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Solid state electrolytes: overview of materials and applications during the last third of the Twentieth Century

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Abstract

Solid state ionics has been a very active field of science during the last third of the century. However, the first observations of conductivity in solid electrolytes occurred over 150 years ago. Faraday reported the transport of silver ions through silver sulfide in 1834. The present report describes some of the more recent investigations of solid state ionic materials and devices, with emphasis on room temperature materials and solid state batteries. Prof. Osamu Yamamoto and his colleagues discovered the most conductive room temperature solid ionic material that is known up to the present time. This compound is $Rb_4Cu_{16}I_7Cl_{13}$ with a specific conductivity of 0.34 S/cm at 25°C.

Keywords: Solid electrolyte; Solid state ionics; Batteries; Silver ion conductor; Copper ion conductor

1. Introduction

Solid state ionics has been a very active field of science during the last third of the century. However, as has been pointed out by a number of authorities in this field (for example, Refs. [1,2]) the first observations of conductivity in solid electrolytes occurred more than 150 years ago. Faraday reported the transport of silver ions through silver sulfide in 1834. The purpose of the present report is to describe some of the investigations of ambient temperature solid electrolytes and development of related devices that have occurred during the period from 1960 to 2000. The author does not intend this to be a critical review of the field, but rather will present a selective overview on recent developments in solid state ionics, with emphasis on room temperature materials and solid state batteries.

2. Historical events

2.1. 1790–1960

Charles Mantell presented an overview of significant battery related events that occurred between 1790 and 1960, [3]. Whittingham [1] and Salkind [4,5] also identified key battery developments from this time period. The author has selected events from these summaries to show in Table 1 a listing of some battery events leading up to 1960. Prior to 1960, the industrial battery technologies were based on aqueous electrolytes.

Solid state batteries were of limited interest for specialty applications, but no conductive electrolytes were known. Mrgudich [6] wrote a short review of solid electrolyte batteries in which he pointed out that a major shortcoming of solid electrolyte batteries was the high internal resistance of the cell. Table 2 shows the five solid electrolyte batteries that were under development and as indicated the very high internal resistance values ranged from 50 kΩ up to 40 MΩ. This high internal resistance of the cells was a direct result of the lack of any ambient temperature solid with fast ion conduction. The most ionically conductive material at that time was AgI with a conductivity value of about 10^{-6} S/cm at 25°C.

This was the status of batteries prior to those relevant changes that were coming in the field of solid state ionics which enabled the development of solid state batteries, thin film batteries and lithium-ion batteries, all operable at normal ambient temperatures.

3. Events during the last third of the century

3.1. 1960–1970

As illustrated by the battery electrolytes of Table 2, room temperature solid electrolytes did not conduct current

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Table 1
Overview of battery events, prior to discoveries of fast ion conduction in solids at ambient temperature

Time	Event	Name
1791	Frog Leg Experiment	(Galvani)
1792	Voltaic piles, First batteries	(Volta)
1827	Ohm's law	(Ohm)
1833	Ionic mobility in Ag_2S	(Faraday)
1836	$Cu/CuSO_4$, $ZnSO_4/Zn$	(Daniell)
1839	Principle of the Air Cell	(Grove)
1859	Lead Acid Battery	(Plante')
1868	$Zn/NH_4Cl/C$ Battery	(Leclanche')
1874	Telegraph	(Edison)
1878	Air Cell	(Maiche)
1885	Zn/Br_2	(Bradley)
1888	Dry Cell	(Gassner)
1891	Thermodynamics of Dry Cells	Nernst
1900	Ni Storage Batteries	(Edison)
1905	Ni Iron Batteries	(Edison)
1911	Automobile Self-starter	(Kettering)
1927	Silver Zinc	(Andre)
1930	Nickel–zinc Battery	(Drumm)
1943	Cuprous Chloride Battery	(Adams)
1945	Mercury Cell	(Ruben)
1950	Sealed Mercury Cell	(Ruben)
1956	Alkaline Fuel Cell	(Bacon)

very well. A value of 10^{-6} S/cm was a high value of conductivity for a solid electrolyte. In the 1960s, this situation was to change dramatically. Reuter and Hardel [7] investigated the structure and transport properties of Ag_3SI and Ag_3SBr. They reported a conductivity value of 0.01 S/cm for Ag_3SI at room temperature. Takahashi and Yamamoto recognized the possibility of a new class of solid state batteries capable of much higher rates than those batteries in Table 2. In 1964, Takahashi and Yamamoto described the solid state battery

