

# 17th International Meeting on Lithium Batteries

## Highlights of the latest research on post-lithium-ion battery chemistry

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### 1. Introduction

Within the last 20 years, publication numbers in the field of lithium battery research have increased from a few hundred in the mid 1990s to more than 4500 publications in 2013 (Figure 1). It has grown to a major research topic, with many universities, state laboratories and commercial research and development (R&D) facilities involved. The number of meetings dedicated to battery work has

increased likewise. The International Meeting on Lithium Batteries (IMLB) has been held biannually since 1982 and is one of the top meetings in the Li battery community. It is organised by an international executive committee, currently comprising of 24 international scientists. Following Jeju, Korea, in 2012, this year's meeting was held in Como, Italy. It was co-organised by the Electrochemical Society (ECS) which will also publish dedicated special issues in *Journal of the Electrochemical Society* and *ECS Transactions*. Around 1000 people attended the meeting with 40+ keynote speakers, presenting in nine plenary sessions and three large poster sessions with more than 500 contributions. Further details on the 17th IMLB meeting including details of the scientific programme and biographies of the invited speakers can be found on the conference website (1).

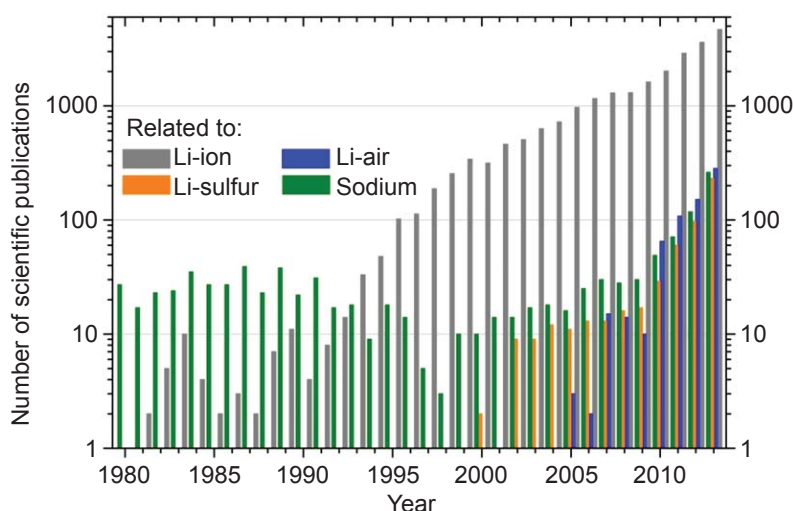


Fig. 1. Numbers of scientific publications related to different types of battery. The search was run on keywords in the manuscript titles and abstracts. Note that the numbers for sodium batteries include the (high-temperature) molten salt and Na-sulfur systems

In recent years there has been increasing interest in next-generation, 'beyond lithium-ion' battery technologies, especially in Li-air, Li-sulfur and sodium based chemistries. A major theme of the meeting addressed recent advances in beyond Li-ion batteries, where novelty was a key requirement for paper acceptance. The main areas of interest were Li battery related science and technology such as, but not limited to: electrode materials, electrolytes, Li-air, Li-sulfur, sodium batteries, new analytical tools, computational work and safety.

Due to the huge amount of contributions during this conference, only a few highlights of each main topic are included in this review. For a detailed overview of the conference contents, the interested reader is referred to the conference homepage (1).

## 2. Lithium-Oxygen Batteries

No other battery system is the subject of such controversial discussion as Li-oxygen. The list of 'unsolvable' problems is long and small successes are contrasted by big setbacks. The many reports on stability issues of electrolyte solvents are just one example (2–4). Reaction mechanisms of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) are still not explained satisfactorily (5) and side reactions are omnipresent. Contamination originating from the cathode, which is open to the environment, cannot be blocked sufficiently (6).

