Fundamental considerations on energy density, power density and safety of batteries

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Outline

- **The trivial, but impossible requests to a battery**
- **The possibilities of the periodic table give us for construction of batteries with high energy densities**
- **Examples of practical and hypothetical batteries**
- **Differences between fuel cells, flow batteries and batteries – originating mainly from the operation modes of the electrochemical cells**
- **Safety aspects**
- **The demands imposed by the competitors**
- **Power density - relations to characters of electrolyte and electrodes (liquid, solid, porosity, structure) and of the electrode reactants (solid, liquid, gaseous) and consequences**

The trivial, but difficult requests to batteries

- A cell consist of two electrodes separated by an electrolyte

- A battery often comprise two or more cells stacked in series

- The requests to a car battery are something like:
  - Highest possible safety, close to zero risk is demanded
  - Lowest possible cost; as low as an oil tank in case of applications for the transport sector
  - Highest possible energy density; a 70 kg, < 50 L battery should provide a driving range for a car of > 600 km $\Rightarrow \sim$ 500 kWh = 1750 MJ $\sim$ 25 MJ/kg
  - Highest possible power density; a 70 kg battery should be able to deliver ca. 100 kW over extended time spans $\Rightarrow \sim$ 1.5 kW/kg

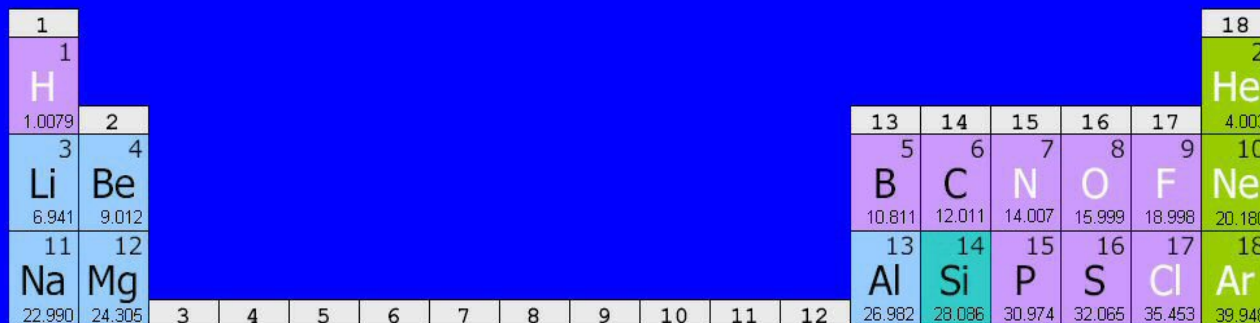
The periodic table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.0079																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.64	33 As 74.922	34 Se 78.960	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.904	54 Xe 131.293
55 Cs 132.905	56 Ba 137.327	57 La 138.905	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.084	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (267)	105 Db (268)	106 Sg (271)	107 Bh (272)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)							
				58 Ce 140.116	59 Pr 140.908	60 Nd 144.242	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.925	66 Dy 162.500	67 Ho 164.930	68 Er 167.259	69 Tm 168.934	70 Yb 173.054	71 Lu 174.967
				90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Apparently many possibilities but …….

By courtesy of Renie Birkedal

Periodic Table



Only the small part above, from element 1 (H with mass 1) to element 17? (Cl with mass 35.4) is worth studying with respect to gravimetric energy density for "big energy" purposes. Several of these cannot be used much in practice due various reasons. Be and F are too poisonous; He, Ne and Ar are inert. Other are generally having low reactivity (B, C, N, Si) and as they have high potential the R&D of providing sufficient electrode reaction rate = power density is a great challenge for battery researchers.

