

A new type of electrolyte for galvanic elements

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Abstract

Solid composite ionic conductors (CIC) with $\sigma_{r,i}$ as high as 10^{-2} S/cm are obtained by immobilizing solutions of lithium salts in aprotic solvents in inert, inorganic powders with a large specific surface area, such as pyrogenic silica. Cell capacities of Li|CIC|CuO, Li|CIC|FeS₂ and Li|CIC|MnO₂ cells compared with cells using conventional liquid organic electrolytes show increases between 11 and 126%. The lower polarization of a Li|CIC|polypyrrole cell proves that CICs can also be used for cells where cations and anions are involved in the cell reaction.

Zusammenfassung

Feste, zusammengesetzte Ionenleiter (CIC) mit $\sigma_{r,i}$ bis zu 10^{-2} S/cm erhält man durch Immobilisieren von Lithiumsalz-Lösungen in aprotischen Lösemitteln in inerten, anorganischen Pulvern mit grossen spezifischen Oberflächen, wie etwa pyrogenem SiO₂. Zellkapazitäten von Li|CIC|CuO-, Li|CIC|FeS₂- und Li|CIC|MnO₂-Zellen zeigen verglichen mit Zellen mit konventionellen, organischen Elektrolyten Zunahmen zwischen 11 und 126%. Die geringere Polarisierung einer Li|CIC|Polypyrrol-Zelle beweist, dass die CIC auch für Zellen verwendet werden können, bei denen Kationen und Anionen an der Zellreaktion teilhaben.

Introduction

In conventional secondary batteries, such as lead storage batteries or alkaline accumulators, the sulfuric acid or alkaline electrolytes are sometimes immobilized, e.g. by gelling. On the other hand the so-called high energy cells with alkali metal anodes always contain solvent-based liquid electrolytes. Mostly Li or Na salts of univalent anions like BF₄⁻, AlCl₄⁻, PF₆⁻, AsF₆⁻, ClO₄⁻ or CF₃SO₃⁻ are dissolved in solvents such as propylene carbonate, acetonitrile, γ -butyrolactone or methyltetrahydrofuran [1]. These electrolytes have room temperature specific conductivities $\sigma_{r,i}$ in the range 10^{-3} to 10^{-2} S/cm [2]. For more reliable solid batteries up to date polyether complexes of alkali salts of the general type poly[(ethylene oxide)_nM⁺X⁻], are suggested as the most positive representatives of solid ion conductors for practical purposes [3]; they have, however, $\sigma_{r,i}$ values of only $\leq 10^{-5}$ S/cm, i.e. definitely 2–3 orders of magnitude

too low for realistic applications. Therefore, there is an urgent need for easy to handle, low cost solid electrolytes with improved conductivities.

Various modifications of these polymer ion conductors have been proposed, but have not produced practical (useful) conductivities combined with thermal or chemical stability [4–6]. Additional attempts to provide solid ion conductors which are suitable as electrolytes and separators for solid batteries can be found in the patent literature.

Phenol-resin-based ion-exchange membranes which contain Zn^{2+} ions for the mobile phase which are used as electrolytes for galvanic solid-state elements with zinc anodes were proposed [7] as well as a pure Na zeolite (e.g. in a Cu/Zn element) functioning as an ion-conducting separator, and in addition to this, a Cu^{2+} zeolite which functions as a catholyte produced by a partial exchange of Na^+ ions [8]. By heating LiI together with aluminum oxide to 500 °C a solid ionic conductor with $\sigma_{r,t} = 10^{-4}$ S/cm was synthesized [9], which was supposed to function by surface conductivity [10].

Recently Scrosati and co-workers [11] reported on composite electrolytes formed by addition of 10 wt.% $\beta''\text{-Al}_2\text{O}_3$ to $(\text{PEO})_8\text{LiClO}_4$. While no improvement with respect to conductivity was possible, the authors observed a much lower passivation at the lithium/solid composite electrolyte interface than with usual PEO–LiX electrolytes, an observation which we can support from our results with complete test cells.