From the start, the question of the preferred morphology of  $\text{Li}_2\text{O}_2$  deposition was heavily discussed amongst the speakers. Together with her co-workers, Yang Shao-Horn (Massachusetts Institute of Technology (MIT), USA) studied the effect of solvation on Li- $\text{O}_2$  redox reactions. The results revealed the formation of very small  $\text{Li}_2\text{O}_2$  particles at high discharge rates and/or when using a solvent with low solvation power (here: dimethylether (DME)). At low rates and/or when using solvents with higher donor numbers (here: dimethyl sulfoxide (DMSO)), larger, disc-like particles (**Figure 2**) are formed (7). Lower overpotential (i.e. higher discharge voltage) was observed in the latter case. Increased solvation power due to high donor numbers lowers the energy levels of the  $\text{Li}/\text{Li}^+$  redox reaction and increases that of the  $\text{O}_2/2^*\text{O}^{2-}$  reaction. Larger particles seemed to improve the kinetics and better fill the volume of carbon pores, whereas smaller particles have a reduced overpotential (5).

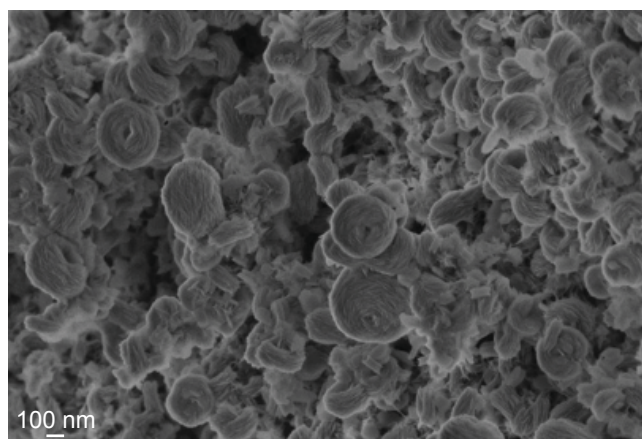


Fig. 2.  $\text{Li}_2\text{O}_2$  toroidal discs on a porous carbon electrode

Large, toroidal shaped discs in high donor number solvents were also found by Peter Bruce's group (University of Oxford, UK). According to his theory, high solubility of the superoxide radical in the electrolyte leads to  $\text{Li}_2\text{O}_2$  growth from the solution rather than from the electrode surface. The addition of redox mediators was discussed to aid the dissolution of  $\text{Li}_2\text{O}_2$  on charge and therefore increase the rate capability (8). Also focused on the donor abilities of electrolyte solvents, K. M. Abraham's (Northeastern University, USA) approach was based on the 'hard and soft acids and bases' (HSAB) concept. Ionic liquids (ILs) with soft cations (such as 1-methyl-1-butyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide ( $\text{Pyr}_{14}\text{TFSI}$ ) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI)) reduce the  $\text{Li}^+$  acidity in organic electrolytes and therefore increase the lifetime of initially formed  $\text{O}_2^-$  (9). The potential of  $\text{Pyr}_{14}\text{TFSI}$  was demonstrated by Jakub Reiter (BMW Group, Germany) when he presented results of an ionic liquid electrolyte ( $\text{Pyr}_{14}\text{TFSI}/\text{LiTFSI}$  (9:1)), applied in a Li-air battery using a Super-P<sup>®</sup> cathode and a Li-metal anode (10).

Tailoring  $\text{Li}_2\text{O}_2$  morphology by providing an optimised cathode structure was the idea of Xin-Bo Zhang and co-workers (Chinese Academy of Sciences, China). A free-standing honeycomb-like palladium modified hollow spherical carbon was applied as Li-air cathode, which led to organised, toroidal nanosheets of  $\text{Li}_2\text{O}_2$ . More than 100 cycles at a current density of  $300 \text{ mA g}^{-1}$  and a specific capacity limit of  $1000 \text{ mAh g}^{-1}$  were presented (11). In contrast to the results discussed before,  $\text{Li}_2\text{O}_2$  was observed to form rapidly if the superoxide binds

well on the cathode surface. Atomically dispersed Fe/N/C composite as bifunctional catalysts showed better performance, exhibiting fewer side reactions than a classic  $\alpha$ -manganese(IV) oxide ( $\text{MnO}_2$ ) catalyst (12).

