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Glassy materials for lithium batteries: electrochemical properties and devices performances

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Abstract

Amorphous or glassy materials may be used as electrolyte or electrode materials for lithium primary or secondary batteries. A first generation proceeded from classical coin cells in which the organic electrolyte was replaced by a high lithium conductive glassy electrolyte. The solid components were assembled under isostatic pressure. The main advantages of such cells are a good storage stability and ability to operate until 200°C. Nevertheless, the high resistivity of the glassy electrolyte below room temperature and a limited depth for charge and discharge cycles makes these cells not competitive compared to conventional lithium-ion batteries. More promising, are the thin films solid state microbatteries realised by successive depositions of electrodes and electrolyte. The low resistance of the electrolyte amorphous layer allows cycling at temperatures as low as -10°C. The total thickness of thin film batteries, including packaging is less than 100 µm. A capacity of about 100 µAh cm⁻² with over 10⁴ charge–discharge cycles at 90% in depth of discharge is well suited for energy independent smart cards or intelligent labels, which represent for these devices a large and unrivalled market. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many new secondary batteries systems have been studied in the last 20 years for a wide range of applications. At the present time, the so-called Li-ion batteries are widely used in portable devices. In the near future an extension of lithium batteries applications towards higher energy supplies (electric vehicle) or lower consuming systems (smart cards, implantable medical devices) is expected.

Conventional lithium batteries systems contain a liquid electrolyte, generally a concentrated organic solution of a lithium salt. The liquid state offers good contacts with the solid electrodes and an ionic conductivity which is slightly temperature dependent, allowing stable performances in the temperature range from -20 to +60°C. On the other hand, lithium cations, and also its associated counter anion and solvent molecules are mobile and give rise to the formation of passivation layers at the electrode/electrolyte interfaces.

The use of a solid electrolyte may overcome these difficulties. In a lithium crystalline or glassy solid electrolyte, the

only mobile species is the Li⁺ cation, because its associated anion is immobilised in a crystalline lattice or in a rigid macromolecular network. Examples include LiI, lithium solid electrolytes of NASICON-type structure, and inorganic oxide or sulphide glasses. Their use in all solid state batteries are described in previous review articles [1–3]. The blocking of the anion and solvent prevents the detrimental passivation of the electrodes, subsequently enlarging the practical red/ox stability domain of the solid electrolyte far above the range fixed by thermodynamics. Under these conditions, the electrolyte can coexist with red/ox couples which are highly reducing at the negative electrode and highly oxidising at the positive one.

Basically, a solid state battery corresponds to an electrochemical chain characterised by the continuity of the cationic transport from one electrode to the other. During discharge, this chain enables the transfer of lithium from a high chemical potential (anode) to a lower chemical potential (cathode). The electrical energy, EF , which is the product of the potential E (V) by the Faraday constant F , liberated while discharging, is equal to the change in lithium free energy $\Delta\bar{G}_{\text{Li}}$ associated with this transfer.

$$EF = \Delta\bar{G}_{\text{Li}} \quad (1)$$

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Practically, part of this electrical energy is dissipated by Joule effect in the electrolyte and at each positive and negative interfaces. Optimising the available energy requires to minimise the electrolyte resistance and to decrease the current density at the interfaces which can be done by increasing the contact areas.

For these reasons, glassy materials as solid electrolytes are of special interest, because several glass compositions present good lithium conductivities (10^{-4} to 10^{-3} S cm $^{-1}$ at room temperature) [4]. In addition, thin film technologies allow the manufacturing of solid state batteries with thin electrolyte thickness and large electrochemically active interfaces. In many cases, these techniques lead to the preferential formation of amorphous phases for the electrolyte or mixed conductive electrodes.

At this point a remark on terminology will be useful. The term ‘amorphous solid’ is the more general, applicable to any solid having a non periodic atomic array. The term ‘glass’ is conventionally reserved for an amorphous solid actually prepared by quenching a liquid melt. Since there are other ways (sputtering, CVD, sol–gel techniques, etc.) to prepare amorphous solids, the conventional term ‘glass’ is restrictive and, in this paper, both terms will be used synonymously.

2. Glassy electrolytes

Ionically conducting glasses generally associate three compounds: (1) a network former; (2) a network modifier and (3) a doping salt. The absence of structural constraints allows to easily modify their relative content to optimise electrical and electrochemical properties.

