

Nonaqueous electrolyte solutions: New materials for devices and processes based on recent applied research

H. J. Gores and J. M. G. Barthel

Institute of Physical and Theoretical Chemistry, University of Regensburg,
D-93053 Regensburg, FRG.

In order to improve the performance of electrochemical devices or processes, information is needed on the behaviour and the properties of all components including the ion-conducting material, the electrolyte. Electrolytes may be classified into liquid and solid electrolytes. Liquid electrolytes include aqueous and nonaqueous solutions, molten salts, and solid polymer electrolytes consisting of a solvating polymer and a salt. The large number of solvents, salts, and additives generally allows the optimisation of the properties of liquid electrolyte for a given task, when based on information about its bulk and intrinsic properties. Applied and basic research on nonaqueous electrolyte solutions have catalysed progress in the development of competitive devices and processes, especially lithium batteries or wet capacitors and electrodeposition or electrosynthesis. Based on recent knowledge various new suitable ion-conducting materials have been developed extending the range of realised or future applications.

1. Types of ion conductors, merits and drawbacks

Every electrochemical cell consists of three major components: electrodes (anode, cathode), separator, and electrolyte. Electrolytes are ion-conducting materials with negligible electronic conductivity. They may be classified into solid and liquid electrolytes. Liquid electrolytes include molten salts and electrolyte solutions, based on a salt, often called electrolyte too, and an appropriate solvent. With reference to the type of solvent used they are called aqueous (water), mixed aqueous (water and cosolvent), and nonaqueous (organic or inorganic solvent) electrolyte solutions, respectively. Molten salts may be classified according to their useful liquid range as high-temperature and ambient-temperature molten salts, which are often based on mixtures of organic halides with aluminium trichloride. Solid polymer electrolytes (SPE) may be included in this class as they exhibit various properties of liquid electrolytes, due to their composition, a blend of a solvating polymer and a salt or a nonaqueous electrolyte solution.

Every type of ion conductor shows specific benefits and drawbacks, determined by bulk properties of the material and the intrinsic behaviour of constituting species.

When compared with solid electrolytes liquid electrolytes show generally better levelling capabilities for both temperature and concentration discontinuities and allow for small volume changes due to chemical or electrochemical reactions. They generally maintain a permanent interfacial contact at the electrolyte/electrode interface and have generally higher conductivities, cf. TABLE 1, where also some of the few exceptions (RbAg_4I_5 and $\text{RbCu}_4\text{I}_2\text{Cl}_3$) are included, due to their potential use in solid-state supercapacitors, cf. also section 2.2. In contrast to solid electrolytes liquid electrolytes show a non-Arrhenius type temperature dependence of conductivity. A trivial advantage of liquid electrolytes is their capability of dissolving the reaction products; they may hence be used in electrosynthesis as reaction media.

Obvious disadvantages of liquid electrolytes are potential gassing and leakage problems in cells, and the higher effort in assembling cells.

Solid electrolytes (for an application related review, see Ref. (1)) often offer cationic or anionic transport in contrast to liquid electrolytes and solid polymer electrolytes (SPE), where anions and cations are con-

tributing to the conductivity. Their use avoids the need for a separator. However, their electronic conductivity may be detrimental in some applications.

TABLE 1. Conductivities of various types of ion-conducting materials.

Type of electrolyte	materials	κ / (mS/cm)	Remarks	References
aqueous	2.81 M LiClO ₄ / H ₂ O	151.7	maximum	(2)
nonaqueous	0.662 m LiClO ₄ / PC	5.420	maximum	(3)
nonaqueous	1.652 m LiClO ₄ /PC/DME(28.2 w%PC)	14.38	maximum	(4)
high-temperature molten salt	34.5 mol% LiCl / 32.5 mol% LiBr / 33.5 mol% KBr	1700	425°C	(5)
ambient-temperature molten salt	TMPC/AlCl ₃ , X(AlCl ₃) = 0.66	5.0	Li/FeS-cell	(6)
polycrystalline	Cu ₄ RbCl ₃ I ₂	500	Cu+ conductor	(7)
crystalline	RbAg ₄ I ₅ -single crystal	260,270	Ag+ conductor	(8),(9)
crystalline	LiI	0.01,0.042	Li+ conductor	(10),(11),(12)
inorganic glass	AgI / Ag ₂ SeO ₄ (3/1)	60	Ag+ conductor	(7)
SPE	LiCF ₃ SO ₃ /PEO ₆	0.01	60°C	(13)
SPE	EC/PC/LiClO ₄ /PAN (38/33/8/21)(mol%)	1.7	20°C	(14)
gelled electrolyte in polymer matrix	PC/LiClO ₄ /2p-MC-DBS/PEGPM (81.0/7.5/0.9/10.6)(w%)	4.6	25°C	(15)

maximum = maximum of the $\kappa(m)$ function, see eq. (5); PC = propylene carbonate; DME = dimethoxy ethane; TMPC = tetramethylphosphonium chloride; EC = ethylene carbonate; PAN = poly(acrylonitrile); 2p-MC-DBS = 1,3:2,4-di(p-methoxycarbonylbenzylidene) sorbitol, PEGPM = poly(ethylene oxide)-grafted poly(methacrylate).

TABLE 2. Voltage windows of some ion conducting materials.

Solvent	Electrolyte	anodic limit	cathodic limit	working electrode	reference electrode	Ref.
water	HCl	1.1 V	-0.3 V	Pt	SCE	(16)
AN	LiClO ₄	2.6 V	-3.5 V	Pt	Ag/AgClO ₄	(16)
PC	LiClO ₄	2.3 V	-2.2 V	Pt	Ag/Ag ⁺	(17)
PN	Bu ₄ NPF ₆	3.7 V	-3.0 V	Pt	Ag/AgCl	(18)
PN/EtCl ₄ (1/2) (-160°C)	Bu ₄ NPF ₆	3 V	-3 V	Pt	---	(21)
EC/SL, (1/1)	Et ₄ NPF ₆	2.4 V	-2.8 V	glassy carbon	SCE	(19)
---	Li ₃ N	0.44 V (*)	---	Li	---	(20)
---	HUP	1.6 V (*)	---	C	---	(74)
---	RbAg ₄ I ₅	0.66 V (*)	---	C	---	(74)
---	TMPC/AlCl ₃	2.7 V	0 V	glassy carbon	Al	(6)
(DMSO)	(1/2) LiNAGE-SPE	3.5 V	0 V	-	Li / Li ⁺	(31)

SCE = saturated calomel electrode; PN = propionitrile; SL = sulfolane; Et = ethyl; Bu = butyl; (*) = useful voltage range; HUP = H₃OUO₂PO₄ · 3 H₂O; LiNAGE = (LiCF₃SO₃-dimethylsulfoxide -lithium salt of poly (2-acrylamido-2-methyl-1-propane sulfonate));

Nonaqueous electrolyte solutions show various advantages, including a larger usable liquid range extending from about -180°C (21) to > 300°C (22), voltage windows up to about 5V, cf. TABLE 2, a large

range of acid-base properties, often better solubility for many materials, electrolytes and non-electrolytes, and better chemical stability, when compared with aqueous electrolyte solutions. Typical disadvantages include higher costs of the solvents, purification problems, security problems due to their toxicity and inflammability, and distinctly lower conductivities.