Theoretical energy density, full reaction with O_2 from air = ΔG^0 of oxide formation

Type	Valence/ mass	$-\Delta G^0/nF$ 25 °C, V	MJ/l	MJ/kg	B. or M. point °C
Liq. hydrogen	1	1.23	8.4	119	Bp:-253
Lithium	0.14	2.91	22	41	Mp: 181
Boron	0.28	2.06	136	55	Mp:2076
Carbon	0.33	1.02	75	33	Mp:3500
Silicon	0.14	2.22	18	7.6	Mp:1414
DME	-	ca. 1*	22^+	30^+	Bp: - 25
Gasoline	-	ca. 1*	33^+	47^+	Bp: 40 - 200

*A mixture of CO, H_2, CO_2, H_2O and the hydrocarbon will form. $^+$HHV

The fundamental demands and problems

- **High energy density**
- **High power density ⇒ high reactivity of electrode reactants**
- **Safety ⇒ high reactivity of electrode reactants**
- **Li: high energy density and reactivity, ionic compounds are formed ⇒ possibility of high power density and of low safety**
- **B impossible due to very strong co-valent bonds**
- **C also co-valent bonds – but suitable catalysts and increased temperature may help**

Li – $SOCl_2$, SO_3, H, C or HC examples

- **The Li- $SOCl_2$ battery has practical energy density of 400 Wh/L = 1.44 MJ/L – not a rechargeable cell. The cathode reaction is forming LiCl(s) and SO_2(l) and is too complicated to reverse – LiCl is not soluble in SO_2**

- **The Li- SO_3 (4.7 V cell voltage) is estimated to be about 3 times higher, but so far a functional battery has not yet been reported. No stable electrolyte found.**

- **A carbon cell, i.e. C – O_2 cell might be fine (Chris Graves and I have filed a patent application); high temperature above 600 C**

- **H_2 or HC – O_2 (reversible electrolyser/fuel cell) might be similar fine and with potential of lower temperature – in particular for H_2 – O_2 cells (Frank, Christos, Pia and I have filed a patent application)**

When is an electrochemical cell stack a battery and when a fuel cell/electrolyser?

- This is clearly dependent on the application and way of operation

- A hydrogen- oxygen cell is usually called a fuel cell, but if both H_2 and O_2 are stored in tanks and if the cell is fully reversible, this would be a battery, which e.g. could be used for peak-shaving of electricity production for the grid.

- Quite a few scientists and engineers regard a Zn – air battery as a fuel cell and it may be found described in fuel cell books

- Thus, differences between fuel cells, flow batteries and batteries – originating mainly from the operation modes of the electrochemical cells.

Safety aspects

- **High reaction rate of the components at increased temperature will often be a problem if all active materials are positioned in close contact in the battery**
- **Li-cell with propylene carbonate as electrolyte and CoO_2: A "Dream liner" may suddenly turn into a "Nightmare liner" if the temperature is raised to less than double (in Kelvin)**
- **In a rocking chair arrangement the supply of electrode reactant cannot be stopped**
- **In a flow type of battery like a DME – air battery (if we can make it to work) both the DME supply and the air supply may be switched of by safety valves automatically**
- **Similarly the air supply may in principle by switched off in a Li- air battery.**

More safety

- **Safety may be improved significantly if the electrode reactants are stored separately, i.e. only small amount in contact with the electrodes**

- **This is possible if the reactants are gaseous, liquid or in powder form, e.g. oxygen (air is naturally best as available without storage) for the positive electrode, and hydrogen, gaseous or liquid hydrocarbons, carbon powder**

- **In these cases it will be fairly easy to stop the supply of reactant in case of malfunction of the battery using valves and electronic surveillance of e.g. temperature.**

- **Flammable (organic) electrolytes are always problematic from a safety point of view**

