, you can make a very
high-temperature crimped-seal battery that lasts for a very
long time, for special very high-temperature use, like surface-
mount or military applications.

2.11. Question A. Kozawa, ITE

I would like to ask a short question regarding safety. Dr
Ohta, have you seen any explosions or dangerous situations
with primary lithium batteries in the past several years?

2.12. Answer A. Ohta

All lithium batteries are tested before being released to
the market. There are no serious safety problems in these
commercial primary lithium batteries.

2.13. Question A. Kozawa, ITE

What is the current regulation for how much metallic
lithium is allowed for airplane transportation?

2.14. Answer S. Megahed

I can give you my short answer. Most of the audience
knows it is half a gram of lithium per cell; that is DOT
regulations for transportation, and that has not changed for a
long time.

3. Future of rechargeable Li batteries — Dr Ishikawa

3.1. T. Osaka

The next topic is the future of rechargeable lithium
batteries, introduced by Dr Ishikawa.

3.2. R. Ishikawa

Thank you Mr Chairman. I am very honored to take part
in this panel discussion on lithium batteries and would like
to present the topic of ‘Rechargeable Lithium Anode Batter-
ies’. The specific capacities of anode active materials are
shown in Fig. 4. The theoretical value for graphite is 372
mAh g⁻¹, and that of lithium metal is more than 3800 mAh
g⁻¹. The specific capacity of amorphous tin oxide, which was
recently announced by the Fuji Photo Film, is higher than
that of graphitic carbon.

Lithium metal offers the possibility for the highest energy
density batteries, because of its high theoretical specific
capacity. On the other side, the problems with rechargeable
lithium batteries using lithium metal anodes are short cycle
life and low thermal stability. Many papers studying the
mechanism of lithium dendrite growth and suppression were
reported in this symposium.

Several types of rechargeable lithium anode batteries are
shown in Table 1. The representative commercialized lithium
battery was the Li–Mo3 system by MoLi-Energy. Li–amor-
phous vanadium oxide is being developed by NTT. The poly-
mer battery is being developed by 3M and Hydro-Quebec,
under contract with the USABC. The Li alloy–FeS2 system
density, energy density, cycle life and stability at high
temperatures (up to 70°C)?

3.4. Answer R. Ishikawa

It is very difficult to offer the priority of safety, cost, power
density, energy density, cycle life, stability at high tempera-
ture and others. Safety is the first priority and cost usually is
the second issue. However, the priorities of cost, energy den-
sity, specific energy, power density, cycle life and stability
depend on the battery application.

3.5. Question G. Blomgren, EBC

I have two questions: (i) what will be the energy density,
voltage and specific energy of lithium-ion cells five years
from now (2001)? (ii) can safety and rechargeability limi-
tations of the lithium anode be overcome in the next five
years?

3.6. B. Owens

These questions will be addressed in the next discussion
section on the future of lithium-ion batteries.

4. Future of Li-ion batteries — Dr Gibbard and
Dr Nakajima

4.1. F. Gibbard

I have just a couple of overheads, in which I have tried to
summarize some of the issues in technology and, because the
lithium battery business is driven by the marketplace, my
second overhead will deal with markets. My comments are
fairly conservative, I think, for a long-time R&D person. First
of all, I would say that for the next several years lithium ion

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<th>Electrolyte</th>
<th>Battery system</th>
<th>Organization</th>
<th>Remarks</th>
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<td>Toxicity of As</td>
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<td>Li/LiAsF6-PC + co-solvent/MS2</td>
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<td>Li/LiAsF6-2Me-THF+EC/TiS2</td>
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<td>Li-Al/LiPFe4 MeDOL + DME + additive/TiS2</td>
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<td>Li-Al/LiClO4 PC/polyvinyl</td>
<td>Bridgestone-Seiko</td>
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<td>Polymer</td>
<td>Low reactivity, mechanical effect</td>
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<td>Low ion conductivity</td>
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<td>Li/PEO-CF3SO2//(SRS)1</td>
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<td>Li/LIX-PEO-based polymer/V2O5</td>
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<td>Molten Salt</td>
<td>Li/Li+Li3PO4+P2S7/TIS</td>
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<td>Li-alloy/LiCl+LiBr+KBr/FeS2</td>
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is going to be the premier battery technology. Based on the discussions and the papers that have been presented at this meeting, and based on the present position of lithium ion in the market, it would be difficult to argue with that.

My second point is an extrapolation of the trend of the past few years, based on the performance of Sony cells and, more recently, of Sony’s competitors. That is, that energy density, both volumetric and gravimetric, has been growing at the rate of 10–15% per year. The technology is still, relatively speaking, in its infancy; and I think that the most conservative estimate would be to say that it will continue to grow linearly, at about 10 to 15% per year for the next few years. One trend that has already been seen (for example, in a report from Nomura in Japan) is that of cost decreases. As more and more production comes on, and competition increases with new producers of lithium ion, the cost per cell is coming down, and we could foresee the time when the price could approach that of nickel–metal hydride, for example.