Network formers are covalent oxides or sulphides as SiO $_2$, P $_2$ O $_5$, B $_2$ O $_3$, SiS $_2$, P $_2$ S $_5$, etc. They form strongly cross-linked macromolecular chains facilitating the glass formation by quenching from a liquid or vapour phase. When the quenching rate is fast enough, the macromolecular chains are frozen and cannot reorganise to a stable ordered crystalline structure. The obtained solid phase, out of thermodynamic equilibrium, is called a glass. This glass is kinetically stable at low temperature. Above a so-called glass transition temperature, T_g , the thermal energy allows local chain movements and the glass may develop to the thermodynamically stable crystalline phase.

When lithium oxide or sulphide, Li $_2$ O or Li $_2$ S is added to the network former, it chemically reacts, breaking the oxygen or sulphide bridges. For this reason, they are called network modifiers. Each lithium oxide (or sulphide) molecule introduce two ionic bonds formed by non bridging and negatively charged oxygen (or sulphur) which is associated to a lithium cation. This chemical reaction decreases the average length of the macromolecular chains. Increasing the amount of modifier makes the glass less stable and decrease the glass transition temperature.

Ionic salts (LiI, Li $_2$ SO $_4$, etc.) are often added to a glassy matrix, since such an addition significantly enhances the

ionic conduction by several orders of magnitude compared to that of a glassy matrix made of only network formers and network modifiers. It has been shown that these doping salts do not chemically react with the network former [5] and their dissolution only occurs by dipole–dipole interactions. It has been also shown that the associated anion has a very low transference number [6].

A lithium-ion conducting glass usually contains one or two network formers, one network modifier and eventually one doping salt. Ionic transport measurements, as well as cyclic voltammetry, show that the Li $^+$ transference number is unity. Below the glass transition temperature, the ionic conductivity, σ_+ , obeys the Arrhenius law expressed by

$$\sigma_+ T = A_+ \exp\left(-\frac{E_\sigma}{RT}\right) \quad (2)$$

where A_+ is the pre-exponential factor and E_σ the conductivity activation energy and T the absolute temperature. Interestingly, for all glass compositions, the A_+ values are almost constant and the wide range of conductivities observed at room temperature is the result of the dependence of E_σ with composition, typically varying from 0.35 to 0.70 eV.

The chemical composition of some Li $^+$ glassy electrolytes used in lithium batteries and their conductivities at room temperature are reported in Table 1. A microscopic understanding of the ionic transport in glasses may be proposed by extending to these materials the point defect approach usually applied to ionic crystals. In this model, the ionic transport mechanism could be attributed to the formation and migration of interstitial cationic pairs [12].

3. Mixed conductive glasses

Oxide glasses containing transition metal oxides are known to exhibit electronic conductivity. Because pure transition metal oxides do not easily form a glass alone, the stability of glassy phases is obtained by the addition of a conventional network former, such as SiO $_2$, P $_2$ O $_5$, or TeO $_2$. They may also incorporate in their structure intercalated alkali metals. In case of lithium, the Li $^+$ cations are dispersed in the voids of the glassy matrix and the associated electron is located in the d-orbitals of the transition metals. Due to the disordered structure, the electron displacement is generally interpreted by the small polaron model [13].

Table 1
Chemical compositions of some Li $^+$ glassy electrolytes and their conductivities at room temperature

Glass composition	$\sigma_{25^\circ\text{C}}$ (S cm $^{-1}$)	Reference
0.45LiI–0.37Li $_2$ S–0.18P $_2$ S $_5$	1.0×10^{-3}	[7]
0.6Li $_2$ O–0.3B $_2$ O $_3$ –0.08SiO $_2$	1.2×10^{-6}	[8]
0.45LiI–0.34Li $_2$ S–0.02Li $_2$ O–0.18P $_2$ O $_5$	5.0×10^{-4}	[9]
0.01Li $_3$ PO $_4$ –0.63Li $_2$ S–0.36SiS $_2$	2.0×10^{-3}	[10]
Li $_{3.3}$ PO $_{3.8}$ N $_{0.22}$	3.3×10^{-6}	[11]