$$Ag/Ag_3SI/I_2$$

that incorporated this new electrolyte Ag_3SI for which they reported the value of 0.015 S/cm at room temperature for the ionic conductivity [8,9]. This cell was capable of current densities in the mA/cm^2 range whereas the cells of Table 1 only pulsed currents in the range of $\mu A/cm^2$. This major step in the development of ambient temperature solid state batteries was the direct result of identifying a solid in which the ionic conductivity at 25°C exceeded that of silver iodide by four orders of magnitude.

In 1965, following the work of Takahashi and Yamamoto on Ag_3SI, Owens and Argue investigated solid state batteries incorporating the electrolyte $RbAg_4I_5$. In 1965, this electrolyte was discovered to have an ionic conductivity of greater than 0.1 S/cm. Interestingly, this electrolyte was discovered independently in 1965 at two laboratories, based on work performed by Bradley and Green in England and Owens and Argue in the USA. The first publication of this new electrolyte was in 1966 by Bradley and Green who reported a value of 0.12 S/cm at room temperature [10]. The following year, Owens and Argue reported a value of 0.21 S/cm for their material [11]. They subsequently reported the value of 0.26 S/cm at 25°C for polycrystalline $RbAg_4I_5$ [12]. A review article by Owens described the work on silver ion conducting solid electrolytes and their application to batteries [13].

3.2. 1970–1980

It was in Italy, in March of 1972, in the city of Ferrara that for the first time a cardiac pacemaker, powered by a Li/I_2 battery, was implanted into a human being. This battery worked even though the electrolyte was solid LiI, an electrolyte known to have a conductivity of only 10^{-7} S/cm at room temperature [14]. This very low electrolyte conductivity did not prevent the successful development of the $Li/LiI/I_2$ pacemaker battery in the 1970s. The cell was a Wilson Greatbatch Model 702/C [15]. The battery worked because it was well suited to the application, which required isothermal operation at 37°C, at a very low rate (10-year rate). This event was key to the subsequent development of small, reliable implantable medical devices, and today there are several million persons who have benefited from implantable devices that are powered by various designs of the Li/I_2 battery.

Also in Italy in 1972, the NATO Advanced Study Institute for ''Fast Ion Transport in Solids, Solid State Batteries and Devices'' was held in Belgirate, Italy from September 5th to the 15th. The proceedings of this conference were published the following year [16]. Eighty-three scientists attended this first international conference on solid state ionics, 27 years ago. The introductory lectures were presented by Professor Hans Rickert on General Properties of Solid Electrolytes and by Dr. Charges Liang on Solid State Batteries. These were followed by sessions that dealt primarily with materials properties, with a limited number of papers talking about batteries. The batteries were limited to silver ion conducting electrolyte systems.

In 1976, Professor Bruno Scrosati led the organization of an international symposium on ''Solid Ionic and Ionic–

Table 2
Solid state batteries as of the year 1960 [6]

Battery system	Nominal cell voltage	Cell internal resistance, Ω	Development organization
$Ag/AgI/V_2O_5$	0.46	4×10^5	National Carbon
$Ag/AgBr/CuBr_2$	0.74	4×10^7	General Electric
$Ag/AgBr–Te/CuBr_2$	0.80	1×10^7	Patterson–Moos Research
$Ag/AgCl/KICl_4$	1.04	5×10^4	Sprague Electric
$Ni–Cr/SnSO_4/PbO_2$	1.2–1.5	2×10^6	P.R. Mallory & Rayovac

Electronic Conductors'' that was held September 1–3, 1976 in Rome [17]. This conference was instrumental in initiating the series of conferences on Solid State Ionics (ultimately known as the SSI series), that continue to this day, as well as the establishment of the International Society for Solid-State Ionics (ISSI). Approximately 40 papers were presented at this first conference. In addition to papers dealing with the highly conducting silver ion electrolyte materials, there were reports of high ionic conductivity in copper solid electrolyte materials, the beta alumina solid electrolytes and batteries based on not only those materials but also lithium-ion conducting electrolytes. These included descriptions of the LiI solid electrolyte pacemaker batteries that were in commercial products.