One tendency that I think we will see is greater temperature range of operation. Some of the cells now are sensitive to storage or operation at 65°C, and that is important for a couple of reasons, for the largest applications. We find from the laptop computer manufacturers that the cells are exposed to higher and higher operating temperatures. As the computing power of the processor increases, the internal heat generation and the temperature of the computer go up. There are already places within the laptop where temperatures of 45–50°C can be found. So it is extremely important, both for the cycle life, and possibly for the safety of the battery, that it be able to tolerate those temperatures.

I think that the next trend that we will begin to see is the ability of lithium-ion batteries to operate the new generation of cellular phones. Since those operate on digital technology, which requires quite high current pulses, it is necessary that any new battery, or modification of an existing battery system, be able to sustain those high-current pulses.

Now, moving along to the specific components of the battery, the capacity of carbon materials, as well as new materials such as tin oxide and perhaps other metal oxides, are expected to be in excess of 500 mAh g⁻¹. As Professor Besenhard told us the other day, metal alloys still have great promise, if someone can figure out how to make them work. The trend for negative active materials is toward higher capacity. For achieving higher capacity in the battery, it would be very desirable to eliminate the irreversible capacity loss on the first cycle. If it were possible to do that, it might also be possible to eliminate the gassing on the first charge, which would be quite convenient. So I expect to see some developments in these areas.

With respect to electrolytes, we will see developments both in the area of gelled electrolytes and in true polymer electrolytes. I expect to see, because there is a great economic incentive to do it, the development of less expensive and less chemically sensitive salt components than lithium hexafluorophosphate.

In the area of positive electrodes, we have had a large number of papers on manganese oxide spinel, which could greatly lower the cost of the positive electrode, if the material can be made sufficiently stable. My guess would be that within two years we will see large-scale production of the lithium manganese oxide spinel. I cannot tell you which company that will be, but I know several of them that are working on it. That is good for the consumer, because we can expect decreases in the cost of the system. Additionally, we have had a good deal of talk about new positive active materials that have lower equivalent weight and therefore lower battery weight. Looking forward to the next five years, we will probably have such a material in production.

In the case of the cell hardware, it seems likely that we will see flexible packaging appearing in the marketplace in large quantity. There are certainly many technical issues in doing that, but in addition to flexible packaging, we can also have extremely thin and light packaging, such as the aluminum case that Sid Megahed was talking about.

That concludes the remarks I wanted to make about technology. A few comments on markets. The big question for lithium ion is whether the growth is limited to premium markets, that is, markets in which consumers are willing to pay extra money for its greater energy density and specific energy. Certainly, if the system has no more energy density than nickel–metal hydride — and that is the case with volumetric energy density, where the new nickel–metal hydride is at 300 Wh/l⁻¹ — and if the cost of the nickel–metal hydride product is considerably lower, there is very little incentive on the part of a device manufacturer to use lithium ion. So the question is, will there be adequate availability of lithium ion, and will the price go down? My own opinion is that lithium-ion costs will continue to decrease significantly. There are other forces that might mandate the use of lithium ion in specific markets, such as environmental considerations — the ‘green’ trend so prevalent in Europe and Scandinavia. I have talked to companies that say they want to use lithium ion as opposed to nickel–cadmium or nickel–metal hydride, simply because their customers expect them to be ‘green’ and they intend to do so.

The market for ‘3C’ applications, which consists of portable computers, communications, and consumer electronics such as camcorders, has been growing at a combined annual growth of 16%, and can be projected to continue to grow at about that rate on the basis of known new product introductions. But the lithium-ion segment has been growing much faster than that, at the expense of the market share of nickel–metal hydride, particularly; and it is projected to grow at a combined annual growth rate (CAGR) of more than 50%, which is a very healthy growth rate indeed.

The electric-vehicle market will not be discussed by Klaus Brandt, who was unable to attend the conference, but by Michel Broussely, so I will not say anything about that market.

A new area in which lithium ion could make a significant impact is that of aerospace. The US Air Force is already
funding research for aerospace applications. For large aerospace companies which launch 50 to 100 satellites per year, the savings if the battery weight can be halved runs into the hundreds of millions of dollars. So there is an enormous incentive for developing lithium ion for this application; it is very likely that lithium ion will be the next generation of power sources in space after nickel–hydrogen. If you are a high-reliability manufacturer of lithium-ion batteries who is accustomed to selling batteries for US$ 1000 to US$ 10,000 per kWh, then the prospect of getting up to two orders of magnitude more for an aerospace battery might be quite attractive.

Military applications are also attractive. Several companies are already being funded to develop lithium-ion batteries for terrestrial uses such as military communications by the US Army and for underwater applications by the US Navy.

And finally, for smaller batteries, there is the consumer-appliance market. Consumer appliances are a very cost-competitive market for rechargeable batteries, and so they tend to use nickel–cadmium or, recently, nickel–metal hydride. There is, however, the environmental pressure for lithium ion; and some manufacturers of electric shavers and tooth brushes may adopt lithium ion, provided that it can deliver the power to operate the motors of the devices.

Within the last year we have seen what may be the first niche market for this type of battery, with the development of a relatively high-temperature lithium-ion polymer battery for down-hole oil well logging.

That concludes the comments that I wanted to make concerning the technology and the development of the markets.

4.2. Question B. Owens

There was the second part of George Blomgren's question — you have addressed it I think. What would be the limits for energy density, voltage, and specific energy in about five years from now?