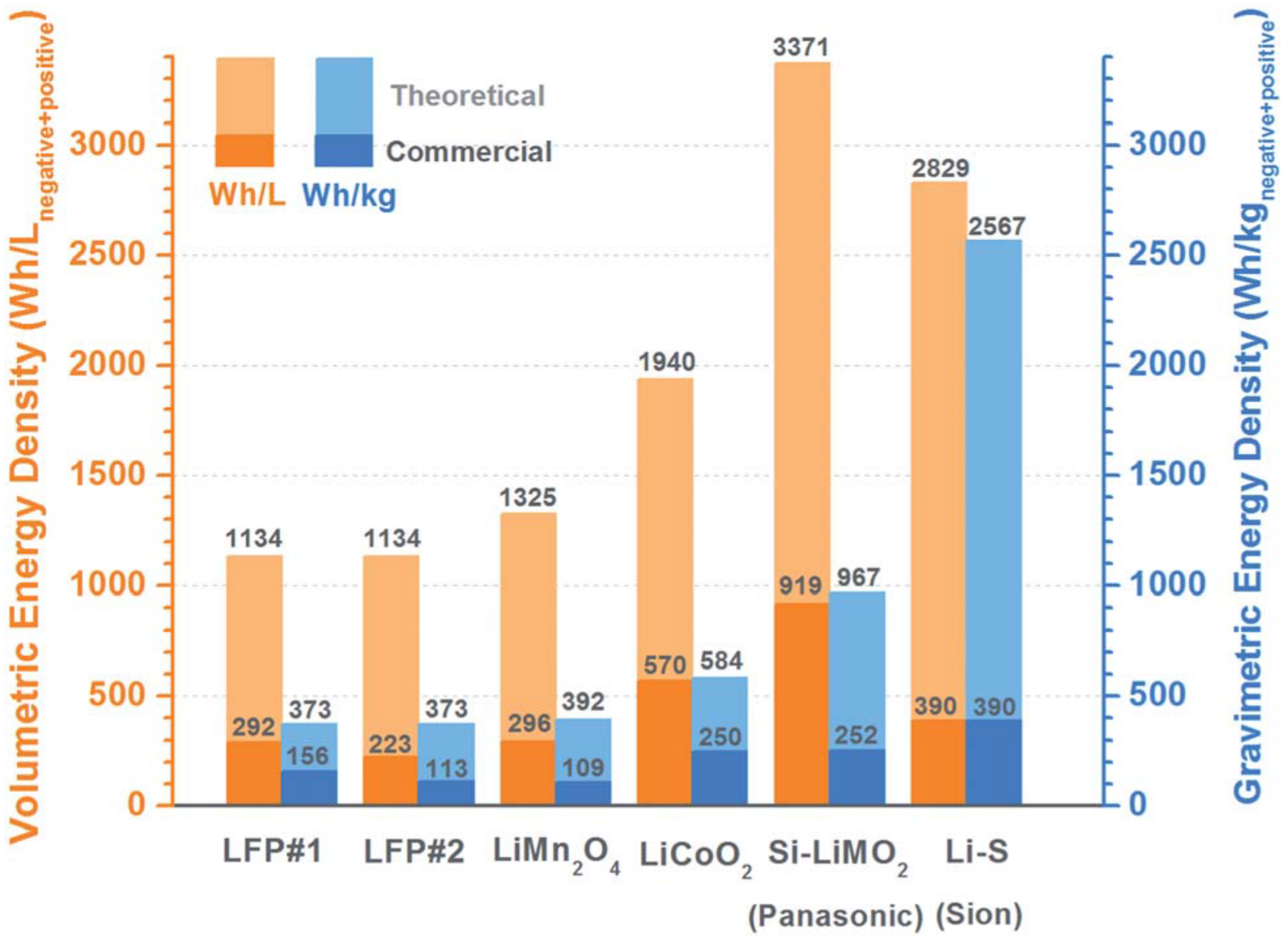
Power density requirements from the competitor

- Gasoline filling rate of 20 L/min equivalents <u>11 MW</u> of power and means it takes 2½ min to get 50 l = 1650 MJ on board, typical 600 km driving range.

- For comparison: Li-batteries usually requires 8 h to get recharged. For a 300 kg battery package (0.5 MJ/kg) this means a power of ca. 3.5 kW i.e. it takes 8 h to get 150 MJ on board.

- The ratio between their driving ranges is only ca. 5, because the battery-electric-engine has an efficiency of ca. 70 % - the gasoline engine has ca. 25 %.

Practical versus theoretical energy densities



Factor of 2 - 6

Gravimetric and volumetric energy of lithium batteries: theoretical vs. commercial single cells.
From:Yi-Chun Lu et al., Energy Environ. Sci., **6** (2013) 750

Practical energy density – Li-air perspective

When realized some day, 5 – 8 times lower than the theoretical power density may be expected because:

1. **Extra protection of the lithium against exposure to water and especially the combination of water and nitrogen. The latter posing a serious safety risk.**

2. **High overvoltage of the oxygen electrode**

Practical energy density – in case we can make a functional liquid methanol – air battery