Solid polymer electrolytes combine various advantages of nonaqueous electrolyte solutions and solid electrolytes, acting as reliable separators and allowing for volume changes during cell operation. Due to recent progress based on new polymers (23,24,25), salts (26,27), and included plasticizing agents, such as dipolar aprotic solvents (14,28), a major drawback of SPEs - their lower conductivity when compared with liquid electrolytes - has been continuously reduced (29,30,31,32,33,34). The recently reported conductivity for lithium salts in dipolar aprotic solvents, immobilised with polymers and gelling agents, reach already liquid-like conductivity for free standing films at ambient temperature, see TABLE 1. In addition, better elastic properties of the new materials insure a good permanent contact with electrodes in contrast to typical solid ion conductors such as polycrystalline materials and ceramics.

Nonaqueous electrolyte solutions immobilised with the help of inert inorganic materials (35,36), such as SiO_2 or Al_2O_3 , are a new class of ion-conducting materials showing also properties similar to those of the parent electrolyte solution, but no leakage problems.

2. Applications of nonaqueous electrolyte solutions

In many fields of applied research nonaqueous electrolyte solutions are actually competing with other ion conductors, especially at ambient and at low temperatures. The high flexibility of nonaqueous electrolyte solutions based on numerous solvents, additives, and electrolytes with widely varying properties generally allows an optimisation for a given technical problem.

The following section shows examples from the literature proving the successful application of nonaqueous electrolyte solutions as ion conductors in devices and processes, including lithium primary and secondary batteries, wet double-layer capacitors and supercapacitors, electrodeposition and electroplating. Other fields where nonaqueous electrolyte solutions are used, e.g. electrochromic displays and smart windows, photoelectrochemical cells, electromachining, etching, polishing, and electrosynthesis, are not considered here.

Some recent advances are based on the development of new or modified electrolytes and solvents or solvent mixtures, and the use of knowledge concerning the intrinsic properties of the solution. Intrinsic properties refer to the structure and the dynamics of the ion conductor, which are affected by the interactions of the constituent ions and molecules, their volumes and shapes. Obviously intrinsic properties of electrolytes strongly influence the bulk properties of the electrolyte. However, only a few examples are known from the literature, showing the importance of structure and dynamics of the electrolyte solution for their behaviour in devices and processes. Some examples of the importance of intrinsic properties of nonaqueous electrolyte solutions for their bulk properties and their behaviour will be given in the last section of this review. Based on recent knowledge on liquid ion conductors, various new suitable materials have been developed which have extended the ranges of possible application by improving the behaviour of the electrolyte. For example, new lithium salts containing large organic anions with delocalised charge for lithium battery electrolytes, have been synthesized, which have the potential to replace the usual ones, offering advantages concerning stability, safety or environmental aspects; nonaqueous electrolytes for the investigation of the superconductor-solution-interface at ultra-low temperatures and for the electrodeposition at very high temperatures have been developed, and new solvents showing better electrochemical stability are now available.

2.1 Nonaqueous high energy batteries

A battery is an electrochemical device, consisting of a single or several electrochemical cells, which directly converts the chemical energy of the electrode material couple into electric energy by coupled, but spatially separated electrochemical reactions, taking place at the anode (oxidation) and cathode (reduction) respectively, when the electrodes are connected by an external load. If the two half-cell reactions are reversible, charging of the battery is possible, too. Rechargeable batteries are called secondary batteries in contrast to non-rechargeable primary batteries. So-called high-energy density batteries (37) utilise materials with high electrochemical equivalents (Ah/g) and high ΔG (J) values for the respective electrode reaction, reaching theoretical energy densities based only on the electrode materials of more than 1000 Wh/l or Wh/kg. High energy batteries thus are based upon low equivalent-weight metals as the anode materials and nonaqueous electrolyte solutions (Li, Ca), salt melts (Li) or solid electrolytes (Na, Li) as ion conductors. The most attractive features of nonaqueous lithium batteries include high energy density and working voltage broad use-

ful temperature range down to about -50°C and very low self-discharge rate due to the formation of protective films at the lithium electrode.

Primary lithium batteries are for more than 20 years (first cell by SAFT: $\text{Li}/\text{LiClO}_4, \text{PC}/\text{Ag}_2\text{CrO}_4$) successful competitors as power sources in the market, e.g. watches, cameras, calculators, other mobile electronic equipment, including defence and aerospace applications due to their high reliability and long shelf life. They are produced by many manufacturers based on various cathode materials and appropriate nonaqueous electrolyte solutions (38,39,40,41). In Japan, the production of primary cells has reached already about 2.5×10^8 units in 1989, i.e. more than half the number of alkaline MnO_2 cells, which are leaders on a number basis. The average increase of the value of produced primary lithium batteries in the period 1984 to 1989 was about 26% in Japan (42). Actually lithium batteries share 8 to 10% of the battery-market for transportable energy sources, world-wide, having a value of 600 million US \$ (43).

Concerning secondary batteries with lithium anodes the research efforts have achieved remarkable progress in the following fields. Electrolyte solutions showing an improved cycling behaviour for lithium anodes, better chemical stability and higher conductance especially at low temperatures, many intercalating electrode materials with 2D and 3D lithium-ion mobility exhibiting fast and reversible lithium ion intercalation, and substitutes for the lithium anode (carbons, and other low potential intercalation materials and alloys with lithium) showing a better compatibility with the electrolyte solution are now available. The results are promising. After the short EXXON episode, MOLI offered the first rechargeable lithium battery (Li/MoS_2), (44,45,46,47,48,49) in 1986. However, despite considerable progress, problems caused by the dendritic growth of lithium and the inherent thermodynamic instability of nonaqueous solutions with lithium have not been completely solved so far. Hence the achievable cycle numbers are rather low when the cell is discharged to an appreciable depth, e.g. < 300 cycles at full depth of discharge and about 1000 cycles at 50% depth of discharge (50), reducing thus the superior performance of rechargeable lithium cells (51,52,53,54). Nevertheless, new nonaqueous lithium cells such as the AA-size ReLi@-cell manufactured by EIC outperform the energy density and hence the service life of Ni/Cd cells, e.g. 130 Wh/kg vs. 45 Wh/kg (50), and are only inferior at high power densities, when compared with Ni/Cd-cells. Recently, rechargeable "lithium-ion" batteries (55,56,57) based on the rocking-chair concept (58,59) using a carbonaceous material (60,61,62,63,64,65,66), which electrointercalates lithium ions during reduction as the anode and Li_xMO_2 as the intercalating cathode, where $\text{M} = \text{Co}, \text{Mn}, \text{or Ni}$, have reached the market (55). A Ni/Cd-secondary battery attains only 1/3 of the voltage of the lithium battery, only 1/3 of its volumetric energy density and 2/3 of its cycle life. It shows double the self discharge rate and is inferior when environmental aspects are taken into account (55).

2.2 Capacitors

A capacitor is in contrast to batteries, which store more or less permanently the electrical energy as chemical energy in anode and cathode materials, mainly a transient electrical charge and energy storage device.