4.3. Answer F. Gibbard

I will stick to my answer of a linear increase in energy content of 10–15% per year, which would give a range for specific energy of 180–200 Wh kg⁻¹ in five years time, and on the volumetric basis it would give 420–490 Wh l⁻¹. Some people are already talking about those kinds of numbers.

4.4. Question B. Owens

Where do you think the voltage will go?

4.5. Answer F. Gibbard

My guess is that the voltage does not go much higher than it is now — it is not necessary for it to go much higher. Take the cellular phone, for example. Once you get down to the voltage where a cellular phone can be driven by a single cell, there is no incentive for further increase of the voltage of a cell. So I am guessing that the voltage does not go much over about 4.2–4.3 V.

4.6. Question T. Imai, Fujikura

What is the possibility for polymer electrolytes in these batteries. Do you see any real advantage or disadvantage to the use of a polymer electrolyte in this type of battery?

4.7. Answer F. Gibbard

Yes, Sid Megahed and I spent about five minutes putting together an overhead on that. Since the panel is pretty much in agreement that safety is a primary consideration, the first advantage that I see is that of safety. The polymer or gelled electrolyte lithium-ion battery should be intrinsically safer than something that comes in a hard metal package, where you can develop significant internal pressures leading to explosions. It is very difficult to see how you get an explosion in a bag.

The second thing that I think is extremely important is the fact that consumer electronics is demanding flat packages. They want thin cellular phones that you can put in your pocket. Laptop computers are constrained to have a footprint about like that (indicates with hands a size about that of a letter-size sheet of paper) because of the keyboard and the screen. And so the only way that you can shrink the size and weight of a laptop computer is to decrease the thickness. 'Thin is in' as far as new power sources are concerned. The big applications — laptop computers and cellular phones — are looking for flat packages. It is very difficult with a liquid–electrolyte system to go to a large, thin, flat package. And you simply cannot do a cylindrical cell smaller than an AAA, because the energy density goes down considerably for the smaller sizes.

There is also the potential with polymer electrolyte lithium-ion batteries to go to lower manufacturing costs, and I think that is why, for example, Bellcore is being quite successful in selling licenses to their technology right now — their licenses see the possibility of lower manufacturing costs.

The true polymer battery has high high-temperature stability, as compared with the liquid system. But the high-temperature stability of the gelled-electrolyte system should be no better than that of the liquid system because they have the same chemicals in the electrolyte. Another disadvantage is that I do not believe that anyone has completely solved the problem of packaging of flexible lithium-ion polymer batteries. Power density remains a question. Bellcore has recently given out data which indicate that they have sufficient power density to operate the GSM digital phone. It remains to be seen whether there is an issue there or not.

I think energy storage was mentioned at the end of the question. I do not think that polymer electrolyte lithium-ion batteries are suitable for energy storage applications — and here we are talking about bulk energy storage like utility load.
leveling — because cost is a driving issue. Lithium-ion batteries in general, and polymer electrolyte batteries in particular, are probably too expensive for that application. There is some question also as to whether they can float indefinitely, as may be required in some power storage applications, but I will just leave that as an unanswered technical question. The polymer battery would, however, still have the advantage of safety and cost over the liquid system.

4.8. Question H. Karokawa, Sanyo Electric Company

Are the manganese oxide cathodes stable or not stable above 4 V?

4.9. Answer S. Megahed

I have a couple of slides on this. Based on some of the work Sam Levy had published, using Rayovac data, the lithiated nickel oxide is safe, the cobalt oxide is safer, and the manganese oxide is safest. In terms of thermal stability, as you see on the slide on TGA analysis (Fig. 5), the decomposition temperature of the nickel oxide is about 220 °C, the cobalt about 260 °C, and the manganese about 460 °C. So the manganese oxide is more thermally stable than the others. There is no oxygen evolution of the manganese material on overcharge, in contrast to the other oxides. On the next slide (Fig. 6), if you take the systems which are commercially available today — this is hard carbon and lithiated cobalt oxide, similar to Sony's — on overcharge, we consider what happens to the cell at the anode and cathode sides. At the anode side, these are the possible reactions that will occur, and on the cathode side, the Co₄⁺ is unstable, and you get oxygen evolution. The same thing happens to graphitic material with lithiated cobalt, no matter which of the various companies it is from. Also, oxygen evolution at the nickel electrode is the resulting byproduct of overcharge. If you compare that to the manganese, with graphite, the manganese is stable, and you get MnO₂ and there is no oxygen evolution. And it is the same thing whether you use LiMn₂O₄ spinel or other manganese compounds. So on overcharge of the lithiated manganese oxide, in the absence of oxygen evolution, we consider that the manganese material is safer than the other oxides.

The other thing that is of interest here, in terms of safety of the oxide, is the fact that when you discharge the oxides, you take 0.5 Li from the cobalt and the nickel, and most of you know what happens to the nickel if you go below 0.5 Li. The same thing happens, to a lesser extent, with the cobalt; whereas, with the manganese, you take all the lithium out. So the discharge product with manganese is safer than with the other oxides.

With the manganese material, you possibly can make cells that require no vents. In terms of environmental concerns, we believe that the manganese material is less of an environmental risk than the other two oxides. Overall, from what we know today, the manganese oxides are safer than the other two oxides.