The possible instability of the carbon cathode and the related importance of the  $2e^-$  per  $\text{O}_2$  ratio for the ORR and OER was a key message from Peter Bruce (13–15). Arumugam Manthiram (University of Texas, USA) suggested hybrid Li-air batteries as a solution to the aforementioned problems. The benefits of an aqueous cathodic compartment and a non-aqueous anodic compartment can compensate for the increased complexity of the system (16, 17). Novel catalysts like iridium(IV) oxide ( $\text{IrO}_2$ ) (18), low-temperature  $\text{Li}_{1-x}\text{CoO}_2$  or  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  were successfully employed (19). Other workers used a cobalt phthalocyanine-derived catalyst to enable the full reduction of  $\text{O}_2$  to  $\text{Li}_2\text{O}$ , thus utilising the full theoretical range of a Li-air cell (20). To reduce safety issues, replacing the Li metal anode with SnC,  $\text{Fe}_{0.1}\text{Zn}_{0.9}\text{O}$  or SiC was suggested (10).

### 3. Lithium-Sulfur Batteries

Lithium-sulfur (Li-S) batteries are expected to be closer to a marketable product than Li-air batteries. A major remaining challenge, addressed in many contributions, is the high solubility of polysulfide intermediates formed during the stepwise (but in no case straightforward) reduction from  $\text{S}_8$  to the final discharge product  $\text{Li}_2\text{S}$  (21, 22). These polysulfides migrate to the anode, ending up as a self-discharge promoting redox shuttle or as a deposit blocking the anode surface (23, 24).

Yi Cui (Stanford University, USA) started with a quick overview of the recent evolution of Li-S cathodes (from sulfur/carbon mixtures to encapsulated hollow particles) and he summarised by stating that no satisfying solution to 'capture' the sulfur has been found yet. Tin-doped indium oxide was found to fix polysulfide to carbon (25). Core-shell material showed increased sulfur 'trapping' but still lost polysulfides during cycling (26, 27). Yu-Guo Guo (Chinese Academy of Sciences) tried to start from smaller sulfur homologues ( $\text{S}_{2-4}$ ) which could be successfully trapped inside microporous carbon or carbon nanotubes (CNTs) (28). The group of Linda F. Nazar (University of Waterloo, Canada) replaced the carbon support with titania ( $\text{TiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and titanium oxide ( $\text{Ti}_4\text{O}_7$ ) and successfully reduced the fade rate (29).

A second approach to stop polysulfide migration would be an electrolyte which would act as a polysulfide barrier. A polymer electrolyte made from poly ethylene(oxide) with 10 wt%  $\text{ZrO}_2$ ,  $\text{LiCF}_3\text{SO}_3$  and  $\text{Li}_2\text{S}$  was presented by Jusef Hassoun (Sapienza University of Rome, Italy). Cells had to be operated at  $70^\circ\text{C}$  to deliver  $900 \text{ mAh g}^{-1}$  (30). Doping the electrolyte (tetraglyme) with a polysulfide ( $\text{Li}_2\text{S}_8$ ) proved to decrease the internal resistance and seemed to buffer further polysulfide dissolution (31). The incorporation of ionic liquids might also be a viable solution to the problem. Aleksandar Matic (Chalmers University, Sweden) presented imidazolium- and pyrrolidinium-based electrolytes (32), some of them mixed with 1,3-dioxolane or glymes (33). Linda F. Nazar could achieve decreased polysulfide dissolution in electrolyte systems based on 1,3-dioxolane, 1,2-dimethoxyethane and bis(trifluoromethylsulfonyl)imide (TFSI) salts (34). She also presented an *in operando* X-ray absorption spectroscopy technique to identify the different sulfur species (35). As an alternative approach, a membrane-free polysulfide flow battery was presented by Yi Cui (36).

### 4. Sodium Batteries

High-temperature Na batteries were developed as molten Na-S or Na- $\text{NiCl}_2$  (ZEBRA) batteries in the 1980s. However, these systems were quickly pushed aside by the success of Li-ion batteries. Low-temperature sodium systems, like Li-ion technology, have now started to gain interest within the last few years (Figure 1). They can certainly benefit from experience in the Li-ion field but knowledge transfer will not be as straightforward as it may seem.