In the course of our study of potential solid ionic conductors [12], we found that solid to paste-like mixtures of inert materials (like SiO_2 , Al_2O_3 , TiO_2 , B_2O_3 , MgO as well as salts such as Na_2SO_4 and AlPO_4) with already mentioned ‘organic’ electrolytes (i.e. lithium or sodium salts dissolved in suitable organic, aprotic solvents), exhibit conductivities as high or even somewhat higher than the selected aprotic electrolyte systems alone and lead to solid, easily obtainable and inexpensive ion conductors with $\sigma > 10^{-3}$ S/cm at room temperature or even $> 10^{-2}$ S/cm at higher temperatures up to 100 °C. Depending on the basic aprotic solvent a temperature range from c. –50 °C to temperatures near the boiling point of the pure solvent can be used. It is essential to use solids with extensive surface areas.

Experimental

The chemicals used were commercial products, dried prior to use by conventional means, and kept under dry N_2 . The inert oxidic solid supports were products of Degussa AG, Frankfurt/Main, and have the essential properties given in Table 1.

The composite ionic conductors (CIC) are prepared by mixing the inert solid support (A) with the liquid electrolyte (mostly 1 M solutions of Li or Na salts in the selected aprotic solvent) (B) under N_2 . Between 1 and 10 ml of B are used per g of A. In order to be able to compare the conductivities of all preparations, as a rule, mixtures were made which were still ‘just pourable powders’ or (with regard to practical application in battery manufacturing) already ‘just paste-like’, – which are admittedly rather vague terms. It is interesting to observe that 1–2 drops (< 0.1 ml) of additional electrolyte solution suffice to change the consistency from powder to paste.

The ‘still pourable powders’ are obtained – as shown exemplarily from 1 M LiClO_4 /propylene carbonate solutions – with different mixing ratios: ml solution/g solid, Table 2.

The resulting specific conductivities, σ , or rather the resistances R were measured several times per sample for discs of a thickness of 0.7–1.0 mm and a diameter of 13 mm as pressed solids or as pastes in a PTFE ring at different temperatures using

TABLE 1

Some characteristic properties of inert support materials

Support material	Surface area (m ² /g)	Particle size (nm)	Method of synthesis	Composition
Aerosil 90	90 ± 30	20	pyrogenically	SiO ₂
Aerosil 200	200 ± 25	12	pyrogenically	SiO ₂
Aerosil 380	380 ± 30	7	pyrogenically	SiO ₂
Sipernat 50	450	50.000	by precipitation	SiO ₂
Aerosil COK 84	170 ± 30		pyrogenically	SiO ₂ + Al ₂ O ₃ (4:1)
Al ₂ O ₃ C	100 ± 15	20	pyrogenically	Al ₂ O ₃
TiO ₂ P 25	50 ± 15	30	pyrogenically	TiO ₂

TABLE 2

Solution (ml)/solid (g) ratios for obtaining pourable powers

Aerosil 90	4.8/1
Aerosil 200	6.0/1
Aerosil 380	8.1/1
Aerosil COK 84	7.0/1
Al ₂ O ₃ C	5.9/1
TiO ₂ P 25	3.6/1
Sipernat 50	3.9/1

an a.c. bridge (4 kHz) or the resistance R of the electrolyte alone was determined by conventional impedance spectroscopy in the frequency range 0.1 Hz to *c.* 500 kHz. All tabulated σ values are quoted as round figures in mS/cm. Temperature variation was in 10 °C steps with 30 min intervals to allow for thermal equilibration before measuring.

The apparatuses used were: a.c. bridge, Conductimètre CD 6 N (Fa. Tacussel), precision current source (Fa. Knick), Multimeter model 172 A (Fa. Keithley), Eurotherm temperature controller model Therm 4200 (Fa. Ahlborn), and x/t recorder model Servogor 220 (Fa. BBC Goerz) for the two-point measurements, otherwise an IM5d impedance spectrometer (Fa. Zahner-Elektrik, Kronach, FRG) combined with temperature control system Therm 4227 and Therm 4190 with Ni/Cr/Ni thermo sensor (Fa. Ahlborn), with peripheral units.

The measuring cells were constructed from Turbotherm steel 1613 NB (Fa. Böhler) and the pressure stable parts from RUS steel, vacuum hardened to 61 Rockwell. The inner parts of the cells were made from aluminum oxide ceramic (Fa. Hoechst CeramTech) or from PTFE.

The cell study was carried out using button cells size 2025. The standard cells used for comparison consisted of working electrode, 1 Celgard 3501; 1 Kodoshi 334103 and the lithium counter electrode. They were vacuum-filled with 1.0 M LiClO₄/propylene carbonate.