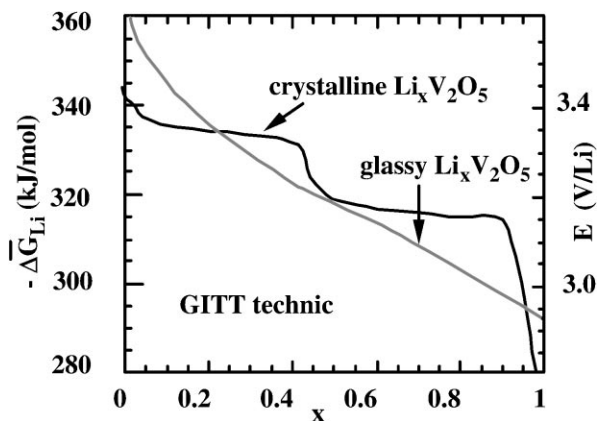


Fig. 1. Variations in the partial free energy of lithium cation as a function of the intercalation ratio x in crystalline and glassy $\text{Li}_x\text{V}_2\text{O}_5$, after Gavriluk [19].

The intercalation reaction of lithium in an electronically conducting glass has been thermodynamically and kinetically studied on several V_2O_5 containing glasses, for instance in the $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$, $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3$, $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5\text{-B}_2\text{O}_3$ systems and pure V_2O_5 glass [14–19]. The variations in $\Delta\bar{G}_{\text{Li}}$ as a function of the intercalation ratio x in crystalline and glassy $\text{Li}_x\text{V}_2\text{O}_5$ are compared in Fig. 1.

The monotonic variation of $\Delta\bar{G}_{\text{Li}}$ observed with the lithium content in glassy $\text{Li}_x\text{V}_2\text{O}_5$ lead to suppose that the inserted lithium-ions are distributed over energetically non-equivalent sites in the glass matrix.

By impulse technique or impedance spectroscopy, it has been possible to determine the lithium diffusion coefficient \bar{D}_{Li} and the usual values at room temperature, for V_2O_5 containing glasses lies between 10^{-8} and 10^{-13} $\text{cm}^2 \text{s}^{-1}$.

Cyclability of glassy cathode materials has been tested. More than 500 cycles have been obtained for a $\text{Li/PC-DME-2MeTHF-LiAsF}_6/\text{V}_2\text{O}_5$ glass cell under a charging–discharging current density of 0.5 mA cm^{-2} . A better stability in the specific capacity is observed on glassy V_2O_5 compared to crystalline V_2O_5 [19].

Most of mixed conductive glasses currently contain V_2O_5 as active component and are studied as positive electrode materials. Some compositions may also be of interest as

negative electrodes. It is the case of amorphous Fe_3O_4 deposited as a thin layer by rf sputtering [20] or glasses in the $\text{SnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ system obtained by quenching [21] or mechanochemical synthesis [22]. For these glasses, it has been shown that, during the first discharge, SnO is reduced as metallic tin and lithium form Li_2O . Metallic tin is dispersed as clusters in a $\text{Li}_2\text{O-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glass. The tin reacts with further lithium to the composition limit $\text{Li}_{4.4}\text{Sn}$, which corresponds to a specific anodic capacity of 991 mAh g^{-1} , and during charge, Li is removed from lithium–tin alloy. During cycling, however, tin cluster size increase and simultaneously an important loss in capacity is observed [23]. A similar behaviour has been observed on thin films of amorphous silicon–tin oxynitride anode deposited by rf magnetron sputtering. While charging this compound with composition, $\text{SiSn}_{0.87}\text{O}_{1.2}\text{N}_{1.72}$ is reduced as Li_xSn and Li_xSi dispersed in an amorphous matrix of Li , Sn and Si oxynitrides [24].

4. Glassy electrolyte lithium coin cells

The first attempt to produce a primary lithium battery using a glassy electrolyte has been done in 1981 by the French SAFT Co. [25] using the pressed powder of a glass with the composition $0.29\text{LiI-0.47Li}_2\text{S-0.24P}_2\text{S}_5$ ($0.55\text{LiI-0.45Li}_4\text{P}_2\text{S}_7$), a lithium anode, and a composite cathode (36% TiS_2 , 7% graphite, 30% glass electrolyte). An alternative battery consisted of $\text{Bi}_4\text{B}_2\text{O}_9$ as cathode, leading to the irreversible formation of Bi , Li_2O and B_2O_3 .