The constant capacitance C of an ideal capacitor is defined by

$$C = q / \Delta E \quad (1)$$

or the time derivative

$$I = C(dE / dt) \quad (2)$$

where q (A s) is the accumulated charge on one electrode and ΔE (V) is the potential difference between the electrodes, I (A) is the charging current and dE/dt is the sweep rate in a cyclic voltammetry experiment. For electrochemical capacitors C is generally a complicated function of the potential difference. The storable energy ΔG (J) is

$$\Delta G = 1/2 C(\Delta E)^2. \quad (3)$$

Capacitors are based on various physical principles, including electrostatic charge separation {e.g. mica capacitor, ($C = 1 \text{ pF}$ to $0.01 \text{ } \mu\text{F}$)(67), ceramic capacitors (10 pF to $1 \text{ } \mu\text{F}$) and electrolytic Al or Ta capacitors ($0.1 \text{ } \mu\text{F}$ to 1.6 F , due to the high dielectric permittivity of the thin solid dielectric film}, electrochemical double-layer charging (dlc), (double-layer capacitors (DLCs), $C = 0.1 \text{ F}$ to 10 F), on dlc and faradaic pseudocapacitance based on underpotential deposition at 2D or quasi-2D electrodes or even 3D-redox reactions within the electrodes (68,69,70,71,72)(supercapacitors, C up to more than 1000 F/g electrode material). Supercapacitors represent hence an intermediate between "normal" capacitors and thin film secondary batteries. Unfortunately, the term "supercapacitor" is not excessively used for capacitors utilising faradaic processes for charge storage, but also for double-layer capacitors of high specific capacitance (73,74,75). Electrolytic, double-layer, and supercapacitors may be produced with nonaqueous electrolyte solutions in order to reduce decomposition and corrosion problems and to increase the useful working voltage ΔE and

hence the energy density, see eq.(3). The required performance characteristics of electrochemical capacitors, a high capacitance with small frequency dependence, a low series resistance, a high-energy density, a low leakage current and a high thermal stability, are closely related to the properties of the solution. Hence many reports and patents concern this topic, especially for DLCs and electrolytic capacitors.

In wet electrolytic capacitors, the solution fulfils various tasks, maintenance and/or formation of the dielectric film (e.g. Al_2O_3 , the oxide of the anode material), and electrical contact. Its capacitance C is: (76)

$$C = 8.855 \times 10^{-12} \varepsilon A / d \quad (4)$$

,where ε is the permittivity of the film, A (m^2) is the area of the electrodes and d (m) their distance. Electrolytic capacitors are mostly operated as polar devices with the oxidised anode as the positive electrode at medium voltages (<600V). The working voltage is limited by sparking which is closely related to the resistivity of the solution (77). Electrolytic capacitors are used as power-supply filters and recently for various applications in the fastly growing electronic markets where devices are required which are compatible with surface mount technology (SMT) withstanding the high temperatures of soldering processes (76). Recent patents show that in addition to the well known glycol-based borate solutions, better conducting solutions based on dipolar aprotic nonaqueous solvents (e.g. γ -butyrolactone, BL) and quaternary salts of polycarboxylic acids for improving the conductance, low temperature behaviour and heat resistance, have gained increased interest.

When the electrode surface is high at rough electrodes such as at active carbon fibres (ACF) from phenolic resins (up to 3000 m^2/g (78)), the double-layer capacitance which reaches only about 40 $\mu\text{F}/\text{cm}^2$ (79) at smooth Hg-surfaces, could attain large values of up to more than 1200 F/g, if the same surface charge density could be attained (73). The specific capacitance realised in commercial double-layer capacitors (DLCs) is lower, up to more than 100 F/g electrode material (70). Commercial DLCs with a capacitance up to 1500 F will reach the market in the near future (80). These huge capacities will enlarge their current use as backup power sources for memories such as DRAMs to power sources in electrical cars together with batteries, where the capacitor is used for large power demands at currents exceeding 100 A, increasing the cycle life of batteries (80). In contrast to electrolytic capacitors, double-layer capacitors are, just like batteries, low-voltage devices (0.9V (aqueous, typical electrolyte H_2SO_4)) (81,70) and up to about 5V (nonaqueous organic or SPE (82)). As they reach already 1/20 of the energy-density of lead-acid rechargeable batteries they are strong competitors for Ni-Cd batteries and Li batteries in those fields where their superior cycle life of $>10^6$ cycles is required; 10000 cycles at less than 20% capacity decline (83) at large charging and discharging currents can be obtained. Typical nonaqueous DLCs (83,84,70,85,86) are employing dipolar aprotic solvents, e.g. PC and tetraalkylammonium or lithium salts with stable anions (e.g. BF_4^-). Nonaqueous DLCs show a two times larger working voltage, but a ten times higher resistance when compared with aqueous DLCs (87,88). The radii of the ions are closely related to the capacitance, smaller cations leading to higher capacitance (19). As nonaqueous ACF based DLCs use similar electrode materials and electrolytes as the carbon/ MO_x -based nonaqueous rocking chair-type batteries, they obviously utilise the pseudocapacitance in excess to dlc, e.g. the C/ LiClO_4 ,BL/C capacitor (89), where intercalation has been postulated.

Supercapacitors utilising the pseudocapacity of electrode materials such as RuO_2 and aqueous electrolyte solution show a capacitance which reaches values of up to 100 times of the dlc for the same electrode area a high kinetic reversibility similar to electrostatic capacitors (68,69), and a low useful working voltage as DLCs. The pseudocapacitance, C_{pc} is given by:

$$C_{pc} = dq / dE = q_0 d\theta / dE \quad (5)$$

where q_0 is the charge required to form a monolayer and θ is the fractional surface coverage of the electroactive species involved. The use of nonaqueous electrolyte solutions for increasing the working voltage, and useful electrode materials for intercalation electrodes which are not stable with water, has only seldomly been considered so far (81,71). In contrast to electrolytic capacitors, DLCs and supercapacitors have a relatively large equivalence series resistance and a strong decrease of capacity with frequency. They are hence restricted to DC applications (73).

2.3 Electroplating and electrodeposition

Electroplating is the electrochemical deposition of an adherent metallic coating upon an electronically conducting surface of a given object in order to improve its surface properties, including corrosion-, heat-, or abrasion resistance, its solderability or boundability, its electrical or magnetic properties, or its appearance. Electroplating is restricted by definition to metal deposition, whereas electrodeposition includes the deposition of non-metallic materials. However, in the literature, the notions are often used synonymously. Plating baths are characterised by their specific conductivity, which should be high to reduce Joule heating and

permit a good current distribution, and resulting good throwing power. Hydrogen evolution instead of metal deposition and hydrolysis of starting materials or substrates, prohibits the deposition of several important metals from the better conducting aqueous solutions.

The use of nonaqueous electrolyte solutions allows (90,91,92,93,94,40,95) the electrodeposition of metals including alkali metals, alkaline-earth metals, B, Al, Ge, lanthanides, actinides, valve metals (Ti, Zr, Hf, V, Nb, Ta), and other materials such as semiconductors (96), e.g. Si (97,98,99,100,101,102,103,104), CdS (105,106,107), and GaAs (108) or precursors for high-temperature superconductors (96,109,110). In addition nonaqueous electrolyte solutions may be used to electroplate water- and reduction-sensitive materials such as superconductors (111,112,113,114) or for electroplating metals platable from aqueous solutions only at low current efficiencies due to hydrogen evolution (e.g. Cr), which may cause hydrogen embrittlement in steel.