4.10. Question J. Schoonman, Delft University of Technology

Dr Nishi of Sony presented a synthesis of LiCoO₂ particles with diameters between 15 and 20 μm. Conventional powders are in the range of 1–5 μm. In order to achieve homogenous intercalation smaller particle size distributions are advantageous. Is there a reason not to focus on submicron powders with a very small particle size distribution?

4.11. Answer K. Nakajima

Regarding the question about the particle size of the cathode material, we are using particles with an average diameter of 20 μm. Why we are using such large size particles is mainly because we can make a cathode mix paint easier with the large particles. When we get small size particles, we have larger surface area and we cannot neglect the surface effect in the mix rheology. In general, the solid with a diameter of less than about 20 μm is in the range of so-called powder and in this region, surface energy is influential in the paint rheology. We choose an easy rheology instead of inter-
calculation efficiency since we have an alternative solution for this. So the main reason is to facilitate the handling process.

Concerning the future of lithium-ion rechargeable batteries, Dr Gibbard already sufficiently described it. What Sony thinks is almost the same. Sony is the pioneer of the lithium-ion battery and since we are profoundly related to this field, I would like to make some comments on it from our viewpoint. Fig. 7 is the growth curve of energy density of lithium-ion battery with hard carbon system in which the cathode material used is only LiCoO$_2$. In the near future we will be able to reach 400 Wh l$^{-1}$ with several promising materials such as LiNiO$_2$ as the cathode material and higher capacity anode candidates such as hard carbon and also graphite. In addition, Fuji Film Celltech recently announced that they are going to produce high performance cells using tin oxide.

We should not forget the other component technologies such as the electrolyte, the separator, the binder, the current collector and the case, which will be supporting the lithium-ion future technology.

Also, the solid polymer electrolyte definitely adds value to the reliability in the electrolytes area. The polymer electrolyte with plasticizer is now one step from a practical liquid electrolyte system.

5. Future electric-vehicle batteries with lithium anodes
--- Dr Atanasoski

5.1. B. Owens

Two types of lithium batteries are being developed for the electric-vehicle (EV) battery market, metallic lithium anodes and Li$^+$-intercalation anodes. We will first consider EV batteries based on the use of metallic lithium anodes; this topic will be introduced by Dr Atanasoski.

5.2. R. Atanasoski

As far as presenting an overview of the progress in the USABC programs, there are more qualified people in the audience who may address this question. Hence, I will restrict myself to the development within the 3M program, which is based on the lithium polymer battery system. As you know, 3M has been working on the development of this system together with Hydro-Quebec (which provided the basic technology) and with Argonne National Laboratories. Let me start by addressing Dr Ishikawa's question concerning the future for the lithium battery technology as far as EV application goes. Our answer is positive; we do believe that the lithium polymer battery has a future in this application. Let us consider the key elements of the technology upon which we are basing our optimism, beginning with the cathode.

In the area of cathode materials both programs in principle should benefit equally from the development of new cathode materials. A system with metallic lithium might have a small advantage over the Li-ion system and this advantage consists of the fact that the cathode material for lithium metal systems does not have to be lithiated. Hence, there is a larger window of opportunity as far as the choice of cathode materials.

The second advantage for the lithium polymer battery is the possibility to substantially increase the energy density. Here we have two other battery elements to work with, the thickness of the polymeric separator and the thickness of lithium metal itself. Polymeric films can be coated very thin (and coating thin is one of the basic competencies at 3M) and the excess of lithium metal can be reduced to a minimum resulting in substantial increase in the volumetric energy density. The total thickness of the cell is less than 100 μm.

The most controversial issue as far as the use of metallic lithium in the battery is the interface between the metal and the electrolyte. The good news coming from this Conference is, as somebody put it, the renaissance of metallic lithium in battery research and development. In that regard, positive results concerning the lithium-electrolyte interface were presented in both Professor Matsuda's and Professor Takehara's Symposiums. An interesting observation from the present Conference is that almost all of the fundamental work on the lithium interface is being carried out in Japan, while the most serious development work is in the USA.

The properties of the lithium-electrolyte interface are usually associated with the safety of metallic lithium systems. In that regard the lithium polymer battery system has an advantage since, unlike in gel, plasticized or liquid electrolyte-conventional separator designs, we are using dry polymer and therefore, no liquid gets in contact with the lithium.

As of present, the lithium polymer battery technology is not suitable for the consumer market since the operational temperature of the polymer is slightly above ambient. However, when it comes to EV application, this is easily an advantage. The electric car drains large currents which as a consequence require a cooling system for batteries running at ambient temperature.

At the previous IMLB, Dr Gauthier presented test results obtained on 10 Wh cells. I can inform you that many of these types of cell have been produced and successfully tested for many hundreds of cycles during Phase I of our program.
Currently, we are six months into Phase II, the final goal of which is to produce and successfully test 2 kWh modules.

5.3. Question T. Tanaka, Cryspi

What is the progress on the research and development programs for lithium batteries as funded by the USABC?

5.4. Answer R. Moy, Ford

USABC programs were started in 1991 and the programs we have are development and engineering rather than research. We have concentrated in all our programs on safety verification, process development, materials verification, etc. In the first phase of USABC programs which are now coming to conclusion, the emphasis was on larger size hardware and feasibility demonstration and testing.

