Li or Na

Cord-Henrich Dustmann

Battery Consult sagl, 6839 Sagno, Switzerland)

Abstract
An overview on the battery technology of lithium and sodium batteries is compiled. Lithium based batteries power our mobile phones, lap tops and power tools. But does this mean that this is also the best technology for electric vehicles? Facts of physics, chemistry and material show a more differentiated picture. This is compared with the complex requirements on the electric vehicle battery pack. Large batteries are price sensitive. Sodium batteries promise larger potential for lower cost for those applications where the operating temperature of ca. 300°C is not prohibitive.

Introduction
For future mobility and for the integration of an increasing contribution of renewable energies into the electricity supply grid the availability of electric energy storage at reasonable cost is essential. The main candidates that are expected to play this part are lithium batteries and sodium batteries. They both have a very different development background:
The Li-battery project was started in a systematic way by Sony in Japan 1987 for the use in video cameras of which the market introduction started 1991 ($_1$). For such small units a sodium system could not be considered because of the elevated operating temperate required for the beta alumina electrolyte.
The first sodium battery was the NaS system invented already 1967 by the Ford Motor Company in connection with the discovery of the Na-Ion conductivity of beta alumina ($_2$). In the mid seventies the other sodium battery system $NaNiCl_2$, also known as ZEBRA, was invented by C.S.I.R. in Pretoria, South Africa ($_3$). In these days the Na battery technology was regarded as interesting enough to invest R&D money but there was no real market pull from a product which needs this battery for its market introduction. Electric vehicles were not regarded as a necessity.
Such basic differences of the environment during the initial phase of a technology may have a long lasting influence on its further evolution, but for an evaluation of this technology only its potential based on facts should count. Therefore it is the intention of this report to collect and analyze the basic data of physics, chemistry and materials on the background of the future demand for large battery packs for mobile and stationary applications.

Target Battery Parameters
For the considerations of this paper a reasonable and typical electric vehicle specialized for urban mobility demands is used with the following parameters as a reference:

Table 1 Reference Vehicle Parameters	
Vehicle Weight without battery	500 kg
Payload 2 persons	150 kg
Battery weight 20 kWh	150 kg
Battery cycle life (80% SOC)	1000 cycles
Acceleration 0 to 100 km/h	10 s
Electric energy consumption	0,12 kWh/km per t
Electricity price average	0,15 €/kWh
Total efficiency (charger, battery, inverter, motor)	80%

Using these parameters and the condition that the cost for the battery plus electricity is equal to the fuel cost for a thermal vehicle the battery price target is calculated. It is shown in figure 1 as a function of the fuel price and the fuel consumption of the vehicle as parameter. For the reference case of today's condition of a fuel price of 1,5 €/l and a low fuel consumption for such a car of 4,5l/100km a battery price of 413 €/kWh or 8260 € is calculated. In case of a higher fuel price or/and a higher fuel consumption a higher battery price would result from this model. Interest rates and other cost are not included. This selling price of 413 €/kWh would require a production cost target of ca. 200 €/kWh.