The most important processes based on nonaqueous solutions are aluminium electroplating, and electrorefining (115). The major benefits of aluminium coating are its high corrosion resistance, superior to that of Zn and Cd, the excellent mechanical properties of Al-films (ductility, thermal conductivity), and the possibility to anodise aluminium, yielding a surface of high hardness (116). In addition, the purity of the deposits is high (> 99.99% or better). Some baths even allow electrorefining of aluminium (117,118,119). Higher purity when compared with zone melted material is obtained (99.9999% purity) at low energy consumption (0.1 to 3.5 kWh/kg (120)). The most important solvents used are ethers such as tetrahydrofuran and diethylether, aromatic hydrocarbons such as toluene and other alkylbenzenes. The major aluminium sources include AlH_xCl_y ($x + y = 3$), AlBr_3 , and aluminooorganic compounds such as Ziegler's salt, $(\text{Na}[\text{Et}_3\text{AlFAI}\text{Et}_3])$. Recently several ambient temperature molten salts or their mixtures with toluene or benzene have been investigated as potential plating baths, cf. (6,121). Some bath formulations show both reversible aluminium plating and stripping; hence aluminium anodes can be used allowing continuous operation. As the difference between formal potentials of more noble metals and aluminium are very small in aromatic solvents, Al-alloys can be plated, even those which cannot be made by metallurgical processes (122,123,124,125).

In a series of papers (126,127,128,129) and two patents (130,131) the benefits of nonaqueous cryogenic electrolytes for electroplating, electrodeposition, and electrosynthesis have been stressed by Sadoway. Cryoelectrodeposition eliminates problems typical for high-temperatures such as formation of metastable structures, nonuniformity of deposited layers and thermally induced stresses of the substrate. Electrolytes for electrodeposition and electrowinning are based on solvents with low boiling points and molar weights; e.g. valve metals are deposited at cryogenic conditions from HF/KF and $\text{HCl}/\text{Et}_4\text{NCl}$ mixtures and compounds containing them, e.g. KNbCl_6 .

3. Optimization of nonaqueous electrolyte solutions

The requirements for suitable electrolyte solutions are sufficiently high conductivity and high mobility of active species, low temperature dependence of conductivity, good chemical thermal and electrochemical stability of the solution, sufficient solubility of electrolytes and non-electrolytes, a large liquid range, and low vapour pressure. Numerous examples in the open and patent literature from the last two decades show that solution chemistry offers a large number of tools, for the optimisation of a nonaqueous electrolyte solution for a given task (40,132). The following examples, especially from lithium battery research and hence referring mainly to nonaqueous lithium salt solutions, may exemplify that.

3.1 Stability of solution

A high electrochemical stability of the solution is related to the use of nonaqueous solvents and relatively inert anions of the lithium salt, which are not easily oxidised or reduced at electrodes. Suitable solvents are mainly the following (40): high-permittivity dipolar aprotic solvents (e.g. organic carbonates such as PC or EC (lithium batteries, capacitors)), low permittivity-high donor number solvents (e.g. ethers such as DME, THF, or dioxolane (lithium batteries, electrodeposition, capacitors)) and low permittivity, high polarisability solvents (e.g. aromatics such as toluene or mesitylene (electrodeposition)). All these solvents are thermodynamically unstable with lithium; kinetic stability determines their usability. For example, AN is among the solvents showing the highest electrochemical stability range when mixed with appropriate electrolytes, cf. TABLE 2. AN solutions provide the high conductivity, due to low solvent viscosity and sufficiently high dielectric permittivity. However, AN is very unstable with lithium (133,134). THF-based solutions show, despite low solvent permittivity high conductivities (17 mS/cm, LiAsF_6 , 1.5M, (135)); however, lithium reacts with THF forming ring opened products (135), and THF is polymerised by Lewis acids from electrolyte-anions or protons (136). A chemical modification of the solvent by methylation in the 2-position (2-Me-THF) prevents the solvent from polymerisation, as also shown by thermodynamic calcula-

tions (136). Unfortunately, 2-Me-THF based electrolyte solutions show only 20% of the conductivity of THF-based solutions, c.f. section 3.2.

Typical electrolytes used in early studies included coordinatively saturated large anions such as ClO_4^- , BF_4^- , PF_6^- , and AsF_6^- , which are not easily oxidised or reduced at electrodes and which are therefore the anions of lithium or tetraalkylammonium supporting electrolytes for electrochemical studies, cf. TABLE 2. The problems associated with these anions have stimulated the search for substitutes (137). E.g. lithium perchlorate solutions are thermally unstable and show explosion risks, especially in ethers, the hexafluorophosphate is itself thermally unstable in the solid state and decomposes in solvents to yield the scarcely soluble LiF and the Lewis acid PF_5 , which initiates polymerisation of cyclic ethers and hence degrades the solution, if this process is not inhibited by additives; hexafluoroarsenate shows environmental risks while the tetrafluoroborate yields poorly conducting solutions, and leads to polymerisation with cyclic ethers. In addition, all anions are thermodynamically unstable with lithium, e.g. LiAsF_6 generates about 1600 kJ/mol heat upon reduction (50). Anions like triflate CF_3SO_3^- , other perfluoroalkyl or perfluoroaryl sulfonates (137), closoboranes ($\text{B}_{10}\text{Cl}_{10}^-$, $\text{B}_{12}\text{Cl}_{12}^-$) (138) or borates such as BMe_4^- (139) show no stability problems, but yield lower conductivities. Borate-ions of the type BR_4^- , where R is the perfluorinated alkyl or aryl show increased stability versus oxidation when compared with unfluorinated borates (140).

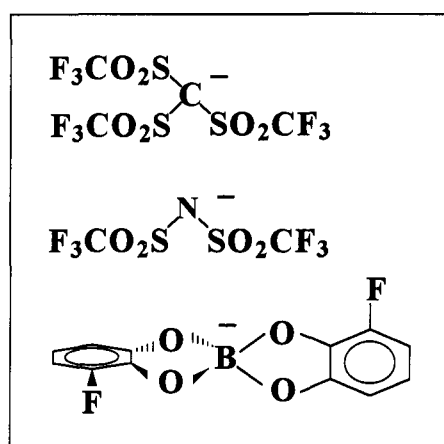


Fig. 1 New anions for lithium salts; from top to bottom the methide, imide (141) and borate (142); for details see text.

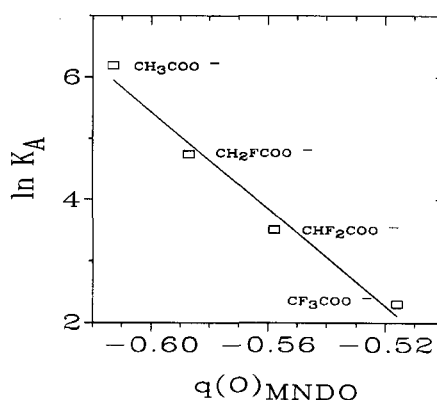


Fig. 2 Logarithm of the association constant K_A of $\text{LiO}_2\text{CH}_x\text{F}_y$ salts in DMSO as a function of mean oxygen charge from MNDO-calculations.

Recently new lithium salts with choice of anions based on common principles of solution chemistry have been developed and are actually studied, i.e. the bis(trifluorosulfonyl)imide, the tris(trifluorosulfonyl) methide and the family of fluorinated borate ions based on various fluorinated diols and boric acid, such as bis(3-fluoro-1,2-benzenediolato(2-)-O,O')borate anion, (141,143,144,145,142) see Fig. 1. All these molecular ions with covalent bonds, show higher chemical stability than the Lewis acid based salts, large radii and hence lower lattice energies leading to good solubilities, low polarisability of the anion, especially when perfluorinated, due to the low polarisability of fluorine. They show low anion solvent interaction and generally a large charge delocalisation resulting in both an excellent electrochemical stability and a weak anion-lithium interaction entailing better conductivities, see section 3.2. Electrochemical stability against oxidation may be estimated with the help of semi-empirical quantum-mechanical calculations; the HOMO energies and oxidation potentials are linearly related (146,142). All salts exhibit good safety characteristics and high thermal stability. For example, the lithium methide is stable up to 340°C (141) a very high, when compared to lithium hexafluorophosphate (30°C) (147) such salts are useful electrolytes for SPEs (148,141,26). The imide is already commercially available, a pilot plant for the production of the methide is projected (137).