A similar glassy electrolyte with a higher content in LiI ($0.71\text{LiI-0.29Li}_4\text{P}_2\text{S}_7$) is used in a commercially marketed solid state battery by Energizer Co. [26,27]. The battery is manufactured by first pressing a composite cathode (50–85% TiS_2 and the rest with glassy electrolyte) and then pressing a thin layer of pure electrolyte onto the cathode. Finally, a Li metallic disk is added and the complete stack is isostatically pressed and sealed in a coin cell package. These batteries can be discharged at current density up to 300 mA cm^{-2} , showing good pulse performance and operating from -40 to $+150^\circ\text{C}$ (Fig. 2a). Later, part of the

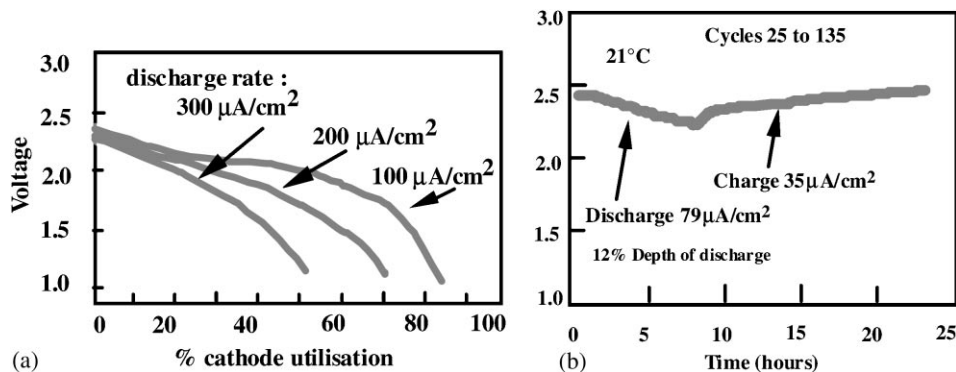
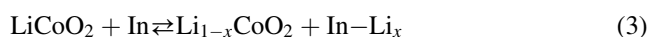


Fig. 2. (a) Efficiency of a Li/TiS_2 coin cell with a glassy electrolyte at different current densities, after Akridge and Vourlis [26]. (b) Secondary performance of a $\text{Li/glassy electrolyte/TiS}_2$ cell, after Akridge and Vourlis [27].

sulphur atoms were substituted by oxygen and the following glassy electrolyte $0.71\text{LiI}-0.29\text{Li}_4\text{P}_2\text{O}_{0.125}\text{S}_{6.875}$ was synthesised and used, allowing a good reversibility at 12% depth of discharge as shown in Fig. 2b.

More recently, Matsushita Battery Co., Japan has realised solid state batteries using a sulphide based glass as the electrolyte with a composition of $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$ obtained by twin roller quenching. The doping of the sulphide glass by a small amount of Li_3PO_4 increases the ionic conductivity (up to 10^{-3} S cm^{-1} at room temperature) as well as the electrochemical stability [10]. The absence of I^- in the glass structure, which may be slowly oxidised, allows the use of highly oxidising positive electrode materials.

A solid state lithium battery was fabricated with $\text{Li}_{1-x}\text{CoO}_2$ as the positive, and metallic indium as negative, allowing the total reaction.



Coin type cells of 20 mm in diameter and 1.6 mm in thickness, were assembled with 15 mAh in capacity and 104 mWh cm^{-3} in energy density. The charge–discharge efficiencies were almost 100% and no degradation was found after 100 cycles. A lithium ‘rocking chair’ cell was also constructed using $\text{Li}_{(4/3)+x}\text{Ti}_{5/3}\text{O}_4$ as negative electrode showing an excellent cyclability [28].

For all solid state lithium cells described above, the glassy electrolyte is ground as a fine powder and pressed into pellets of about 200 μm thick between the two electrodes. Compared to the bulk glass, the pellet’s conductivity is about one order of magnitude lower, and this technique is hence restricted to high conductive sulphide glasses which cannot be handled in air because of extreme sensitivity to oxygen and moisture.

In addition, this technique does not allow good and stable interfacial contacts between the different solid components of the cell. The volume changes which accompany the intercalation–deintercalation processes or lithium dissolution lead to an irreversible decrease of the efficiency of the electrochemically active interface [29]. It is probably the reason why all cycling tests reported on solid state coin cells do not exceed 20% for depth of discharge. To overcome these two inconveniences, i.e. loss in ionic conductivity and poor interfacial contacts, glass polymer composites electrolytes have been recently investigated [30].