A review of the field of Solid Electrolytes was published the following year [18]. This book was part of the continuing series *Topics in Applied Physics* and described theoretical aspects, materials properties and applications of solid electrolytes.

A symposium on the History of Electrochemistry was held at the ECS meeting in the spring of 1977. Whittingham [1] presented a review of ''rapid ionic mobility in solids''. This article traced the development of solid state ionics from work by Faraday in 1833 up to more recent interests in the highly conducting silver ion materials and in sodium beta alumina. As observed by Whittingham, the field had moved from one of scientific curiosity, through an extensive period of scientific investigations, in particular work by Professor Carl Wagner, and then the discoveries of sodium beta alumina electrolytes. Whittingham points out that one of the problems in developing a room temperature high-energy battery is related to the need for a highly reversible cathode material. He describes his work on the lithiated titanium disulfide cathode material, which was an important precursor to the present day commercially successful use of lithiated metal oxide cathode materials.

The ''Second International Meeting on Solid Electrolytes'' was held at St. Andrews, Scotland in 1978. Two noteworthy events from that meeting are recalled here.

First, Prof. Takahashi reported that his research group had discovered the most conductive room temperature solid electrolyte that has ever been known [19]. Research carried out primarily by Prof. Osamu Yamamoto had resulted in the discovery of the compound $Rb_4Cu_{16}I_7Cl_{13}$. This material is a pure Cu^+ ion conductor with a room temperature ionic conductivity equal to 0.34 S/cm (25°C) and an electronic conductivity of 10^{-12} S/cm (60°C) [20].

Secondly, at this same conference Dr. Michel Armand proposed that the most useful solid state battery of the future might be based on a thin film cell,

Alkali Metal/Polymer Electrolyte/Intercalation Compound

with electrode films of about 100 μm each separated by a 50 μm electrolyte layer of ionically conducting polymers, which might ultimately be the most useful solid electrolyte for an all solid-state battery [21]. Today, more than 20 years later, the rechargeable lithium polymer battery is the focal point of several major electric vehicle battery development programs.

3.3. 1980–1990

In 1980, the technical monograph ''Applications of Solid Electrolytes'' was published [22]. The co-editor Professor Takehiko Takahashi was well known as both an expert in the field of solid ionics and a key contributor to this field for many years. It was in 1960 that Professor Takahashi and his co-worker Prof. Osamu Yamamoto proposed the use of the term ''Solid State Ionics'' to represent the emerging scientific field of solid electrolytes. In this volume there is included a summary of Professor Takahashi's contributions to science and technology [23]. The book also includes some interesting chapters on devices such as sensors based on oxide conductors and timers and memory cells based on silver ion conducting electrolytes.

In 1984 the review chapter ''Solid-Electrolyte Cells'' was published in ''Handbook of Batteries and Fuel Cells'' [24]. This chapter incorporates a brief summary of solid electrolyte materials that had been incorporated into solid state batteries. The chapter describes lithium solid-state primary batteries and the commercially successful lithium/iodine pacemaker battery. It is noted in this chapter that the commercial development of solid state batteries had been realized with lithium-ion conducting materials, and interestingly, the first application of a lithium high-energy battery was in the cardiac pacemaker. The silver ion conducting based solid electrolyte batteries were not commercially viable because of the intrinsic low energy density and high cost associated with these materials.

In 1986, a workshop on ''Materials For Solid State Batteries'' was held in Singapore. The proceedings volume includes many papers dealing with the growing field of solid state ionics [25]. Professor Yamamoto presented a summary of the field of ambient temperature copper ion solid electrolytes [26]. He compares the physical properties of $RbAg_4I_5$ to those of the highly conducting copper ion solid electrolyte $Rb_4Cu_{16}I_7Cl_{13}$. The room temperature conductivities of these materials were reported as 0.28 and 0.34 S/cm, respectively.

In 1987, a Symposium on the History Of Battery Technology was organized by the Electrochemical Society [5]. The first paper by Professor Salkind [4] presented a chronology of important scientific events in the battery field. Some of that material was incorporated in Table 1 of the present article. Professor Salkind's chronology covered the period from 1791 (with Galvani) up to the 1980s with sealed lead acid batteries and lithium primary batteries.

The status of Solid State Ionic Devices as of 1988 was the subject of an international seminar held in Singapore.