3.2. Optimisation of conductivity

The specific conductivity κ (S/cm) of electrolyte solutions is another major topic for the optimisation of nonaqueous electrolyte solutions, cf. section 2. Measurements of concentration dependence of the specific conductivity $\kappa(m)$ are favourably evaluated with the help of the Casteel-Amis (149) empirical equation:

$$\kappa = \kappa_{\max} \times (m / \mu)^a \times \exp \left[(b \times (m - \mu)^2 - a / \mu \times (m - \mu)) \right] \quad (6)$$

where κ_{\max} is the maximum conductivity for a given temperature and solvent composition, μ is the molality at maximum conductivity, and a and b are empirical parameters. Only measurements including a wide concentration range, a large temperature range and for mixed solvent systems the complete composition range, are needed to obtain an adequate description of the conductivity behaviour. κ_{\max} and μ are strongly affected by temperature and solvent composition. The occurrence of the maximum in $\kappa(m)$ -functions which is attained at sufficiently high solubility has been discussed elsewhere (40,3). At high concentrations, where the association constant is small, κ is mainly determined by the hydrodynamic properties i.e. the solvent viscosity and Stokes-radii of cations and anions. As a consequence, κ_{\max} is proportional to μ . The mobility functions κ/m or κ_{\max}/μ are approximately linear functions of solvent fluidity and of Stokes-radii changing only when solvation changes as observed in mixed solvents of different donor numbers (3,40). Walden-rule like behaviour is hence also observed in mixtures of high permittivity solvents (e.g. PC and AN) with similar donor numbers (150). When the ion-solvent and ion-ion interaction are only slightly changed in mixed solvent systems, e.g. when cosolvents of the same solvent class are used, the viscosity change of the solvent also is the predominating effect. For instance, 1:1 mixtures of sulfolane and glymes ($\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_n\text{CH}_3$, $n = 1, 2, 3, 4$) show a linear relationship for the conductivity of 1 molar LiAsF_6 as a function of the fluidity (151). The common behaviour for the temperature dependence of μ , $(d\mu/dT) > 0$, is another consequence of the viscosity change, decreasing with temperature, $(d\eta/dT) < 0$.

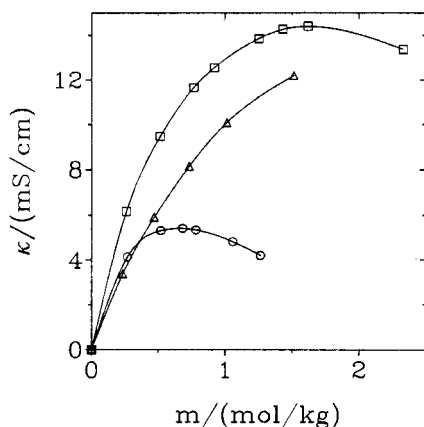


Fig. 3 Specific conductivity of LiClO_4 in PC (O), PC/DME, 28.2 weight% DME (□), and PC/DME, 12.9 weight% DME (Δ) at 298 K (4).

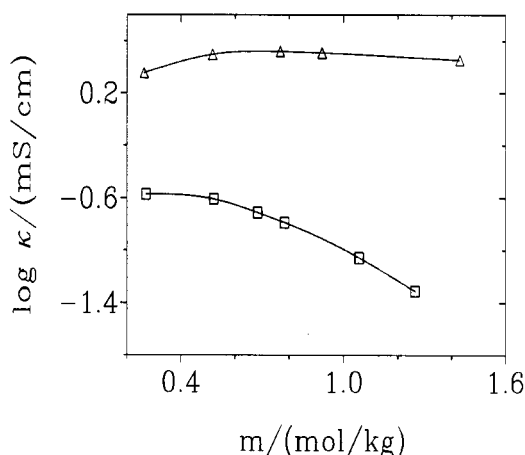


Fig. 4 Logarithm of specific conductivity of LiClO_4 in PC (□) and PC/DME, 28.2 weight% DME (Δ) at 228 K (4).

Strong ion-association, as observed in ethers, lower the κ_{\max} -values when no strong solvation, which competes with ion-association and restricts it, takes place (152). In the series of electrolyte solutions of LiClO_4 in alkylformates, from methylformate to butylformate, where again ion-ion interaction and ion-solvent interaction are similar, but the viscosity is doubled, κ_{\max} decreases nearly linearly with increasing chain length (17). However, the large conductivity decrease from about 30 mS/cm to 5 mS/cm (17) shows, that other effects, namely association due to decreasing permittivity and increasing molecular volume of the molecules, diminishing their ability for solvation, cannot be neglected. Unfortunately, it is nearly impossible to change only one parameter in studies of this type. In the series of measurements of the conductivity of LiClO_4 in PC/DME mixtures for example, the increase of DME entails a change in the Stokes-radius of the lithium ion, which is preferentially solvated by DME (4).

Taking into account that solvent viscosity, solvation of ions and interaction of ions are the determining factors for κ_{\max} two strategies for improving the conductivity are available.

The first is the mixed solvent approach, which has been exemplified by us and others (4,17,132,153,154,155,156,151). Lowering the solvent viscosity by the addition of a low viscosity cosolvent, e.g. the addition of DME ($\eta = 0.407$ cP) to PC ($\eta = 2.512$ cP at 25 °C) yields an increase of κ_{\max} , at

least at concentrations up to about 80 w% of DME, see Fig. 3. At higher DME-content ion-association overcompensates the viscosity effect due to decreasing dielectric permittivity of the solvent mixture. For Me-THF based LiAsF₆ solutions, a more than 300% conductivity increase is observed when the mixed solvent EC/Me-THF is used (50).

The mixed solvent approach is especially useful at low temperatures where a conductivity increase of about 1000% can be obtained, cf. Fig. 4. Another benefit is the increase in solubility of the electrolyte, which is often observed in mixed solvents (132).

The second approach is based on the modification of the mixed solvent or of the anion which interacts with lithium. It is known since Gilkerson's and co-workers pioneering work (157,158,40), that the use of additives with good solvating properties for the cation, as evidenced by a high donor number, leads to huge conductivity increases at low electrolyte concentrations in low permittivity solvents. The ligand-molecules successfully compete with anions for a site in the vicinity of the cation, thus reducing ion pair formation. However, this feature results in only a smaller conductivity increase at high concentrations and may even have detrimental effects for intercalation electrodes if the donor molecule is a strong ligand for the cation and hence cointercalated into the cathode.

The chemical modification of anions may be performed with the help of fluorination or use of fluoro-ligands in synthesis. We have recently found (159) that the charge distribution at anions strongly influences the association behaviour of the electrolyte despite the fact that the cation-anion contact distance does not change. In the series CF_yH_xCOOLi / DMSO, (x + y = 3), the association constant increases from 10 (y = 3), 37.4 (y = 2), 115.0 (y = 1) to 488 (y = 0) at 25°C in accordance with expectation. The "electron-withdrawing" inductive effect of the F-substituents decreases the electron density at the carboxylate ions as can be confirmed from semiempirical quantum-mechanical calculations with the help of MOPAC (160). This effect reduces cation-anion interaction, and hence the association constant. The plot of ln(K_A) versus the mean oxygen charge q(O) is linear in accordance with expectation from electrostatic models of the association process, cf. Fig. 2. Unfortunately, the solubility of these salts is not sufficiently high to obtain a maximum for the correlation of K_A with κ_{max}. Currently studies with more soluble electrolytes are made to study the influence of the association on the conductivity-maximum without change of other parameters. It is interesting to note that the new electrolytes mentioned in section 3.1 also follow this strategy i.e. the delocalisation of the anionic charge.