We are now preparing Phase II which is still an engineering program wherein the focus includes cost reduction. In addition to the current programs, USABC has also picked up the electrochemical energy storage responsibility for PNGV (Partnership for New Generation Vehicles) and hardware programs. We announced one contract with SAFT America and we have some other PNGV contracts that are under discussion.

In terms of lithium batteries, we initially started with a lithium molten salt battery with SAFT; two programs went to 3M/Hydro-Quebec and one to W.R. Grace and their association, and most recently, an Li-ion program with Duracell-Varta, a total of four programs.

5.5. Question R. Yazami, LEPMI–ENSEEG

What was the target of the first phase of the 3M program and what was achieved up to now in terms of energy density and cycle life?

5.6. Answer R. Moy, Ford

The technology milestones of all our programs are confidential within the USABC.

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Fig. 8. Safety box for design analysis of new battery systems.

6. Future electric-vehicle batteries with lithium ion anodes — Dr Broussely

6.1. B. Owens

The next topic, EV batteries based on the use of Li⁺-ion anodes will be introduced by Dr Broussely.

6.2. M. Broussely

The future of lithium batteries for EV application, which can be a huge market, will depend on some important properties such as specific energy and power, reliability, safety and cost. In the presentation that I gave at the beginning of this symposium, you may remember that the required energy and power were demonstrated on full-size prototype batteries. The two other main challenges are safety and low cost.

The cost of such a large battery is mainly driven by materials cost. Low cost means low purchasing price for the customer, but also the actual low cost of the service delivered by the battery (i.e., reliability, cycle life, energy) must be low. Trying to anticipate the future bottom cost for these materials, one can compare the relative cost of the different components. For example for an LiNiO₂/graphite battery, three components are very important: electrolyte, separator and positive material. They each represent roughly about 25 to 30% of the total material cost of the cell stack. More effort must be put on these components, however, the energy must not be reduced to maintain a good cost per Wh.

As an example, the use of a low cost manganese lithiated oxide like spinel LiMn₂O₄ is very attractive (two to three times lower cost than LiNiO₂, itself which is three to four times less than LiCoO₂). However, the concurrent decrease in energy density for the LiMn₂O₄ results in a higher cost per kWh than that for LiNiO₂. Indeed, as the energy of the battery is lowered, we need a larger and more expensive battery to achieve the same service. Safety is a very important subject, and the use of highly energetic materials (oxidant and reducer), may result during abuse conditions in exothermic chemical reactions. The mandatory use of non-aqueous media deprives the battery design of the very interesting properties of heat dissipation and chemical stability found in water. Each component of the battery may or may not react with any other one, and it is then difficult and too simplistic to say 'safe', or 'unsafe' system, based on one item taken separately from the other parts of the battery.

The safety, or condition of thermal runaway, is also closely related to the rate of reactions, which are themselves dependent on the cell technology. As an example, the use of a polymer electrolyte is generally considered as beneficial for safety. However, using liquid electrolyte containing gelled polymers, is not so different from a microporous polypropylene thin membrane filled with liquid electrolyte, in cells which have the same power capability. The nature of the polymer matrix, which may participate in reactions, may have
a detrimental influence on the overall chemical reactions. If you make a small, thin, flat cell, then the heat transfer is so good that there will be no safety issue, whatever the type of electrolyte, liquid or not. But when the size of the cell, energy and power density increase, as required by EV application, then you may face the same problems.

This example was just taken to illustrate that a lot of parameters that must be taken into account in order to design a safe lithium battery. It is clear that this is a top priority when designing an EV battery.

6.3. Question E. Yagasaki, Kansai Electric Power Co.

(i) How large can lithium batteries be? The EV application is in sight now, but will it be possible to use lithium batteries for load-leveling? (ii) What is important in controlling a large number of batteries? To power an EV, we need about 100 cells of Li ion (a couple of hundred for other batteries). What do we have to take care of to control them? (iii) I would like to hear comments on Nissan’s announcement of their selling an EV with Sony’s Li-ion battery next spring.

6.4. Answer M. Brousseley

As far as the battery size, there is no theoretical limit. There is a large R&D program in Japan devoted to load leveling, and the battery might be about the same size of an EV battery. Perhaps Dr Ishikawa would like to comment on that?

6.5. Answer R. Ishikawa

The size of the battery is not yet decided. It depends on the assembly technology and the cost. Presently, we are challenging the technology and later will address the cost.

6.6. B. Owens

The third question from Mr Yagasaki was about Nissan’s announcement of an EV with Sony’s Li-ion.

6.7. Answer K. Nakajima

Recently, Sony announced that concerning the EV business, we are on the level of R&D. Entering into the EV business requires a big investment, so our top management has not yet decided what to do. For Nissan’s announcement of a lease business starting next Spring, we can supply an adequate number of cells from the engineering experimental line.

6.8. Question C.-Y. Yao, Industrial Technical Research Institute/Materials Research Laboratories

(i) For safety reasons, all large-scale lithium batteries are designed by connecting several small units. But more individual unit cells will require more control circuits, and there-fore will not lower the reliability of the large scale batteries? (ii) The performance of the Li-ion battery has improved during the past three years. However, carbon materials play an important role for these progress. New advanced carbon materials were developed with specific capacities larger than 600 mAh g⁻¹. My question is ‘Do we need new high capacity and high voltage cathode materials in the future since cathodes limit the performances?’