The description of devices includes considerable reference to both practical devices such as those that are in production as well as evolving devices [27,28]. Devices described by Professor Hagenmueller include batteries, fuel cells, oxygen sensors, capacitors, memory devices and photochromic devices [27]. As pointed out by Professor Hagenmueller, in addition to the need for highly conductive solid electrolyte materials, one must also characterize and minimize those problems that occur at the interface between the various solid state elements comprising any such solid state ionic device. The need for cooperation between scientists and engineers was also emphasized.

3.4. 1990–2000

An excellent monograph on Solid State Ionics was published in 1990 [29]. The authors credit Professor Takehiko Takahashi for the first use of the term solid state ionics, in 1960 at Nagoya University. In Table 3 is given a chronology of solid state ionics over the time period from 1833 to 1983; this table is based on the review by Kudo and Fueki, as well as other references. The chronology initiates with the observations of Faraday in 1833 and includes some of the more recent battery and device developments that occurred subsequent to 1960.

Professor Scrosati was instrumental in organizing the second Belgirate conference on Fast Ion Transport In Solids [30]. This conference marked the 20-year anniversary of the first International Symposium on Fast Ion Transport In Solids that was also held at Belgirate as a NATO workshop, in 1972. The attendance at the conference was limited to 52 persons, and included a number of the scientists that attended the first conference. Professor von Gool [31] presented the final remarks of this meeting. As pointed out in his summary remarks, the present volume on fast ion transport in solids includes review articles dealing with solid state batteries, fuel cells and other electrochemical devices, intercalation compounds and mixed conductivity.

During the 20 years between these conferences, a large body of work has been completed. This has resulted in advances in materials science and also new types of devices. The use of the electrolytes has been significant not only as a material to maintain a separation between two active electrodes, but also as a key material in sensing electrodes and in reversible electrodes for high-energy batteries. It will be interesting to see what happens during the subsequent 20 years and the possibility of a third Belgirate conference on ion transport and solids for the year 2012 (again to be organized by Prof. Scrosati).

In 1995 the second edition of the ''Handbook of Batteries'' was published. Included in this is a revised review chapter on Solid-Electrolyte Cells [32]. A chronology of solid electrolyte cells up through the time of 1999 is shown in Table 4, and is simply an update of the earlier table. It is interesting to note that the more recent development in solid state ionics and batteries are based on materials that were absent 20 years ago. These are the developments of thin film batteries built around a number of lithium-ion conducting glasses and also the extensive work going on with lithium polymer and lithium-ion gel electrolyte batteries.

A recent reference on new directions in rechargeable high-energy batteries [33] identifies some 14 companies

Table 3
Chronology of solid state ionics (1833–1983)

Time	Event	
1833	Faraday's Law	
1897	ZrO_2Glower (Nernst)	
1920	High Ionic Conduction in a-AgI	
1934	Ion Transport Mechanism for a-AgI	
1943	Ionic Conduction Theory for ZrO_2	
1950–1960	Solid State batteries:	Cell Voltage:
	$Ag/AgI/V_2O_5$	0.46
	$Ag/AgBr/CuBr_2$	0.74
	$Ag/AgBr–Te/CuBr_2$	0.80
	$Ag/AgCl/KICl_4$	1.04
	$Ni–Cr/SnSO_4/PbO_2$	1.2–1.5
1957	Applied Use of ZrO_2 (Wagner)	
1962	High Temperature Fuel Cell Using ZrO_2	
1967	β-alumina; Rb Ag_4I_5	
1969	Electro-chromism in WO_3	
1972	Solid State Li Battery Memoriode	
1976	NASICON Automotive Sensor Using ZrO_2; Secondary Battery Using TiS_2 Intercalation	
1979	High Cu^+ Conductor Organic Polymer Solid-electrolyte	
1981	Plastic Battery	
1983	Commercial ECD	

Table 4
Chronology of Solid-electrolyte cells (1950–1999)
PEO — polyethylene oxide; MEEP — poly(bis[methoxy ethoxy ethoxide]); SPE — solid polymer electrolyte; Lipon — $Li_{0.39}N_{0.20}O_{0.47}P_{0.12}$ glassy electrolyte.