- **If the cell stack is similar to a fuel cell stack, the energy density may come relative close to the theoretical energy density – say a factor of 1.5 - because the tank for the methanol has a low weight.**

- **Example: A 5 kg tank with 50 kg CH_3OH and a cell stack/battery of 45 kg (100 kW) would give a factor of only 2.**

- **With methanol this would give an energy density about 8 – 9 MJ/kg**

- **If methane (SNG) is used instead of methanol then an energy density of 22 – 24 MJ/kg would be obtained**

Power density determinants

- Electrolyte resistance
- Electrode polarization resistance
- Mass transport rate

Electrolyte resistance

- **Liquid electrolytes have most often much better conductivity than solid electrolytes at a given temperature.**
- **The lower the viscosity of a liquid the higher the conductivity**
- **Liquid proton conductors - strong acids like slightly diluted (30 %) H_2SO_4 in H_2O has among the highest electrolyte conductivities known**
- **Ionic liquids/molten salts also have fine conductivity**
- **The aqueous electrolytes are the cheapest and in many contexts best also from a safety point of view**
- **Liquids may be troublesome to handle; immobilization of liquid electrolytes may be helpful**

Electrodode polarization resistance

- **Inherent high reactivity of electrode reactants**
- **Increased temperature**
- **Good electrocatalysts**
- **In case of O_2 as a reactant a good electrocatalyst is always necessary**

Mass transport

- **In order to minimize mass transport limitations:**

- **Best to avoid any diffusion, i.e. direct supply of reactant with preferably solid (but easily dissoluble) reaction products like in the lead acid battery, $Pb/H_2SO_4(aq.)/PbO_2$ with $PbSO_4$ as reaction product**

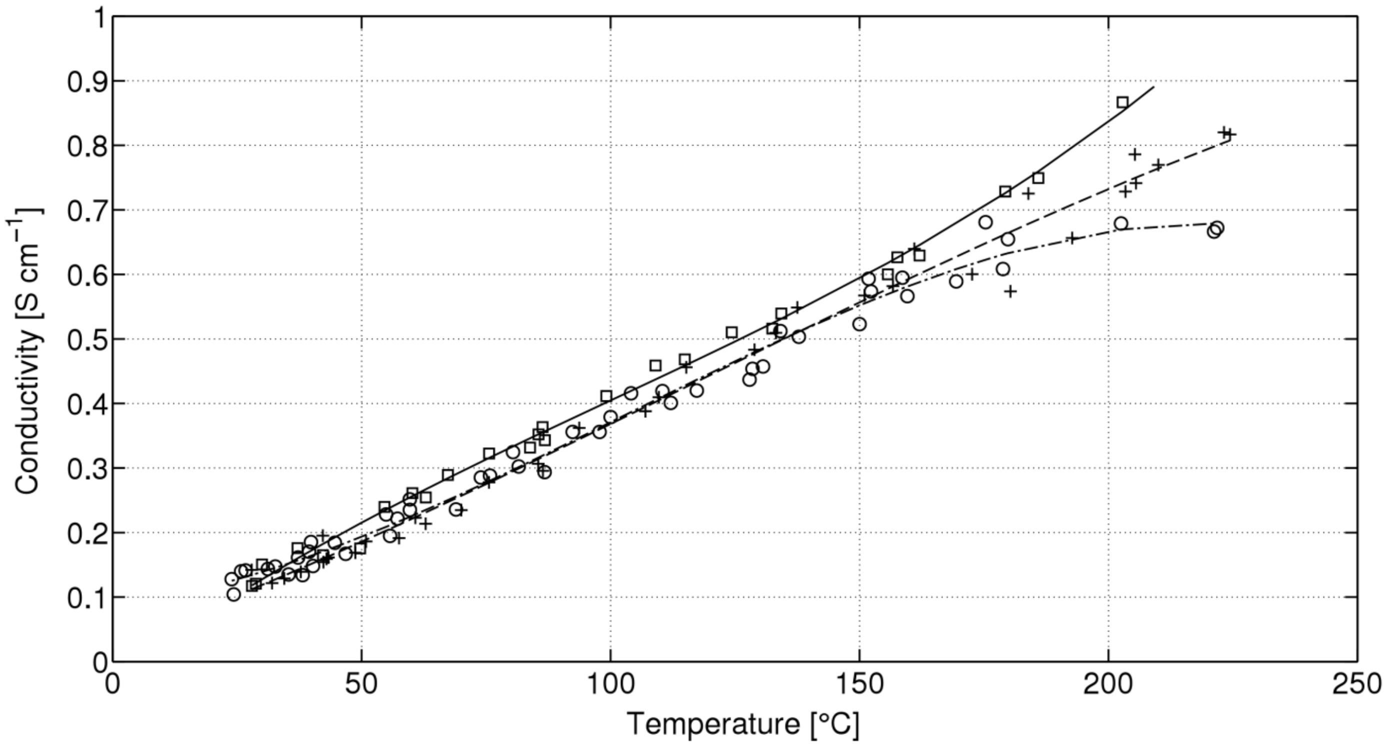
- **If not possible then gas diffusion is much faster than diffusion in liquids or solids.**