5. Thin film lithium batteries with glassy electrolytes

The miniaturisation of electronic devices has resulted in very low current and power requirements for many applications (smart cards, CMOS back up, implantable medical devices, microelectromechanical systems (MEMS)). This has enabled the use of thin film rechargeable microbatteries as power sources for these devices.

As pointed out earlier [31], some of the advantages offered by thin film microbatteries include:

1. they are manufactured by the same techniques as currently used in the microelectronics industry;
2. the very low thickness allows to use oxide glasses as electrolyte, less conductive, but easier to handle than the sulphide glasses;
3. the successive deposition processes allows to provide large and good electrochemical active interfaces.

Interestingly, the use of new techniques, like sputtering, allowed to synthesise new and unexpected compositions for the electrolytes (ex: LiPON glass) or the positive (ex: amorphous titanium oxysulphide).

The first thin film microbatteries have been designed in 1980s [32–34] and three projects have presently reached the pre-industrial level. The first one is a joint project of Bordeaux University [35,36] with Hydromécanique et Frottements (HEF) a French company specialised in thin film technologies. The positive electrode is an amorphous titanium or molybdenum oxysulphide ($\text{TiO}_{0.2}\text{S}_{1.4}$ or $\text{MoO}_{1.6}\text{S}_{1.8}$) film deposited from TiS_2 or MoS_2 targets. The presence of oxygen in sputtered films is due to traces of oxygen in the sputtering chamber and it has been found that the partial substitution of sulphur by oxygen improves the electrochemical behaviour. Glassy oxide based electrolyte film with a similar thickness is then deposited by the same technique and finally the negative lithium electrode (4–5 μm in thickness) is obtained by vacuum evaporation. A hydrophobic polymer film protects the battery from moisture (Fig. 3).

The thickness of the thin film battery is less than 10 μm and the final product, including the air-tight package, is less than 0.1 mm thick. The cells have a surface of about 2 cm^2 and may deliver a maximum current density of about $200\text{ }\mu\text{A cm}^{-2}$ for 10 min under an average potential of 2.0 V. More than 10,000 charge–discharge cycles have been performed.

Energy independent smart cards for safe bank transactions could be the first product to be targeted by these microbatteries. This market is very large since 4 billions smart cards are estimated to be produced in the year 2000. Another important application expected would be related to wireless electronic shelf edge labels soon to be developed for intelligent packaging in supermarkets.

A similar project has been developed at Eveready Battery Co. [37]. Thin film solid state Li/TiS₂ microbatteries are fabricated by sputtered depositions of the metal contacts, TiS₂ cathode and an oxysulphide glass as electrolyte. This electrolyte is sputter deposited from a target with the composition $6\text{LiI}-4\text{Li}_3\text{PO}_4-\text{P}_2\text{S}_5$. The conductivity of the glassy thin films is $2.10^{-5}\text{ S cm}^{-1}$. It has been found that the metallic lithium anode could react with this electrolyte forming a high resistance layer, probably Li_2S . To avoid a direct contact between lithium and the electrolyte, an intermediate LiI layer is deposited by vacuum evaporation. The total ionic conductivity of this two layered electrolyte (glassy electrolyte + LiI) is $2.10^{-6}\text{ S cm}^{-1}$.

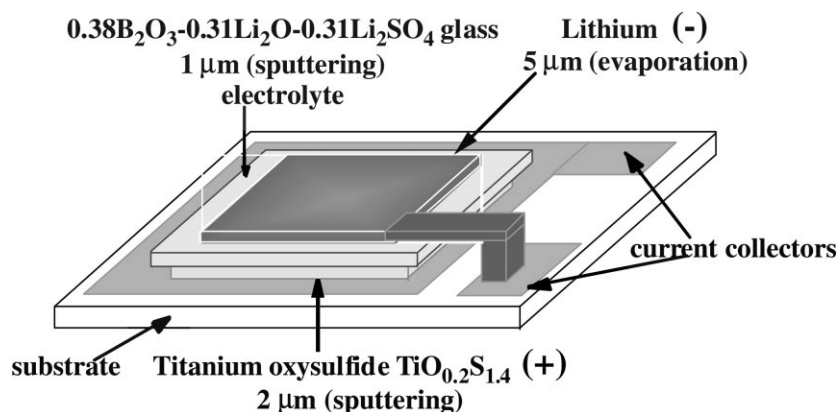


Fig. 3. Thin film Li/glassy electrolyte/TiS₂ microbattery, after Levasseur and Vinatier [35].