Date	Electrolyte	Log s, W^{-1} cm^{-1}	Typical cell system
1950–1960[a]	AgI	−5	Ag/V_2O_5
1960–1965[a]	Ag_3SI	−2	Ag/I_2
1965–1972[a]	$RbAg_4I_5$	−0.55	Ag/Me_4NI_5
1965–1975[a]	Na β-alumina	−1.5	Na–Hg/I_2,PC
1970–1975[a]	$LiI(Al_2O_3)$	−5	Li/PbI_2
1970–1980[a]	LiI	−7	$Li/I_2(P_2VP)$
1978–1999[a]	LiX–PEO	−7	Li/V_6O_{13}
1979–1995[b]	$Rb_4Cu_{16}I_7Cl_{13}$	−0.47	$Cu_2Mo_6S_{7,8}/Cu_2Mo_6S_{7,8}$
1980–1986[a]	$Li_{0.36}I_{0.14}O_{0.007}P_{0.11}S_{0.38}$	−3.3	Li/TiS_2
1983–1987[a]	MEEP	−4	Li/TiS_2
1994–1999[c]	$Li_{1.26}Si_{0.365}O_{0.04}P_{0.01}S_{1.36}$	−2.8	$InLi_x/Li_{1-x}CoO_2$
1985–1992[a]	Plasticized (Gel) SPE	−3	Li/V_6O_{13}
1985–1992[a]	$Li_{0.35}I_{0.12}O_{0.31}P_{0.12}S_{0.098}$	−4.7	Li/TiS_2
1990–1992[a]	$Li_{0.39}N_{0.020}O_{0.47}P_{0.12}$	−5.6	Li/a-V_2O_5
1990–1999[d]	Polymer Gel	−3	$C/LiCoO_2$
1995–1999[e]	Lipon	−5.6	$Li/LiMn_2O_4$

[a] Owens et al. [32].
[b] Kanno et al. [38], Sotomura et al. [39].
[c] Takada et al. [40].
[d] Osaka, [33].
[e] Bates et al. [41].

that are engaged in the advanced development or the production of lithium-ion rechargeable batteries in which the electrolyte is a gel electrolyte rather than a liquid electrolyte (see Table 5). This gel electrolyte is referred to as a polymeric material although it is perhaps more accurately a plasticized polymer. All of these batteries use electrolytes that are modifications of a true solid state electrolyte, but all do include as their cathode material a solid ionic conducting material that permits the reversible insertion and deinsertion of lithium-ions.

The final reference to a review book in the field of solid state ionics is the book *Solid State Electrochemistry* edited by Professor Peter G. Bruce [34]. Professor Bruce introduces a brief history of solid state electrochemistry and gives reference to the origins as lying with Michael Faraday's work on the high ionic conductivity in both Ag_2S and PbF_2 in 1838. As Bruce points out, the emphasis in this field was first on ionic conduction in the bulk phase of the material but that the areas of research had shifted to where the importance of the interface and interfacial studies are being reflected in the types of investigations now being reported.

Prof. Bruce's book includes a chapter on ''Applications'' [35]. It is very fitting that Professor Yamamoto

Table 5
Lithium-ion polymer-gel electrolyte batteries, in production for cell phone and PC applications. Cells are all nominal 3.7 V, prismatic shapes (Osaka [32])

Manufacturer	Country	Cathode	Anode	Electrolyte	Energy density, W h L^{-1}/W h kg^{-1}
Matsushita Battery	Japan	$LiCoO_2$	Graphite	PVDF gel	250/125
Sony	Japan	$LiCoO_2$	Graphite	PVDF gel	245/125
Japan Storage Battery	Japan	$LiCoO_2$	Graphite	PVDF gel	210/125
Hitachi Maxell	Japan	$LiCoO_2$	Graphite	PEO gel	130/90
Sanyo	Japan	$LiCoO_2$	Graphite	PEO gel?	200/120
Toshiba	Japan	$LiCoO_2$	Graphite	PVDF gel	245/115
Yuasa	Japan	$LiCoO_2$	Coke	PEO gel	165/95
Hirion/Mitsubishi Ch.	Japan	$LiCoO_2$	Graphite	PEO gel	280/130
Ultralife	US	$LiMn_2O_4$	Graphite	PVDF gel	185/105
Valence	US	$LiMn_2O_4$	Graphite	PVDF gel	220/110
Thomas and Betts (HET)	US	$LiCoO_2$	Graphite	PVDF gel	220/120
Lithium Technology	US	$LiCoO_2$	Graphite	PVDF gel	240/125
ElectroFuel	Canada	$LiCoO_2$	Graphite	PVDF gel	435/175
Shubilan	Malaysia	$LiCoO_2$	Graphite	PVDF gel	215/120

wrote this last chapter because he has been instrumental in the scientific investigations of solid state ionic materials for many years, and his investigations and ideas have led to the development of technologically important devices. Professor Yamamoto gives an updated review of this field and describes many applications including solid electrolyte batteries. He also describes other types of applications such as the use of solid ionic materials as intercalation electrodes in liquid electrolyte batteries, the solid oxide fuel cells, sensors, electrochromic devices, lithium polymer batteries, the high temperature sodium/beta alumina/sulfur battery and memory devices.