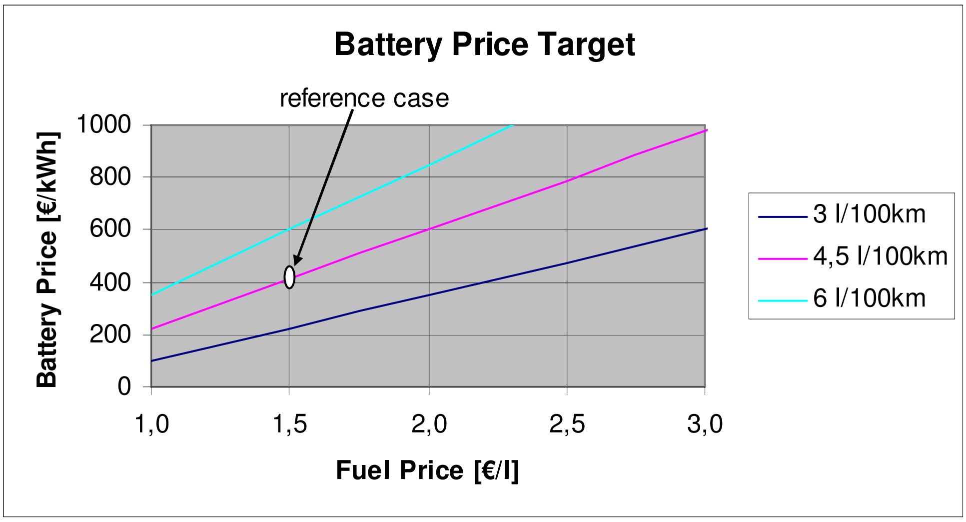

Fig.: 1 Battery Price Target vs Fuel Price

For the reference vehicle the parameters for the corresponding battery are shown in table 2 together with an indication to what degree these parameters are achieved today (green), can be reached with some R&D effort (yellow) or are difficult to be achieved and/or would need substantial R&D (red). The NaS battery is not included in this table because it is used only stationary; its safety concept does not work for mobile applications.

Table 2 Reference Battery	**unit**	**Required**	**$LiCoO_2$**	**$LiFePO_4$**	**$NaNiCl_2$**
Energy (133 Wh/kg)	kWh	20	20		
Peak Power	kW	40	green	green	yellow
Weight	kg	150	yellow	yellow	yellow
Open Circuit Voltage	V	250 – 350	green	green	green
Battery cycle life (80% SOC), statistically proven		> 1000	yellow	yellow	yellow
Calendar Life	Years	> 10	yellow	yellow	green
Production cost	€/kWh	200	red	yellow	green
Safety		crash	red	yellow	green
Ambient Temperature		-30 - 65	yellow	yellow	green
Dust, Water, Vibration, Shock		Car standards	Design task		
Material Availability & cost		No restriction	yellow	green	green
Recycling	%	100	yellow	yellow	green

Also compare (6)

Chemical Options

For a rechargeable battery with high specific energy the following requirements are to be combined:

1. a reversible and stable chemical reaction for charge and discharge
2. a high and symmetric internal energy difference between charge and discharge state
3. light materials for low weight and high specific energy
4. an electrolyte must be available to control the reaction
5. no corrosion for the materials in contact for > 10 years
6. no hazardous materials under operation and abuse conditions
7. no explosion and no fire under abuse or accident conditions

The requirements 1 to 3 bring us to oxidation/reduction reactions between elements up left of the periodic table with those elements up right not considering of cause the inert gases. Fig. 2 shows the most favorable combinations:

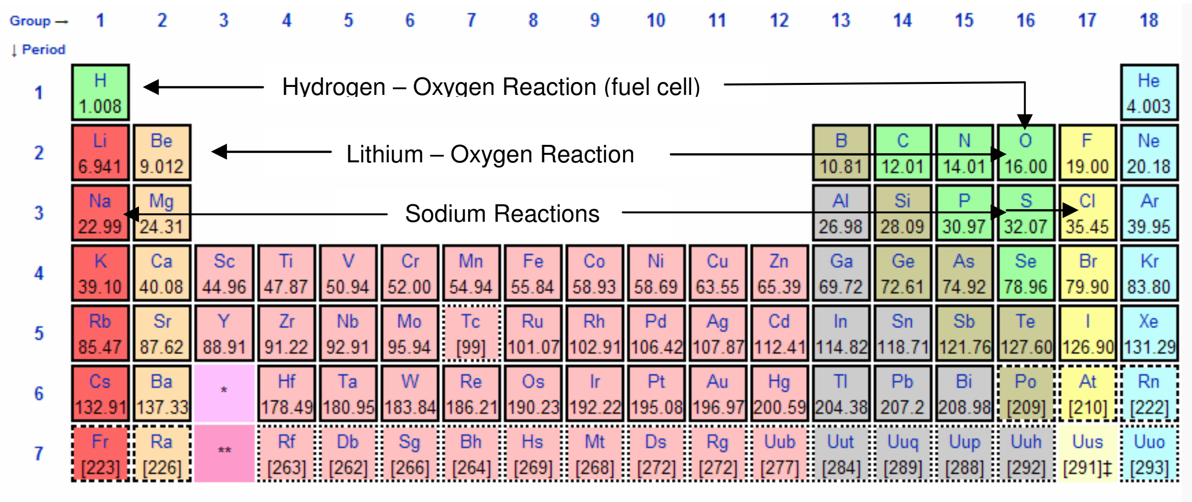

Fig.: 2 Periodic Table with Reactions indicated

The most attractive reactions are the following:

<u>Hydrogen – Oxygen Reaction</u>

$$2 H_2 + O_2 \rightarrow 2 H_2O$$

This reaction is used in fuel cells to convert the energy of Hydrogen and Oxygen into electricity. The reverse reaction is the electrolysis and requires different equipment at least up to now and the efficiency of the cycle is very low at about 50%.

<u>Lithium – Oxygen Reactions</u>

In principle the lithium battery reaction runs between lithium and oxygen but for safety reasons the lithium is intercalated in graphite on the anode side and on the cathode side the oxygen is part of a metal-oxide which forms an alloy with lithium. In this way the uncontrollable direct reaction between lithium metal and an oxide is avoided. Such a reaction would have a specific energy of 8665 Wh/kg which is much more than TNT with 1375 Wh/kg. Therefore the main issue to be solved for a lithium battery system is the safe control of the reaction under all operating and abuse conditions. The solutions are complex chemical systems out of which two are selected as relevant for EV applications:

$$Li_xC_6 + Li_{i-x}CoO_2 \leftrightarrow LiCoO_2 + C_6$$

$$Li_xC_6 + Li_{i-x}FePO_2 \leftrightarrow LiFePO_4 + C_6$$

The $LiCoO_2$ system was first developed by Sony ($_1$) and is now the most widely used chemistry of Li-Ion batteries used for consumer products. For these small units of one or a few cells the control is part of the electronic system whereas for large battery units a separate control per cell is required and thus the reliability standard has to be very high. The theoretical specific energy is 647 Wh/kg if the anode carbon is included into the calculation. The values in table 3 are calculated using the formula

$$E = U * n * F / m$$

with U – potential, n – number of electrons exchanged, F=96485 As/g Faraday constant, m – molecular mass

The more recent system $LiFePO_4$ is favoured because of its better safety record and high power capability in spite of its lower specific energy of 375 Wh/kg. The objective for the further development is to achieve stable reaction partners with a minimum of passive components and low cost materials. For the electrolyte lithium salts such as $LiPF_6$ are used solved in organic solvents like ethylene carbonate.

Sodium Reactions

Sodium batteries have been developed using sulphur first and than chlorine on the cathode side following the reactions:

$$\mathbf{2\,Na + 5\,S \leftrightarrow Na_2S_5}$$

$$\mathbf{2\,Na + NiCl_2 \leftrightarrow 2\,NaCl + Ni}$$

The NaS system is in production for stationary applications ($_4$) with a calendar life time target of 15 years. This requires the suppression of any corrosion to a minimum so that the deeper discharge to Na_2S_3 is avoided. This limited discharge to Na_2S_5 results in a theoretical specific energy of 542 Wh/kg. The NaS batteries are optimized for high energy content and 7 hours charge and discharge so that the power to energy ratio is only 0, 14 h^{-1}. The NaS system is no longer considered for electric vehicles.

The $NaNiCl_2$ system is in production mainly for EV applications ($_5$). The theoretical specific energy is 790 Wh/kg (table 3) and most requirements for an EV battery are already met (table 2). The main difference to Li systems is an operating temperature of around 300°C which is required for the conductivity of the beta alumina electrolyte. For this reason small batteries with a low volume to surface ratio are not feasible. But for large battery units the wide range of operating temperature (270°C to 350°C) has important advantages:

- Any ambient temperature very high or low does not matter due to the thermal enclosure
- 10% of the electric energy can be stored in addition as heat for cab heating without range reduction
- Battery temperature management (cooling or heating) is effective due to the large difference to ambient
- in the cold state the battery is switched off which is a safety advantage

The directly linked disadvantage is a thermal self-discharge if the battery is not used and kept warm.