200 – 300 °C cell types

As part of the initiative called Catalysis for Sustainable Energy (CASE, www.case.dtu.dk) and the 2. generation alkaline electrolyser project other types of electrolysis cells are being researched and developed at DTU energy conversion – and intended to be reversible

- Immobilized, pressurized aqueous K_2CO_3
- Immobilized, pressurized aqueous KOH
- Solid Acids (CsH_2PO_4)

Conductivity of immobilized KOH (aq)

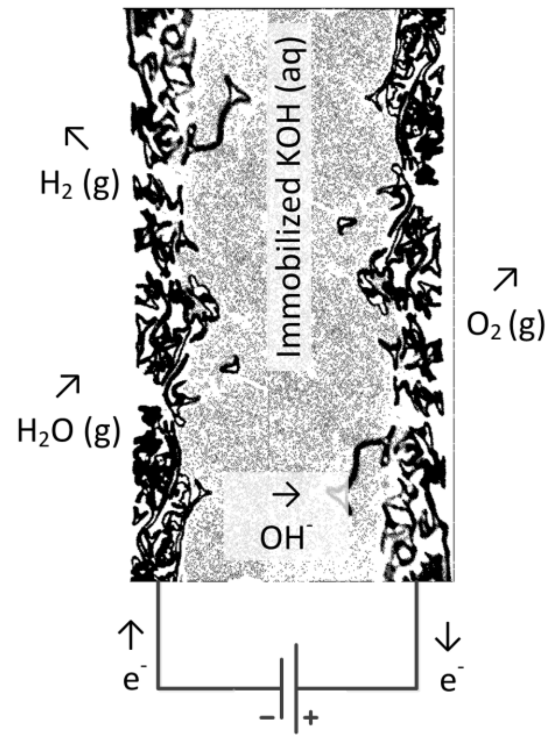


- The electrolyte was immobilized in a porous $SrTiO_3$ structure with a medium pore size of 59 nm and a porosity of ca. 50%
- The conductivity is reduced by a factor of 3-4
- immobilized KOH with 35 wt% (o), 45 wt% KOH (�) and 55 wt% (+) at 200 ˚C showed values of 0.67 S cm^{-1}, 0.84 of S cm^{-1} and 0.73 S cm^{-1}, respectively.

“Frank Allebrod” cell

A cell with an electrolyte of 45 wt% KOH(aq.) immobilized in micro porous ceramic, with gas diffusion electrode made of metal foam partially imbedded in the porous ceramic and impregnated with suitable catalysts operating at 250 °C, 40 bar