4. Conclusions

In this paper I have highlighted a number of the relevant review articles and monographs that have been published during the last third of the century. My selection is not intended as a comprehensive review of all such sources of information. For example, the International Conferences on Solid State Ionics that have been held every 2 years and have attendance in the hundreds also have extensive Proceedings Volumes that are published in the journal *Solid State Ionics*.

My introduction to the field of solid state ionics took place in June of 1965, nearly 35 years ago. It is clearly recalled by the author that the reason for this interest in solid electrolytes was based on two papers that were published in Denki Kagaku the preceding year, 1964. Professor Yamamoto was co-author of these two papers [8,9] describing the solid electrolyte cell, $Ag/Ag_3SI/I_2$. Professor Yamamoto has been working in this field of solid state ionics since the phrase was first proposed in 1960. Their first paper on ionic conduction in cuprous iodide was published in 1963 [36,37].

During the last 35 years there has been a continual quest for new solid electrolyte materials with high ionic conductivity in the bulk phase. The types of materials investigated have ranged from the copper and silver ion crystalline materials, to glassy materials, to crystalline lithium-ion conducting materials, to amorphous lithium-ion composite electrolytes, to thin film lithium-ion conducting glasses and to pure lithium-ion polymer electrolytes and most recently to the ambient temperature lithium-ion conducting gel or gelled-polymer electrolytes.

It is interesting to consider the improvements in the conductivity of ambient temperature solid ionic materials. Prior to 1960, silver iodide was the most conductive electrolyte known, with a value of about 10^{-5} S/cm at 25°C. LiI was the most conductive alkali halide with a value of 10^{-7} S/cm. The ionic conductivities of known materials started to increase dramatically as illustrated in Fig. 1. The most conductive solid state ionic compound discovered and characterized during the Twentieth Century is $Rb_4Cu_{16}I_7Cl_{13}$.

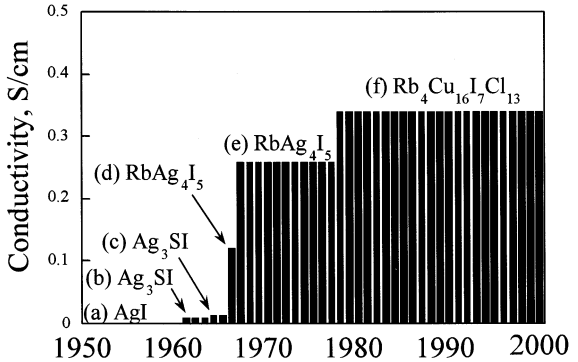

Fig. 1. The highest conductivity solid electrolytes known at ambient temperature (25°C), between the years 1950 and 2000. (a) AgI in amorphous form exhibits an ionic conductivity of 10^{-4} S/cm, and in crystalline form had the value of 10^{-6} S/cm; (b) Reuter and Hardell [7]; (c) Takahashi and Yamamoto [8]; (d) Bradley and Greene [10]; (e) Owens and Argue [11]; (f) Takahashi et al. [19].

Even though ion conduction is a necessary property for ionic devices, it is possible to make commercially successful battery products with solid electrolytes in which the ionic conductivity is much less than the fast ion conduction values shown in Fig. 1. This is a result in part of the ability to form the electrolyte as a very thin film, for example by the thin film techniques done for lithium ion glasses, and the ability to form polymeric-gel electrolytes also as thin films. By minimizing the electrolyte thickness and maximizing the interfacial area between the elements of a cell, one can reduce this ohmic impedance contribution.

The field of solid state ionics has been a very exciting one during the past one-third of the century. Professor Yamamoto, to whom this International Session at the 40th Battery Symposium in Japan is dedicated, has been one of the major contributors into this field. We all look forward to his continuing leadership in this area of solid state ionics.

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