The cells with the composite ion conductor (CIC-cells) consisted of working electrode, the CIC without separator and the lithium counter electrode. The CIC

was prepared by mixing 2.2 g Aerosil 200 with 15.0 ml 1.0 M LiClO₄/propylene carbonate.

Lithium cycling experiments were undertaken at a current density of 1 mA/cm² at one hour rate; Li/coke tests at a current density of 0.5 mA/cm² (0–1.0 V versus Li/Li⁺); Li/polypyrrole (PPy) tests at a current density of 0.5 mA/cm² (2.0–3.7 V versus Li/Li⁺). The primary cells were discharged with 1.0 mA/cm² until a cell voltage of 1.0 V was reached. All cell measurements were made using an in-house-built computer controlled current supply and data logger.

Results and discussion

Table 3 shows the temperature dependence of σ (mS/cm) as measured by impedance spectroscopy of two lithium salts dissolved in three solvents as they are commonly used in high energy battery research. First of all it is evident, that these ionic conductors have much higher room temperature (r.t.) specific conductivities than all other practical solid or paste-like conductors reported. The low temperature range allows for practical application in conventional batteries. Obviously, the choice of salt as well as solvent has an effect. Compared with the values for a pure LiClO₄/PC solution a slight increase in σ can be observed. This might be caused by a marked surface conductivity of our mixtures. However, as Table 4 shows, there is an optimal mixing ratio x ml electrolyte/g solid as exemplified by the system 1 M LiClO₄/PC immobilized in Aerosil 200 at various temperatures.

The amount of LiClO₄ introduced by 6 ml 1 M solution, i.e. the optimal condition, can be estimated to be sufficient to cover the available surface of the solid particles more than six-fold. Therefore, the conduction should occur by migration as a liquid phase. Applying a modified Born equation proposed by Abe [13] one can estimate diameters for spherical cavities around Li⁺ and ClO₄⁻ of 210 and 500 pm, respectively, in bulk solutions. Assuming spherical particles, as they are typical for pyrogenic silicas, and an average size of 12 nm in Aerosil 200 a mean pore size of almost 2 nm should leave ample space for migration of even solvated ions. Therefore, we see the reason for the increased conductivity compared with pure liquid electrolyte as an electroosmotic phenomenon. It is known [14], that the direction of electroosmotic movement follows the empiric rule, that the phase with the higher dielectric constant ϵ is charged positively against the other phase. This effect is even amplified in capillary systems [15, 16]. Combined with specific adsorption of anions at the oxidic surface of Aerosil etc. and ϵ (quartz) = 4.3 and ϵ (solvent) = 36 and more (as used here) it is conceivable, that cations can move more freely in the solution phase of our composite material than in pure solvents. This effect should not be lost even at low temperatures. Additionally it is known from the study of aqueous systems [17] that ions can penetrate into the so-called porous double layer, the penetration depth with silica being *c.* 0.7 nm. Again this effect would enhance the mobility of counter ions in solution. This aspect is supported by the fact shown in Table 5, namely that σ varies with the solid support material.

As can be seen the variation is not a simple function of the specific surface area (cf. Table 1), for Sipernat 50, a silica made by precipitation reaction and having the largest surface area of all tested solids, has the lowest σ value. On the other hand there is no linear correlation with the amount of electrolyte solution immobilized, cf. Table 2. Additionally a pronounced 'maturing' effect is observed on storage of the mixed conductors. Thus, for example $\sigma_{r.t.}$ of 1 M LiClO₄/AN improves as:

TABLE 3

Temperature dependence of σ (mS/cm) of 6 ml 1 M LiX/aprotic solvent immobilized in 1 g Aerosil 200; AN = acetonitrile, BL = γ -butyrolactone, PC = propylene carbonate; measured by impedance spectroscopy 1 week after preparation