References:

- (1) A.R. West, *J. Mater. Chem.* **1**, 157 (1991).
- (2) R. Haase and K.H. Drücker, *Z. Phys. Chem. N.F.* **46**, 140 (1965).
- (3) J. Barthel, H.J. Gores, and G. Schmeer, *Ber. Bunsenges. Phys. Chem.* **83**, 911 (1979).
- (4) H.J. Gores and J. Barthel, *J. Solution Chem.* **9**, 939 (1980).
- (5) T.D. Kaun, P.A. Nelson, L. Reddy, D.R. Vissers, and G.L. Henriksen, *Electrochim. Acta* **38**, 1269 (1993).
- (6) G.E. Blomgren and S.D. Jones, *Proc. Electrochem. Soc.* **92-16**, 379, (1992).
- (7) P. Colomban and A. Novak, in: *Proton conductors*. P. Colomban, (ed.), Cambridge University Press, Cambridge (1992).
- (8) D.O. Raileigh, *J. Appl. Phys.* **41**, 1876 (1970).
- (9) B.B. Owens, in: *Advances of Electrochemistry and Electrochemical Engineering*, P. Delahay, and C.W. Tobias, (eds.), Ch. 1, Wiley, New York (1971).
- (10) B.C. Tofield, (ed.): *Advanced Electrochemical Storage Devices. Final Report for the period 1st January 1978--31st March 1980*. Commission of the European Communities, Energy, EUR 7595 EN Vol. II, p. 111 (1982).
- (11) C.C. Liang, A.V. Joshi, and N.E. Hamilton, *J. Appl. Electrochem.* **8**, 445 (1978).
- (12) C.C. Liang, *J. Electrochem. Soc.* **120**, 1289 (1973).
- (13) J.E. Weston and B.C.H. Steele, *J. Solid State Ionics* **2**, 347 (1981).
- (14) K. M. Abraham and M. Alamgir, *J. Electrochem. Soc.* **137**, 1657 (1990).
- (15) M. Ue, M. Kaitoh, E. Yasukawa, and S. Mori, *Electrochim. Acta* **38**, 1301 (1993).
- (16) C.K. Mann, *Nonaqueous Solvents for Electrochemical Use in Electroanalytical Chemistry*, p. 57, A.J. Bard, (ed.), Marcel Dekker, New York (1969).
- (17) R. Herr, *Electrochim. Acta* **35**, 1257 (1990).
- (18) J. Heinze, *Angew. Chem.* **96**, 823 (1984).
- (19) M. Morita, M. Goto, and Y. Matsuda, *J. Appl. Electrochem.* **22**, 901 (1992).
- (20) R.A. Huggins, *Proc. Electrochem. Soc.* **87-1**, 356 (1987).
- (21) S. Ching, J.T. McDevitt, S.R. Peck, and R.W. Murray, *J. Electrochem. Soc.* **138**, 2302 (1991).

- (22) G. Geblewicz, R.J. Potter and D.J. Schiffrin, *Tans IMF* **64**, 134 (1986).
- (23) X. Andrieux, J.P. Boeuvre, and T. Vicedo, *J. Power Sources* **43-44**, 445 (1993).
- (24) K.M. Abraham and M. Alamgir, *J. Power Sources* **43-44**, 195 (1993).
- (25) J.F. Le Nest, S. Callens, A. Gandini, and M. Armand, *Electrochim. Acta*, **37**, 1585 (1992).
- (26) L.A. Dominey, T.J. Blakley, and V.R. Koch, *Proc. Intersoc. Energy Convers. Eng. Conf.*, 25th(Vol.3), 382 (1990).
- (27) D. Benrabah, D. Baril, J.Y. Sanchez, M. Armand and G.G.Gard, *J. Chem. Soc. Faraday Trans.* **89**, 355, (1993).
- (28) C.W. Walker, Jr. and M. Salomon, *J. Electrochem. Soc* **140**, 3409 (1993).
- (29) K.M. Abraham. in: B. Scrosati *Solid Polymer Electrolytes*, Ch.3, p.75, Chapman and Hall, London, (1993).
- (30) M. Moulton, R.D. Alamgir, and K.M. Abraham, *Proc. Electrochem. Soc.* **91-3**, 131 (1991).
- (31) P.S.S. Prasad, B.B. Owens, W.H. Smyrl, A. Scheaggi, and B. Scrosati, *Proc. Electrochem. Soc.* **91-3**, 170 (1991).
- (32) B.B. Owens and P.M. Skarstad, *Solid State Ionics* **53-56**, 665 (1992).
- (33) M. Armand, W. Gorecki, and R. Adreani, in: B. Scrosati, (ed.), *Second International Symposium on Polymer Electrolytes*, p. 91, Elsevier Applied Science, London (1990).
- (34) M. Armand, J.Y. Sanchez, M. Gauthier and Y. Choquette, in: *The Electrochemistry of novel materials*, J. Lipkowsky and P.N. Ross (eds.), VCH, Weinheim (1994).
- (35) H.P. Fritz, K. Stein, and R. Herr, *J. Power Sources*, **37**, 315 (1992).
- (36) H.P. Fritz and K. Stein, *Offenlegungsschrift DE 39 29 316 A 1*, *Offenlegungstag*: 7.3.91.
- (37) R. Jasinsky, *High-Energy Batteries*, Plenum, New York (1967).
- (38) G. Pistoia, *Bull. Electrochem.* **7**, 542, (1991).
- (39) G. Pistoia, *Chim. Ind.* **73**, 664, (1991).
- (40) H.J. Gores and J. Barthel, VCH Publishers, Weinheim, in press.
- (41) D. Linden, *Lithium Cells*. In: *Handbook of Batteries and Fuel Cells*, D. Linden (ed.) Ch. 11, McGraw Hill (1984).
- (42) F.L. Tye, (ed.), *Progress in Batteries and Solar Cells*, Vol. 9, p. 314, p. 316, JEC. Press, Brunswick, (1990).
- (43) Anonymous in *Rev. Gen. Electr.* (5), 61 (1993).
- (44) Molicel ®, A cell user guide, Moli Energy Ltd., Burnaby, B.C., Canada (1986).
- (45) K. Brandt, *J. Power Sources* **18**, 117 (1986).
- (46) K. Brandt and F.C. Laman, *J. Power Sources* **25**, 265 (1989).
- (47) F.C. Laman, J.A.R. Stiles, R.J. Shank, and K. Brandt, *J. Power Sources* **14**, 201 (1985).
- (48) K. Brandt, and F.C. Laman, *J. Power Sources* **25**, 265 (1989).
- (49) J.A.R. Stiles, *New Mater. New Processes* **3**, 89 (1985).
- (50) K.M. Abraham, *Electrochim. Acta* **38**, 1233 (1993).
- (51) S. James, P. Smith, T. Murphy, and D. Cason-Smith, *Progr. Batt. Sol. Cells* **9**, 238 (1990).
- (52) P. Smith, D. Chua, W. Ebner, S. James, and H.P. Lin, *Progr. Batt. Solar Cells* **9**, 229 (1990).
- (53) S. James, D. Cason-Smith, T. Murphy, and P. Smith, *Progr. Batt. Solar Cells* **9**, 244 (1990).
- (54) J.-P. Gabano, *Proc. Electrochem. Soc.* **88-6**, 311 (1988).
- (55) T. Nagaura, and K. Tozawa, *Progr. Batt. Solar Cells* **9**, 209 (1990).
- (56) T. Nagaura, *Progr. Batt. Solar Cells* **10**, 218 (1991).
- (57) K. Sekai, H. Azuma, A. Omaru, S. Fujita, H. Imoto, T. Enolo, K. Yamaura, M. Yokogawa, and Y. Nishi, 6th Int. Meet. on Lithium Batteries, extended abstract, p. 108, Münster, Germany (1992).
- (58) P. Di Pietro, M. Patriarca, and B. Scrosati, *J. Power Sources* **8**, 289 (1982).
- (59) B. Scrosati, *J. Electrochem. Soc.* **139**, 2776 (1992).
- (60) K. Sawai, T. Ohzuku, and T. Hirai, *Chem. Express* **5**, 837 (1990).
- (61) M. Morita, N. Nishimura, H. Tsutsumi, and Y. Matsuda, *Chem. Express.* **6**, 618 (1991).
- (62) M. Sato, T. Iijima, K. Suzuki, and K. Fujimoto, *Proc. Electrochem. Soc.* **91-3**, 407 (1991).
- (63) T. Ohzuku, and T. Hirai, 6th Int. Meet. on Lithium Batteries, extended abstract, p. 139, Münster, Germany (1992).
- (64) K. Momose, H. Hayakawa, N. Koshiba, and T. Ikehata, *Progr. Batt. Sol. Cells* **6**, 56 (1987).
- (65) M. Mohri, N. Yanagisawa, Y. Tajima, H. Tanaka, T. Mitate, S. Nakajima, M. Yoshida, Y. Yoshimoto, T. Suzuki, and H. Wada, *J. Power Sources* **26**, 545 (1989).
- (66) R. Kanno, Y. Takeda, T. Ichikawa, K. Nakanishi, and O. Yamamoto, *J. Power Sources* **26**, 535 (1989).