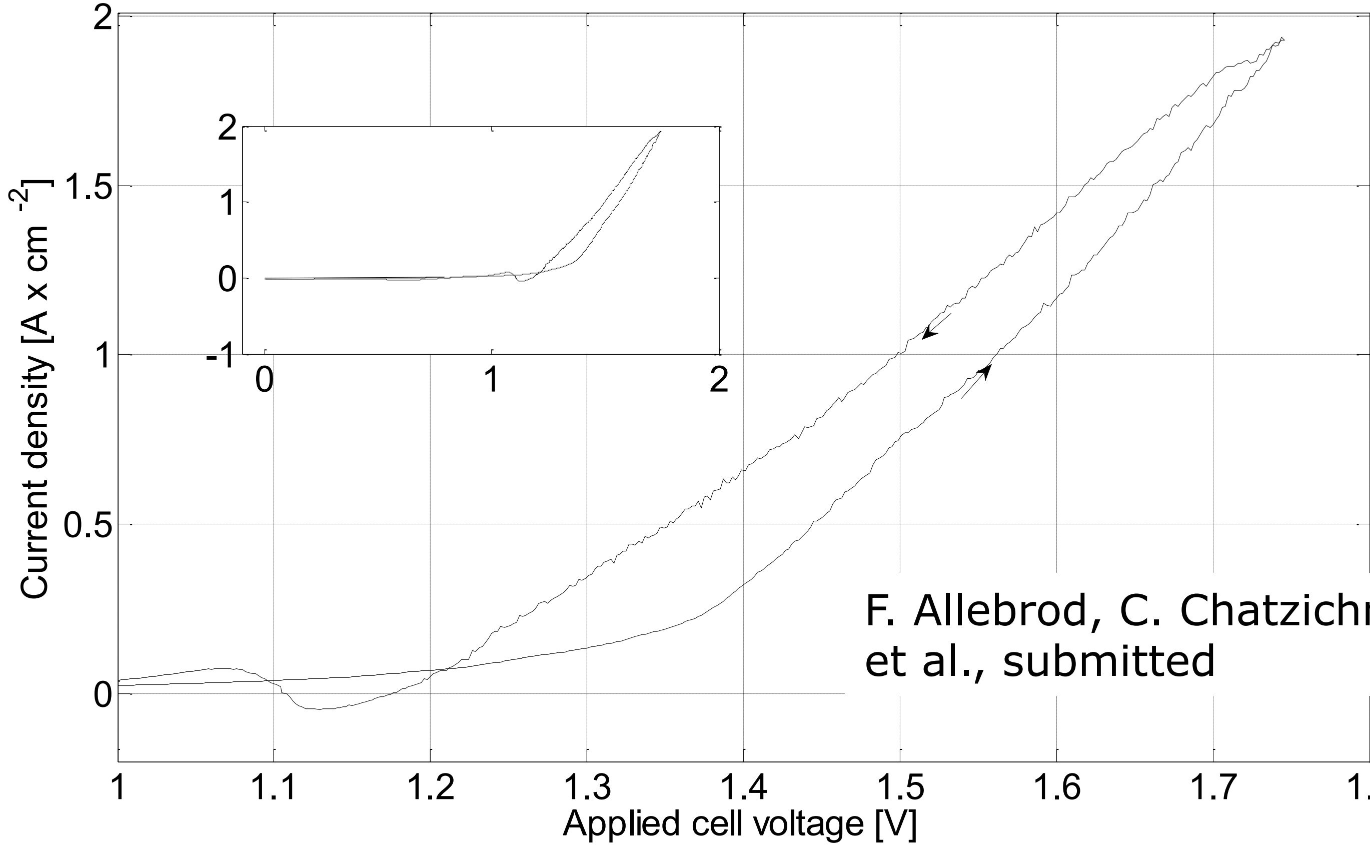
GDE with immobilized Electrolyte



+ decreased ohmic losses
+ no bubble effects
+ Reversible
- simple production method needed to be found

High Temperature and Pressure Alkaline (HT-AEC)

Conductivity of aqueous 45 wt% KOH immobilized in nano-porous structure reached 0.84 $S\cdot cm^{-1}$ at 200 ºC



Cyclic voltage sweep on a cell with nickel-based gas diffusion electrodes. Current densities of 1.0 $A\cdot cm^{-2}$ at 1.5V and 1.9 $A\cdot cm^{-2}$ at 1.75V. 3.7 MPa and 241 ºC. Calculated EMF 1.2 V. 1 cm^2 button cell.

Conclusions

- **Lithium-batteries and in particular Li-air are interesting and have high potential, but there are other possibilities**

- **Carbon, hydrogen and hydrocarbon batteries (reversible electrolyser/fuel cell with fuel tank) may have even higher potential**

- **Efficiencies not discussed, but I hope that it is becoming clear that it does not make any sense to claim that the efficiency of batteries are in general much higher than of fuel cells – because there is no basic difference**