Temperature (°C)	Temperature Immobilized				Pure solution			
	1 M LiClO ₄ /AN	1 M LiCF ₃ SO ₃ /AN	1 M LiClO ₄ /BL	1 M LiCF ₃ SO ₃ /BL	1 M LiClO ₄ /PC	1 M LiCF ₃ SO ₃ /PC	1 M LiClO ₄ /PC	
-50	3.2	3.7	2.4	0.6	1.0	0.2		
-40	4.2	4.4	3.0	0.9	1.2	0.4		
-30	5.7	5.0	3.6	1.1	1.5	0.6	1.2	
-20	7.6	5.7	4.4	1.5	2.0	0.9		
-10	9.8	6.4	5.3	1.8	2.5	1.1	3.2	
0	13.4	7.1	6.4	2.3	3.3	1.4		
10	19.1	7.7	7.4	2.7	4.3	1.8		
22	22.1	8.4	9.4	2.9	5.8	2.1	4.8	
32	24.8	9.2	10.0	3.3	7.1	2.5	5.9	
40	28.0	10.0	10.9	3.7	8.4	3.0	6.8	
50	30.7	11.0	12.1	4.2	9.8	3.4	7.8	
60	32.8	11.9	13.8	4.6	10.8	3.9	8.9	
70	34.4	12.7	15.5	5.1	11.9	4.4	9.9	
80	35.9	13.9	16.9	5.5	13.3	4.8	10.7	
90					14.4			
100					15.6			

Time of storage (weeks)	0	1	10	16
$\sigma_{r.t.}$ (mS/cm)	15	22.1	27.4	28

Presumably the penetration of ions into the porous double layer or the formation of a more uniform distribution of solution in all pores of the solid phase to be 'wetted' is a slow reaction.

To estimate the practical value of the new CICs complete button cells were built and compared with corresponding standard cells (liquid electrolyte + separator). The tests were carried out with six electrode couples (Li/Li; Li/carbon; Li/polypyrrole (PPy); Li/MnO₂; Li/CuO; Li/FeS₂).

The lithium-lithium cycling experiment (one hour rate; 1 mA/cm²) showed a much lower polarization behaviour for the CIC cell in comparison with the standard cell (Fig. 1), while the overall cycling efficiency is exactly equal (79%). When carbon material (coke) is doped and undoped with lithium, the specific capacity of the carbon material in the cell with the CIC electrolyte is higher and much more stable than in the standard cell (Fig. 2).

TABLE 4

$\sigma_{r.t.}$ (mS/cm) as function of the mixing ratio for x ml 1 M LiClO₄/PC immobilized in 1 g Aerosil 200

T (°C)	1/1	2/1	3/1	4/1	6/1	8/1	10/1	Pure solution
22	0.7	3.5	4.2	5.0	5.8	5.8	5.5	4.8
40	0.9	4.8	5.1	6.0	8.4	6.6	6.2	6.8
60	1.3	6.5	7.2	7.4	10.8	8.0	7.1	8.9
80	2.1	8.1	9.1	9.2	13.3	9.6	8.4	10.7

TABLE 5

$\sigma_{r.t.}$ (mS/cm) of 1 M LiClO₄/BL pastes made by immobilizing in different solid supports

Aerosil				Al ₂ O ₃ C	TiO ₂ P 25	Sipernat 50
90	200	380	COK 84			
7.0	9.4	9.7	8.8	8.0	7.9	6.4

TABLE 6

Comparison of (Li/cathode) cell capacities

Cathode material	Standard cell (A h/kg)	CIC cell (A h/kg)	Increase (%)
CuO	184	215	17
FeS ₂	122	276	126
MnO ₂	194	216	11

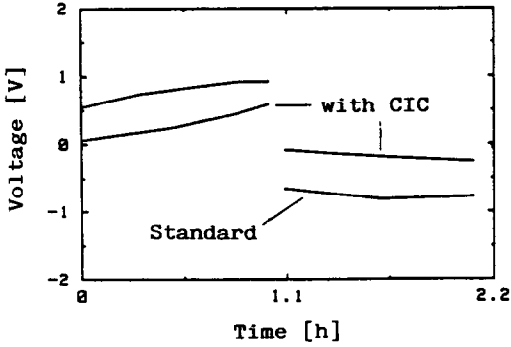


Fig. 1. Polarization behaviour of Li/Li cells during cycling.

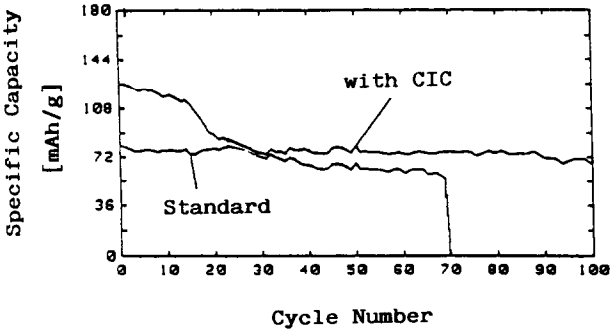


Fig. 2. Specific capacity of carbon in Li/C cells during cycling.