Typically, these microbatteries have a total thickness around 10 μm including the protective package and an OCV between 2.4 and 2.5 V. Their capacity range lies between 5 and 100 μAh cm⁻² depending on the amount of active materials. They routinely go more than 1000 cycles between 1.4 and 2.8 V with greater than 90% cathode utilisation, at current densities as high as 300 μA cm⁻². They cycle at temperatures as low as -10°C at current density of 100 μA cm⁻² and are capable of supplying pulse current of several mA cm⁻². Microbatteries as large as 10 cm² have been fabricated and cycled over 1000 times at close to 100% cathode efficiency [38].

A third example is the solid state rechargeable lithium battery developed at the Oak Ridge National Laboratory [39]. This battery consists of amorphous or crystalline cathodes of oxide lithium intercalation compounds (LiCoO₂, LiMn₂O₄ or V₂O₅) and a lithium metal anode separated by a glassy electrolyte. The first step is the fabrication of a sputtered film of the cathode material, eventually annealed for crystallisation of the amorphous phase for a better Li⁺ diffusion. Then, an amorphous lithium phosphorous oxynitride is deposited by rf magnetron sputtering of Li_{3+x}PO_{4-x}N_x ($x \sim 0.2$) is commonly denominated as 'LiPON glass'. It has a Li⁺ conductivity of about 10⁻⁶ S cm⁻¹ at room temperature and is stable in contact with lithium and oxidising cathode materials like CoO₂. The anode is deposited over the electrolyte by thermal evaporation of lithium metal and the battery is then sealed with a multi-layer coating of parylene and titanium metal. The performance of the battery is determined by the cathode material Li_xV₂O₅, Li_xMn₂O₄ or Li_xCoO₂. For high rate applications, crystalline LiCoO₂, has been found as the best choice. With a 1 cm² × 2 μm layer of LiCoO₂, the battery can deliver about 100 μAh between 4.2 and 3 V at a continuous rate of 1 mA cm⁻². Li/LiPON glass/LiCoO₂ batteries have been cycled over 40,000 times at room temperature with less than a 5% total capacity loss [40].

Recently [41], an improvement of the manufacturing technology has been proposed by forming 'in situ' the

lithium anode by lithium deposition on a copper layer from a LiCoO₂ positive electrode layer.

6. Conclusion and perspectives

This review on glassy materials for lithium batteries is a survey of our present knowledge on the electrochemical properties of these materials and of the present state-of-art of their working up in the all solid state lithium batteries. We have willingly restricted the devices description to those studied at the pre-industrial level. Many other lithium cells have been realised as laboratory prototypes as conventional or thin film batteries. Very often, this pioneering work has initiated further industrial studies.

Considering the performances, it seems that coin cells realised by pressing together electrolyte powders and electrode materials remain less efficient than lithium-ion battery using a liquid electrolyte. Conventional organic solution of lithium salts allows deeper charge and discharge cycles at lower temperatures.

On the other hand, thin film solid state batteries have no conventional competitor and are an attractive possibility for electrical energy supply for smart credit card, electronic labels and applications on a very large industrial scale. Until now, studies were concerned with glasses as solid electrolytes. Glasses may also be used as intercalation electrode materials like the titanium or molybdenum amorphous oxysulphides or V₂O₅ glasses. The decrease in the value of the lithium diffusion coefficient would be compensated by an isotropic intercalation. In addition, a lower expansion coefficient is expected during intercalation–deintercalation cycles and this property would guarantee the mechanical interfacial stability when associated to a solid electrolyte.

Because, glasses may easily incorporate in their structure transition metal ions to form mixed conductive positive or negative electrodes, we may then imagine the realisation of a monolithic 'rocking chair' cell. A common network former for the electrolyte and electrode materials would provide a continuity for the lithium cation surrounding during its

transfer from one electrode to the other and would consequently reduce the interfacial polarisation while transfer. The required thin film technology for the realisation in large surfaces is already well-managed for multi-layers thin film coating.

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