For sodium batteries beta alumina is used as the electrolyte. This ceramic is produced in standard ceramic powder, forming and sintering processes. The advantage is a good stability but an increased operating temperature is needed. The $NaNiCl_2$ system uses $NaAlCl_4$ salt in the molten state as a secondary electrolyte which has important functions for the sodium ion conductivity in the cathode and the intrinsic safety by its capability to allow overcharge protection, a low resistive failure mode and the absorption of the sodium in case of mechanical damage.

The basic data of these systems are shown in table 3. The voltage of Li Systems is higher than Na because of the higher standard potential of lithium. But the anode material cost for sodium is much lower than for lithium, in specific for the $NaNiCl_2$ system where plain salt is used as raw material for production. The theoretical specific energy is an indication of the potential of a system. A ranking shows $LiCoO_2$ as number one if the anode carbon is not included into the calculation and $NaNiCl_2$ as number two. The development task in any case is to keep the passive material at a minimum. For lead acid as a mature technology the active material is 25% of the total (theoretical specific energy 160 Wh/kg, practical 40 Wh/kg) so that the same value is assumed for the new technologies as well. From this point of view the Li-ion systems are already very close to this value whereas the sodium system still has room for improvements. One of the reasons is the geometric shape of the cells. The abundance of the involved elements in the earth crust (fig.7) allows an indication about cost and availability of the elements used.

Table 3 Chemistry Data	**unit**	**$LiCoO_2$**	**$LiFePO_4$**	**Na_2S_5**	**$NaNiCl_2$**	**Comments**
Anode Material		Li	Li	Na	Na	
Anode Standard Potential	V	3,01	3,01	2,71	2,71	
Anode Mat. Spec. Energy	Wh/g	11,7		3,16		
Anode Material Cost	€/kg	35		0,53[1]	0,12[2]	[1]metal, [2]salt
Theoretical Specific Energy	Wh/kg	647	375	542	790	C included
		1122	543			C not included
Practical Specific Energy 25% of theoretical assumed	Wh/kg	162/280	94/136	136	198	C incl./not incl.
Open Circuit Voltage	V	4,1	3,2	2,08	2,58	
Mol Weight	g	169,9	229,7	206,3	175,6	C included
		97,9	157,8			C not included
Abundance Earth	ppm	Li 17	Fe 56000	Na 23600	Ni 84	
		Co 25	P 1050	S 350	Cl 145	