- (67) P. Horowitz and W. Hill, *The Art of Electronics*, Cambridge University Press, Cambridge (1989)
- (68) B.E. Conway, *J. Electrochem. Soc.* **136**, 1539 (1991).
- (69) B.E. Conway, *Proc. Int. Power Sources Symp.*, 34th, 319 (1990).
- (70) I.D. Raistrick, in: J. McHardy and F. Ludwig, (eds), *Electrochemistry of Semiconductors and Electronics*, Noyes Publication Park Ridge, New Jersey (1992).
- (71) L.A. Dominey, T.J. Blakeley, V.R. Koch, D.R. Vujic, and D.M. Schleich, *Proc. Int. Power Sources Conf.*, 35th, 290 (1992).
- (72) B.V. Tilak, C.P. Chen, and S.K. Rangarajan, *J. Electroanal. Chem.* **324**, 405 (1992).
- (73) K. Sanada and M. Hosokawa, *NEC Res. Development* **55**, 22, (1979).
- (74) P. Colombari and M. Pham-Thi, *Chem. Solid State Mater.*, 567 (1992).
- (75) M. Pham-Thi, G. Velasco, and F. Colombari, *J. Mater. Sci. Lett.* **5**, 415, (1986).
- (76) S.Noda, *JEE, J. Electron. Eng.* **28**, 94 (1991).
- (77) F.J. Burger and J.C. Wu, *J. Electrochem. Soc.* **118**, 2039 (1971).
- (78) M. Endo, Y. Okada and H. Nakamura, *Synth. Met.* **34**, 739 (1989).
- (79) D.C. Grahame, *Chem. Rev.* **47**, 441 (1947).
- (80) H. Yoneda, *J. Electron. Eng.* **29**, 102 (1992).
- (81) K. Mund and G. Richter, *Dechema Monographien* **90**, 173 (1981).
- (82) Y. Matsuda, M. Morita, M. Ishikawa, and M. Ihara, *J. Electrochem. Soc.* **140**, L109 (1993).
- (83) T. Morimoto, *Kagaku Kogyo* **43**, 998 (1992).
- (84) A. Nishino, *Tanso* **132**, 57 (1988).
- (85) S. Sekido, Y. Yoshino, T. Maranaka, and H. Mori, *New Mater. New Proc.* **1**, 184 (1981).
- (86) A. Yoshida, A. Nishino, and I. Tanahashi, *New Mater. New Proc.* **3**, 352 (1985).
- (87) I. Tanahashi, A. Yoshida and A. Nishino, *Bull. Chem. Soc. Jpn.* **63**, 3611 (1990).
- (88) I. Tanahashi, A. Yoshida and A. Nishino, *J. Electrochem. Soc.* **137**, 3052 (1990).
- (89) M. Nawa, T. Nogami, and H. Mikawa, *J. Electrochem. Soc.*, **131**, 1457 (1984).
- (90) T.A. Takei, *Surf. Techn.* **8**, 543 (1979).
- (91) A. Brenner in: *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 5, C.W. Tobias, (ed.), Interscience, New York (1967).
- (92) O. Popovych and R.P.T. Tomkins, *Nonaqueous Solution Chemistry*, Wiley, New York (1981).
- (93) U. Landau, *Jahrb. Oberflächentechn.* **46**, 163 (1990).
- (94) S. Takahashi and N. Koura, *Tetsu-to Hagane* **77**, 921 (1991).
- (95) M.P. Delplancke and A. Fontana, *ATB Metall* **29**, 49 (1989).
- (96) P.S. Searson, *Solar Eng. Mat. Solar Cells* **27**, 377 (1992).
- (97) J. Gobet and H. Tannenberger, *J. Electrochem. Soc.* **135**, 109 (1988).
- (98) J. Gobet and H. Tannenberger, *Proc. Electrochem. Soc.* **87-17**, 387 (1987).
- (99) A.E. Austin, US Pat. 3,990,953; Nov. 9 (1976) from: CA 86:10098c.
- (100) A.K. Agrawal and A.E. Austin, *J. Electrochem. Soc.* **128**, 2292 (1981).
- (101) E.R. Bucker and J.A. Amick, US Pat. 4,192,720; Oct. 16 (1980) from: CA 92:10098c.
- (102) Y. Takeda, R. Kanno, O. Yamamoto, T.R. Rama Mohan, L. Chia-Hao, and F.A. Kröger, *J. Electrochem. Soc.* **128**, 1221 (1981).
- (103) Y. Takeda, R. Kanno, K. Ohibayashi, Y. Nagata, and O. Yamamoto, *Denki Kagaku Oyoby Kogyo Butsuri Kagaku* **51**, 215 (1983) from: CA98:20649It.
- (104) T.R. Rama Mohan and F.A. Kröger, *Electrochim. Acta* **27**, 371 (1982).
- (105) A.S. Baranski and W.R. Fawcett, *J. Electrochem. Soc.* **127**, 766 (1980).
- (106) A.S. Baranski, W.R. Fawcett, and A.C. McDonald, *J. Electroanal. Chem. Interfac. Electrochem.* **160**, 271 (1984).
- (107) S. Preusser and M. Cocivera, *Sol. Energy Mater.* **15**, 175 (1987).
- (108) M.K. Carpenter and M.W. Verbrugge, *J. Electrochem. Soc.* **137**, 123 (1990).
- (109) B.N. Bhattacharya, R. Noufi, L.L. Roybal, and R.K. Ahrenkiel, *J. Electrochem. Soc.* **138**, 1643 (1991).
- (110) S.H. Pawar and H.A. Mujawar, *Mat. Res. Bull.* **25**, 1443, (1990).
- (111) J.M. Rosamilla and H.D. Rubin, *Proc. AESF Annu. Tech. Conf.* 76th, H1 (1989).
- (112) J.M. Rosamilla and B. Miller, *J. Electrochem. Soc.* **136**, 1053 (1989).
- (113) J.M. Rosamilla and B. Miller, *J. Mater. Res.* **5**, 1612 (1990).
- (114) H.D. Rubin, J.M. Rosamilla, H.M. O'Bryan Jr., and B. Miller, *Appl. Phys. Lett.* **54**, 2151 (1989).
- (115) H. Lehmkuhl, H. Mehler und U. Landau, in: *Advances in Electrochemical Science and Engineering*, Vol 3, Ch. 4, p.163.