6.9. Answer M. Brousseley

One of the questions was about the size of unit cell. It seems that a proper size for an EV, taking into account the required voltage (200 to 350 V), would be about 50 to 100 Ah. Many unit cells have to be connected in series, and this is an advantage of the lithium-ion battery that has a high cell voltage. Reliability should decrease with the number of cells. With Li ion, each individual cell voltage must be monitored to avoid overcharge or overdischarge, and the control circuitry has to be designed in order that a failure would not impact the safety.

6.10. B. Owens

Another question of Mr Yao had to do with the cathodes of Li-ion batteries. ‘Do you need high capacity cathode materials, which may become a limiting component, to improve battery characteristics?’

6.11. Answer M. Brousseley

I would say yes, the energy density of the positive material has a large influence on the battery characteristics, as I stated during the first session of the Conference, and also on the cost. I would like to make a short comment about the voltage. To insure a good stability, it is not desirable to have a very high voltage such as more than 4.2 V. Electrolytes are too sensitive to oxidation to give a good shelf life. However, for the EV, the voltage should stay high enough to limit the number of cells in series. It is different for a portable application, where a single cell will be used in the future in most of the equipment. At the present time, 3 V is mandatory. Fifteen years ago, it was said that 1.5 V would be enough voltage in the near future with new electronic components. We may still have to wait another 15 years. On the other hand, if we want to get enough energy with a low voltage cathode, the specific capacity must be very high; more lithium must be exchanged per mole. Then problems of reversibility will arise because the higher the number of lithium atoms exchanged in the cathode material, the larger the volume (and crystal structure) changes during cycling. Eventually, a 3.5–4 V voltage range seems a good compromise.


What is the most important issue in order to achieve the Li-ion cell module for the EV, other than the cost? Is it the
improvement of the conductivity of the electrolyte? Is a cathode material with a high voltage such as 4 V necessary for the Li-ion cell?

6.13. Answer M. Broussely

On the first point, the answer is safety. With respect to the electrolyte, we have presently achieved prototypes with attractive specific power levels that meet the requirements. But it is clear that in lithium cells, the main rate-limiting factor is mass transfer in the electrolyte. That is to say, it is not directly the conductivity, but is transport properties such as diffusion coefficients of ions, especially at high concentrations. To overcome this problem, one must make thin electrodes of high surface area and use thin separators. If a stable electrolyte, with properties similar to water was found, then we would be able to increase electrode thickness, which means energy density, cost and safety. So the answer is yes, a better electrolyte would be beneficial, but the improvement must be very large compared with presently known components.

7. Future high performance batteries after lithium and lithium-ion – Professor J. Besenhard

7.1. J. Besenhard

I feel that I have got the most difficult topic in this panel discussion. Of course, I do not know either what the future holds and if I did, I probably would not tell you. For the near future we still have to do a lot to improve Li-ion batteries but once we have done that, what could be next? Some fancy alternatives to batteries for instance, fly wheels, heat reservoirs and so on but I would not really like to talk about these. We are electrochemists and we should keep with the stuff we have some understanding on.

When we look at the periodic table, there are not many possibilities to replace lithium by other promising anode materials may be with the exception of some main group two elements such as magnesium or even beryllium. There are electrolytes which do allow deposition of metallic magnesium reversibly. It is also possible to insert magnesium ions into oxide host matrices such as molybdenum trioxide. However, there is one serious drawback – electrolytes which can be used for plating magnesium are not useful for inserting Mg$^{2+}$ ions into oxide cathodes because the electrolytes for plating magnesium are containing alkyl groups and are very, very tough to oxidation. Nevertheless, electrochemists are used to fighting against thermodynamics, so may be we will find some filtering process allowing the operation of a magnesium electrode in an organic electrolyte system.

A second point I would like to make is that the operating principle of ion-transfer cells (and the lithium-ion cell is just one example of ion-transfer cells) is, of course, a very fascinating one. But these cells will never have very high energy density because they have to carry a lot of matrix material. In the negative side, for instance, carbon or tin oxide, alloys, etc., and also the positive materials we have so far are far from being high energy density.

If we could move to more reactive elements, may be chlorine, bromine or oxygen in combination with lithium or magnesium, we could, of course, have a much, much higher energy density. But it will not be possible to pack these elements in ordinary small and closed battery configurations. There are, however, big fuel batteries, you all know about the zinc–bromine flow battery, and maybe we could design similar things having a reservoir of some negative electrode material and a second reservoir of the positive electrode material and a pumping system.

There is one more thing which is not directly related with batteries but I would like to draw your attention to: d.c.–d.c. converters. These are now available at least for small size applications and they convert d.c. from low voltage to high voltage. You can use batteries with the worst possible discharge characteristics and a d.c.–d.c. converter with about 90% efficiency will make a nice, flat, discharge curve. Maybe in the future we can operate an EV with a 3.3 V battery, everything in parallel, avoiding all the problems with series-connection and a d.c.–d.c. converter will boost the voltage to 300 V which the engine would like to see.