C = anode carbon

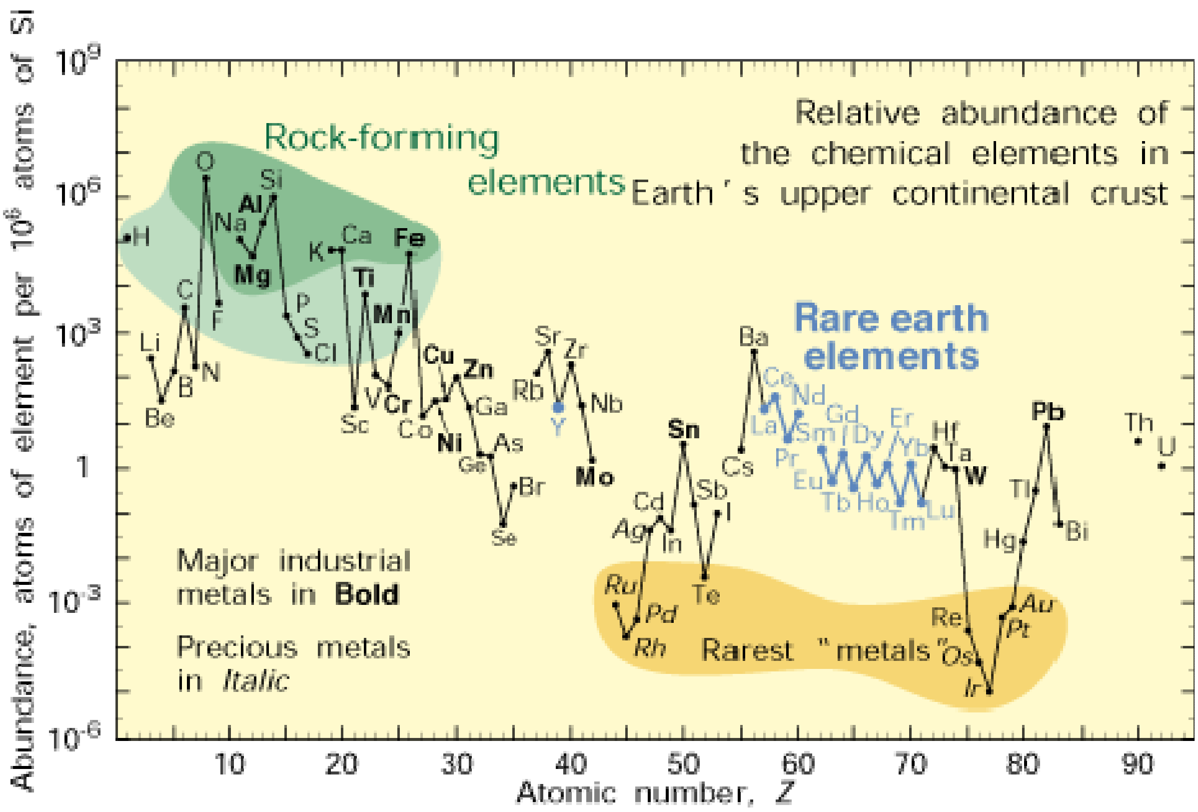

Fig. 3 Abundance of elements on Earth (7)

A ranking for the used elements shows that lithium and cobalt are at the low end followed by nickel. The lithium recourses are estimated to be 28,4 Mt lithium (equivalent to 150 Mt lithiumcarbonate) (8) and the demand for 500 million cars (25 million per year, 20 years) is 0,85 Mt (1,7 kg per car) which is to be added to the present consumption for other applications (16 kt/year) resulting in 0,32 Mt for the same period of 20 years. We can conclude from these numbers that there is enough lithium for the next decades and that recycling could lead to a stable situation long term. The next in the ranking is cobalt which will no longer be needed when $LiFePO_4$ is introduced and number 3 in the ranking is nickel which is recycled already and can be replaced by iron.

Battery Cycle Life

All battery technologies in discussion have demonstrated their ability to deliver ≥1000 80%SOC cycles. But statistical life data out of a production of relevant volume and for vehicle size packs in vehicle environment cannot be available. For this reason the fast introduction of a relevant number of electric vehicles is a big business risk. 100.000 batteries each with a production cost value of 4000€ represent a value of 400 mio€. For this reason accelerated tests are under way but the interpretation of the results is sometimes difficult.

Battery Calendar Life

The calendar life is related to corrosion for which accelerated testing is possible if the corrosion reaction follows the Arrhenius equation. For the $NaAlCl_4$ battery a calendar life test did run more than 10 years which demonstrates that there is no relevant corrosion for this technology. This has not yet achieved by lithium batteries.

Production cost

The production cost depends on the availability and market situation of the used materials, the production quantity and the maturity of the processes. For the $LiCoO_2$ the learning curve has been passed already and the result is 250€/kWh in an optimistic scenario developed by ANL in the year 2000 (9). This has to be increased to ca. 320 €/kWh assuming an inflation rate of 3%. For avoidance of any confusion about exchange rates I take 1$ = 1€.

For the $LiFeO_4$ system it is too early for an estimate but it is expected to be less expensive than $LiCoO_2$ so that it may meet the target of 200 €/kWh.

For $NaNiCl_2$ a cost study concluded in 2003 a production cost of 77 €/kWh (10). This has to be assumed to be increased by 30% for inflation rate and maybe another 30% for redundancy so that a production cost of 130 €/kWh is estimated. Further R&D is expected to reduce the amount of passive material and also will achieve higher specific power.

Safety

USABC and EUCAR have defined safety tests for EV batteries with the intention to understand the safety implications of a battery technology under worst case conditions and to avoid surprises. These tests are: drop impact (fig. 3), deformation, intrusion, turnover, fire, water immersion, over-charge, short circuit, reversal.