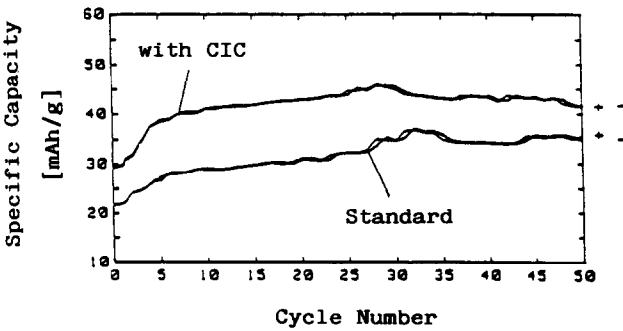


Fig. 3. Specific capacity of polypyrrole in Li/PPy cells during charge (+) and discharge (-).

A Li/CIC/polypyrrole couple shows a superior behaviour, too (Fig. 3). The lower polarization of this cell (Fig. 4) proves, that CICs are not only suitable for cells with cation exchange, but also for systems where anions and cations are involved in the cell reaction.

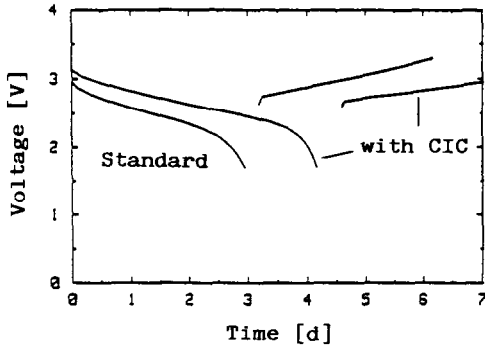


Fig. 4. Polarization behaviour of Li/PPy cells during cycling.

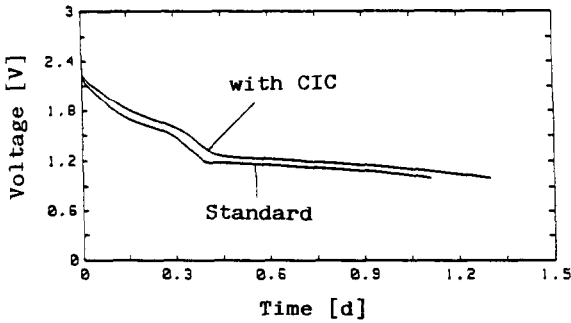


Fig. 5. Discharge curves of Li/cuO cells.

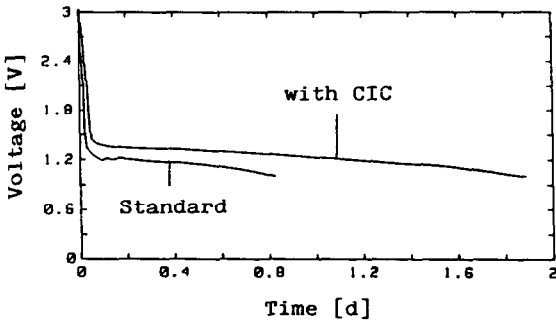


Fig. 6. Discharge curves of Li/FeS₂ cells.

Primary cells with CIC electrolytes have higher discharge voltages than standard cells (Figs. 5-7). The result is an improved capacity of various cathode materials when discharged to a certain cut off voltage (1.0 V).

The improved performance of cells with CIC electrolytes can be explained in terms of a lower concentration polarization due to a higher mobility of the cations.

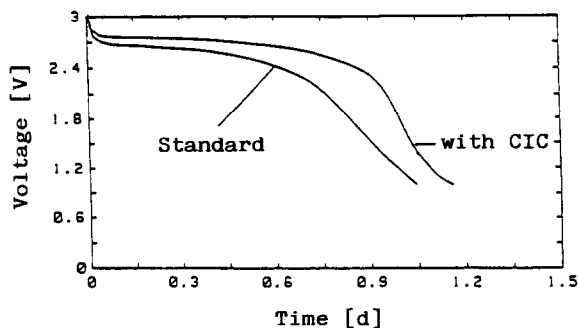


Fig. 7. Discharge curves of Li/MnO₂ cells.

Further investigations will focus on the transference number and the CIC/electrode interface.

Acknowledgements

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