This was a lot of wishful things and I hope there are lots of bright ideas and visions in the audience because I did not have too many of them.

7.2. Question T. Osaka

Does anyone have any comments on this topic?

7.3. Answer A. Ohta

It seems to me the fuel cell (PEM) is one of the candidates for the next future battery.

7.4. Answer E. Peled, Tel Aviv University

Following up on that, the fuel cell can go to about 300 Wh kg$^{-1}$; if we find some good devices to store oxygen and hydrogen for a large system they can go up, in some projections, to 500 Wh kg$^{-1}$ in the near future.

7.5. Question M. Kuroki, Asahi Chemical Co.

For the ZEV (zero emission vehicle), the ‘flywheel’ is sometimes mentioned. Is it a possible alternative or just a joke?

7.6. Answer J. Besenhard

Well, I am certainly not an expert on ‘flywheels’ but I have seen reports about this as early as in the 1970s. In fact one can store lots of energy in a flywheel but obviously there are
problems in the case of an accident. To avoid a runaway of the heavy flywheel, it should be made up of materials that pulverize in an accident. There may be some more problems with the compensation of the rotary momentum of flywheels.

7.7. J. Schoonman, Delft University of Technology

One small comment regards beryllium. I would not like to work with beryllium in batteries from a chemical point of view because that is a very toxic material.

7.8. Question J. Schoonman, Delft University of Technology

Would it be possible to envision a proton-conducting membrane and a battery system working on proton conduction from an anode to a cathode, making use, e.g. of composite materials polymer organic electrode/electrolyte. During this Conference there was one paper on DMcT + PAN (2,5-dimercapto-1,3,4-thiadiazole and polyaniline) composite cathodes and there was also a question from the audience about what happens to the protons during the redox process.

7.9. Answer J. Besenhard

I am sure that this can be done but, of course, at fairly low cell voltage.

7.10. Answer E. Peled, Tel Aviv University

There is a small start-up company in Israel using a proton membrane and two insertion compounds such as MnO₂ that can reversibly insert hydrogen. I do not know the degree of insertion, maybe 0.8 or 0.5. If somebody is interested, I can find the address of this company and give it to them.

7.11. E. Peled, Tel Aviv University

Regarding magnesium or calcium batteries, the problem may be that it is very difficult to make a thin solid electrolyte film on top of magnesium that will conduct magnesium. Most films that are expected to grow on magnesium would conduct anions and then you have the problem of deposition and dissolution of magnesium.

7.12. J. Besenhard

I fully agree, of course. It is an almost unique property of the lithium cation and of the proton to be able to penetrate easily through a solid electrolyte interface. A cation with two positive charges will hardly be able to do that at a reasonable current density.

7.13. R. Yazami, LEPMI–ENSEEG

I think everybody in the audience agrees that there has been much progress these last five years concerning the electrochemistry of carbon. I think there are two communities interested in the electrochemistry of carbon. One is the Li-ion battery and the second is supercapacitor. I think some people can join in between. So I think one idea is to put these people together and have some brainstorming about material designs in the future. What will be good carbon materials that could make the bridge between Li-ion and supercapacitor?

7.14. B. Owens

As supercapacitor performance improves further, it is increasing in power and specific energy and, as you say, approaching that of high energy batteries. Some supercapacitor designs involve faradaic processes at the electrodes so it becomes somewhat academic as to whether the device is a battery or a capacitor.

7.15. S. Levy, SCL Battery Consulting

The future might involve a hybrid system containing a supercapacitor and a battery in combination to cover the high energy and high power requirements that you cannot get with each individually.

8. Safety problems of large scale lithium batteries – Dr Megahed

8.1. B. Owens

The final topic, to be introduced by Dr Megahed, is 'safety'. But first I am going to read the two written questions that were turned in.

8.2. Question K. Tatsumi, Osaka National Research Institute

For high energy density batteries, a high voltage cell is very attractive. However, the safety of a cell decreases with the increase in cell voltage. So the question is, how much voltage is enough for lithium batteries for commercial use?

8.3. Question M. Armand, University of Montreal

Which safety issues in the lithium-ion battery are specific to the negative electrode and which are specific to the positive electrode?

8.4. B. Owens

Dr Megahed, please address these questions as a part of your remarks.

8.5. S. Megahed

Thank you, Dr Owens. Dr Besenhard said that his subject was probably the most difficult; mine is probably the most
controversial. I do not profess to be an expert on the safety of lithium batteries, but I think as we go through the material in the literature, we will see some trends. The major question on safety is this: is there really a truly safe battery anywhere? Does anyone have a battery, small or large, which passes all of the safety tests — UL, abuse and use conditions, and so on? This is a very difficult question to answer.

When you talk about safety, you like to start with things that are known, and to take the least risk to design a safe battery. When you consider a safe battery, you have to look at the selection of safe components. The safe components — there are many — will be those cathodes, anodes, separators, electrolyte systems, etc., that are safer than others. So you will be better off selecting the safer components, and I mentioned, on the cathode side, that the manganese material is 'safer' than other oxides. On the electrolyte side, for example, a polymer or a plasticized polymer could be 'safer' than a liquid electrolyte. With respect to the anode, when lithium ion was invented, number one of the advantages of the system was its safety relative to lithium metal systems. However, we found later on that lithium ion can be unsafe if it is not designed properly. Are lithium-ion batteries with nonmetallic lithium safer than those with lithium metal? This is really the question that has to be answered. The indications are, yes, it may be that they are; this is why we selected the lithium ion and lithium-ion polymer electrolyte batteries as future candidates for safer batteries.