The tests for the lithium technologies are under way. Results are not presented in open literature. The $NaNiCl_2$ batteries passed these tests already in the early nineties and a comprehensive report is published by NREL (11).

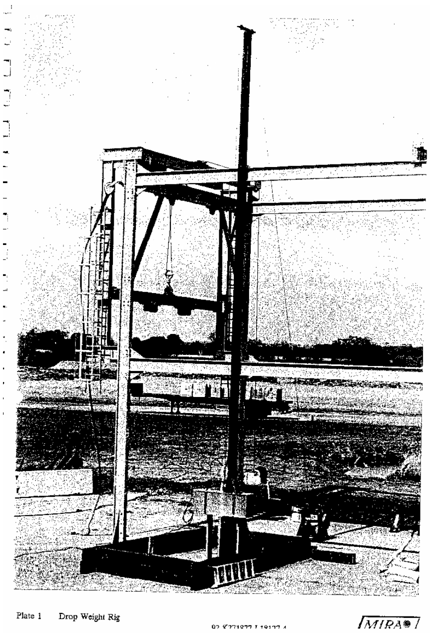

Fig. 4 Rig for drop impact test

Ambient Temperature

Charge and discharge reactions are chemical reactions for which the reactivity is temperature dependent following the Arrhenius law. For this reason the wide temperature range required for vehicle applications is a challenge so that every battery type will require a temperature management. In the case of the $NaNiCl_2$ battery this is naturally included.

Water, Dust, Vibration, Shock

These are conditions of the vehicle environment and are to be solved as a design task for every technology.

Material Availability and Recycling

The material availability is discussed on the previous page and fig. 3. It can be concluded that at least short term there is no material constrain for either technology if the market influence and local

concentrations as for lithium are disregarded. For the $NaNiCl_2$ system there is obviously no material constrain at all.
By law every battery has to be recycled in order to avoid dumping of hazardous material. The objective for recycling is at least to be cost neutral in the way that the process cost are covered by the value of reclaimed material. This is not yet possible for small Li-ion batteries. The market value of reclaimed material depends on its purity. In this respect new material sets the standard. The recycling process of $NaNiCl_2$ batteries is so simple that the market value of reclaimed nickel is higher already today.

Conclusions

With the recent market pull for electric vehicle batteries new technologies are entering the market and existing solutions receive a push if they have the potential to survive. It is shown from the facts presented that the more recent lithium technology is not necessarily better than the older $NaNiCl_2$ technology for which several issues have been solved and paid for already whereas these are under way for the new technologies now. For this reason I expect that also for Na batteries new suppliers may show up to compete with the present one. At the end of the day the market will decide and I expect that in future there will be

Li and Na

References

1. Sony History chapter 24.2 and 24.3, www.sony.net
2. Weber,N. Kummer, J.T. (1967) "Sodium Sulphur Secondary Batteries" Proceedings 21th Annual Power Sources Conference
3. Coetzer,J. Sudworth,J. "Earn your Stripes" Electric & Hybrid Vehicle Technology 2000, UK & Int. Press 2000, ISSN 1362-5217
4. www.ngk.co.jp/english/products/nas
5: www.mes-dea.ch = www.cebi.com
6. Salasoo,L. Kane,A. King,R. Richter,T. Kumar,A. Young,H. "Application of Energy Storage Batteries to Hybrid Locomotive and Mine Trucks" World Electric Vehicle Association, EVS-23, 2007
7. Abundance of the Chemical Elements, www.wikipedia.org
8. Information from Chemetall, www.chemetalllithium.com
9. Gaines,L. Cuenca.R, "Costs of Lithium-Ion Batteries for Vehicles" ANL Report ANL/ESD-42 (2000)
10. Galloway,R. Dustmann,C.-H. "ZEBRA Battery, Material cost, Availability and Recycling" World Electric Vehicle Association, EVS-20, Long Beach, California, 2003
11. Trickett,D. "Current Status of Health and Safety Issues of Sodium/Metal Chloride (Zebra) Batteries" National Renewable Energy Laboratory, November 1998, NREL/TP-460-25553