- (116) R. Dötzer, *Chem. Ing. Techn.* **45**, 658 (1973).
- (117) K. Ziegler and H. Lehmkuhl, *Z. Anorg. Allg. Chem.* **283**, 414 (1956).
- (118) K. Ziegler, H. Lehmkuhl, and E. Lindner, *Chem. Ber.* **92**, 2320 (1959).
- (119) R. Dötzer, *Chem. Ing. Techn.* **36**, 616 (1964).
- (120) A. Böhm, H. Ginsberg, and W. Reuter, *Aluminium* **37**, 267 (1961).
- (121) S. Takahashi, I. Saeki, K. Tanaka, and H. Kanazashi, *Nisshin Seiko Giho* **60**, 36 (1989).
- (122) S. Birkle, *Proc. Electrochem. Soc.* **87-17**, 369 (1987).
- (123) E. Peled and E. Gileadi, *Annu. Techn. Conf. Am. Electroplat. Soc.* 68th, paper G2, (1981).
- (124) M. Elam, E. Peled, and E. Gileadi, *J. Electrochem. Soc.* **130**, 585 (1983).
- (125) G.A. Capuano, *J. Electrochem. Soc.* **138**, 484 (1991).
- (126) D.R. Sadoway, in: *New trends and approaches in electrochemical technology*, N. Masuko, T. Osaka and Y. Fukunaka, (eds.), VCH, Weinheim (1993).
- (127) D.R. Sadoway, *Proc. Elliott Symp. Chem. Process Metall.* MD 1990, 189 (1991).
- (128) D.R. Sadoway, *JOM* **43**, 15 (1991).
- (129) D.R. Sadoway, *Tungsten Tungsten Alloys Recent Adv. Proc. Symp.* 225 (1991).
- (130) R.M. Rose and D.R. Sadoway, US patent 4,517,253, May 14 (1985).
- (131) D.R. Sadoway and R.M. Rose, US patent 4,971,663, Nov 20 (1990).
- (132) H.J. Gores and J. Barthel, *Naturwiss.* **70**, 495 (1983).
- (133) A.N. Dey and R.W. Holmes, *J. Electrochem. Soc.* **126**, 1638 (1979).
- (134) A.N. Dey and R.W. Holmes, *J. Electrochem. Soc.* **127**, 775 (1980).
- (135) K.M. Abraham, in: *Lithium. Current Application in Science, Medicine and Technology*, R.O. Bach, (ed.), Wiley, New York (1985).
- (136) L.A. Dominey, J.L. Goldman, V.R. Koch, D. Shen, S. Subbarao, C.K. Huang, G. Halpert, and F. Deligiannis, *Proc. Electrochem. Soc.* **91-3**, 293 (1991).
- (141) L.A. Dominey, V.R. Koch, and T.J. Blakley, *Electrochim. Acta*, **37**, 1551 (1992).
- (142) M. Wühr, Thesis, Regensburg (1994); German Pat. Appl. 5084253, IPC H01M 6/14 P 43 16 104.9.
- (137) L.A. Dominey, in: *Lithium Batteries*, G. Pistoia, (ed.), Elsevier, Amsterdam (1994).
- (138) J.W. Johnson and J.F. Brody, *J. Electrochem. Soc.* **129**, 2213 (1982).
- (139) L.P. Klemann and G.H. Newman, *J. Electrochem. Soc.* **128**, 13 (1981).
- (140) H.R. Horowitz, J.I. Haberman, L.P. Klemann, G.H.J. Newman, E.L. Stogryn, and T.A. Whitney, *Proc. Electrochem. Soc.* **81-4**, 131 (1981).
- (143) M. Takahashi, S. Yoshimura, H. Watanabe, O. Hiroshi, F. Ryuji, S. Furukawa, Sanyo Electric Co, Japan, *Jpn. Kokai Tokkyo Koho*, JP 05074491, from: CA 119:121268 (1994).
- (144) A. Webber, *J. Electrochem. Soc.* **138**, 2586 (1991).
- (145) M.G. Armand and D. Muller, New electrolyte solutions for batteries, french patent: FR 2606217 from: CA:110:98805 (1994).
- (146) H. Yilmaz, E. Yurtsever, and L. Toppare, *J. Electroanal. Chem* **261**, 105 (1989).
- (147) T.C. Ehlert and M.M. Hsia, *J. Chem. Eng. Data* **17**, 18 (1972).
- (148) S. Sylla, J.Y. Sanchez, and M. Armand, *Electrochim. Acta* **37**, 1699 (1992).
- (149) J.F. Casteel and E.A. Amis, *J. Chem. Eng. Data* **17**, 55 (1972).
- (150) J. Barthel, H. Graml, T. Neumeier, R. Neueder, and V.K. Syal in preparation.
- (151) J.T. Dudley, D.P. Wilkinson, G. Thomas, R. LeVae, S. Woo, H. Blom, C. Horvath, M.W. Juzkow, B. Denis, P. Juric, P. Aghakian, and J.R. Dahn, *J. Power Sources* **35**, 59 (1991).
- (152) J. Barthel, H.J. Gores, G. Schmeer, and R. Wachter, *Top. Curr. Chem.* **111**, 33 (1983).
- (153) J. Barthel and H.J. Gores, *Pure Appl. Chem.* **57**, 1071 (1985).
- (154) J. Barthel, R. Wachter, and H.J. Gores, in: *Modern Aspects of Electrochemistry*, Vol. 13, Ch. 1, p. 1, Conway, B.E. and Bockris, J. O'M. (eds.), Plenum, New York (1979).
- (155) Y. Matsuda in: *Electrochemistry in transition*, O.J. Murphy, (ed). Plenum Press N.Y. (1992).
- (156) G.E. Blomgren, in: *Lithium Batteries*, J.E. Gabano, (ed.), Ch. 2, Academic Press, London (1983).
- (157) W.R. Gilkerson and J.B. Ezell, *J. Am. Chem. Soc.* **87**, 3812 (1965).
- (158) W.R. Gilkerson and E.K. Ralph III, *J. Am. Chem. Soc.* **87**, 175 (1965).
- (159) J. Barthel, L. Kraml, and H.J. Gores, in preparation.
- (160) J.J.P. Stewart, Mopac: A general molecular orbital package. Frank J. Seiler Research Laboratory, Colorado Spring, Colorado (1987).