Even though you may have the safest compounds and components that are going to work in a battery, you have to design the battery in a safe manner. Are your batteries cathode limited or anode limited? What kind of configuration will these batteries take? For example, in lithium metal batteries, we know that coin cells have been successful and safe for over 30 years, and small cylindrical cells with metallic lithium anodes have been commercial markets in the AA and 2/3A size. If you go beyond that size, then the configuration will prohibit you from having a safe design. There are other cases where you can make a bigger battery that is safe. Again, you have to design the battery with safety in mind.

In the last few years, electronics have been added to enhance safety. We can combine chemistry and electronics to make the battery safe. And we all know that there are multi-cell batteries designed with electronic safeguards that will make the batteries safer.

Thermal management, especially in large batteries, is a major issue. We have to deal with this issue for both cylindrical and prismatic cell designs, for all batteries, including lithium ion. You have to be aware of all the safety issues, under use and abuse conditions, taking into account the consumer protection and other relevant regulations.

There are many, many other factors involved in safety, and this is why it is a very complicated issue. In addition to safety and reliability, environmental considerations must be taken into account. I have developed what I call the 'safety box' (Fig. 8) inside which a successful battery design must lie. These are some of the considerations which you must concern yourself with in battery design. With metallic lithium batteries, over the years, the safety issues have been the formation of dendritic lithium growths or films in the presence of cell electrolyte, which is a surface-area phenomenon. As I look back over the development of lithium batteries during the past 30 years, it is a bit of a disappointment, because they have not overtaken some of the battery chemistries we thought they would. If you think back 30 years, when the lithium batteries which were called 'exotic' batteries first were described, you have to ask yourself the question, 'What went wrong?' Safety was the major issue with the lithium batteries. However, it is not a complete loss, because we know you can design primary cells and coin-cell configurations, and they are completely safe. You can design cylindrical cells in the 2/3A and AA size, and both of these are commercial successes, and you also can design primary and secondary cells with metallic lithium anodes that are safe.

Battery design, that is, multi-cell packs, is another issue, and I have talked about the electronic systems that can be added to enhance safety. For non-metallic lithium batteries, we have been talking all this week about liquid—electrolyte, plasticized—electrolyte and true polymer systems — which one of these is the safest? I really agree with Dr Broussee's comments that it is not the components in the cell, for example nickel and cobalt, that render it less safe, because you can take a manganese cathode system and make it unsafe. Similarly, you can take cobalt and make it safe. There are other issues beside the cathode material that must be taken into consideration to make the battery safe.

In the area of non-metallic lithium, cylindrical batteries, such as the 18650, which is the work-horse of the industry, have many safety features in each cell, but even it can be made to be unsafe. Large cells, such as the Sony EV 100 Ah cell or other prismatic cells up to 125 Ah, are made with safety as a primary consideration. When you consider the design of large, multi-cell batteries the issue of mass becomes important, as is the issue of connecting the cells in parallel and series. There are many issues, and we do not have time to consider them all, but let me say a little about just one area of my 'safety box', the area of battery management. In battery management for safety, you have to consider module monitoring, voltage, temperature, current, failure detection, impedance, short-circuit detection, safety features, charge and discharge controls, and many other factors.

The first lithium rechargeable batteries were made with metallic lithium and safety was a major problem. By changing the anode to carbon in 1991, dendritic growth was eliminated and replaced by structural transformation. The primary reason to develop plastic batteries such as that of Bellcore is to enhance the safety.

That concludes the formal part of my presentation. Regarding the two questions, I think the question regarding the cathode materials, cobalt, nickel and manganese, has already been answered. The question regarding the maximum voltage has also been answered. The highest usual voltage is about 4.3 V, and there are electrolytes which will go up to 5.0 V
per cell and that you can cycle safely, for example, LiPF$_6$ with EC–DEC or EC–DMC. There are other salts, the imide family, that are stable up to 5.0 V.

8.6. B. Owens

Thank you very much for your presentation, Dr Megahed.

9. Conclusions

9.1. T. Osaka

I have to close the panel discussion. Thank you very much for the valuable discussions and the presentation of the panel members. Also, thanks to the audience for your patience. I think the cost, reliability and safety are the most important issues in the next coming lithium batteries. We believe that the next new phase of the lithium battery is growing now. Thank you very much for your cooperation.

10. In Memory of Dr Sid Megahed

We were all saddened by the unexpected death of our scientific colleague and good friend Dr Sid A. Megahed. He passed away at his home in Madison, WI, USA, 3 August 1996, just six weeks following this Conference. Many of us in the battery community have known Sid well during the past 25 years and have enjoyed the technical and social interactions with him. Sid’s participation on the Battery Panel at IMLB-8 Conference was his most recent public presentation. We shall remember him as a fine scientist, a teacher and an innovator in this field of battery technology. We shall miss him.

Chairmen
B.B. Owens
University of Minnesota, USA
T. Osaka
Waseda University, Japan