'Walking on the sodium side' was the slogan of Maria Rosa Palacín (Institut de Ciència de Materials de Barcelona-Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), Spain) as she opened the Na-ion related talks. Major safety concerns come with the use of Na metal as anode, which reacts more fiercely with water than Li. Carbon would be one alternative (37), but Ti-based insertion materials, especially  $\text{Na}_2\text{Ti}_3\text{O}_7$ , could also give reasonable performance, with Na insertion potentials as low as 0.3 V vs.  $\text{Na}^+/\text{Na}$  (38, 39). Young-Jun Kim (Korea Electronics Technology Institute) would employ sodium metal in systems like Na-S, Na- $\text{NiCl}_2$ , Na- $\text{O}_2$  and Na-ion when electrolytes like  $\text{NaAlCl}_4 \cdot \text{SO}_2$  or organic liquids would prove

suitable. However, side reactions with the electrolyte are an issue for sodium. Maria Rosa Palacín's group found ethylene carbonate and/or propylene carbonate based solutions with sodium perchlorate ( $\text{NaClO}_4$ ) to be relatively stable (40). Laurence Croguennec (Institut de Chimie de la Matière Condensée de Bordeaux-Centre National de la Recherche Scientifique (ICMCB-CNRS), France) suggested fluorophosphates as high energy density positive electrodes for Na (and Li) batteries. In particular the compound  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  was investigated, since vanadium offers a wide range of stable oxidation states and structures in Na (41, 42) and Li (43) containing compounds.

## 5. Layered Lithium-Ion Battery Cathode Materials

There is a large drive to increase the operating potential of Li-ion batteries in order to increase the gravimetric energy density. The gravimetric energy density is the product of capacity and the mean operating voltage and therefore can be altered by changing either of these material properties. Layered metal oxides have been used as Li-ion battery cathodes since the first commercial battery produced by Sony in the early 1990s. These materials are made up of slabs of edge sharing  $\text{MO}_6$  octahedra (where M is Ni, Co and/or Mn) separated by layers of Li cations (Figure 3). The elemental composition of these materials has changed significantly since Sony first used  $\text{LiCoO}_2$  as

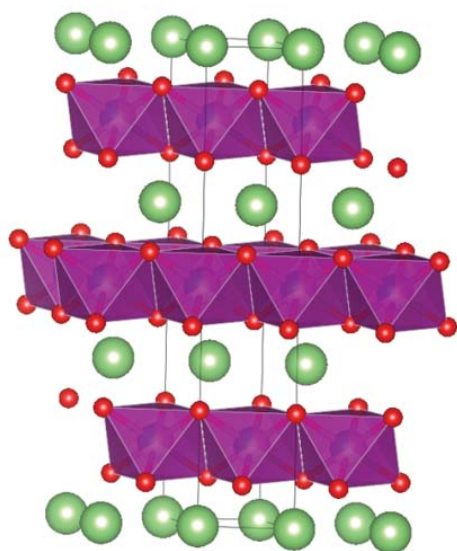


Fig. 3. Structure of  $\text{LiMO}_2$ : green = lithium, purple = metal (M) and red = oxygen (O)

an intercalation cathode. Modern versions are doped with Ni and Mn (known as NMC) with the formula  $\text{Li}[\text{Ni}_x\text{Mn}_y\text{Co}_z]\text{O}_2$ , where  $x + y + z = 1$ . The transition metal ratios can be altered to control properties such as capacity and operating potential.

One major issue with NMC type compounds is structural instability caused by either collapse of the  $\text{MO}_6$  layers on Li removal or by migration of transition metals into the empty Li positions. Increasing the Ni content in  $\text{Li}[\text{Ni}_x\text{Mn}_y\text{Co}_z]\text{O}_2$  leads to increased capacity but also decreased capacity retention and concomitant decrease in structural stability. When  $x$  is as high as 0.85, the material has a higher initial capacity, but 90% of the structure collapses during cycling, leading to fast capacity loss. Therefore Yang-Kook Sun (Hangyang University, Korea) described a core-shell material with increased capacity in the core and good stability (and therefore high safety) on the surface (44). However, these materials do not perform well due to separation of the shell from the core during cycling, caused by different volume change ratios. Applying a gradient throughout the whole particle, using a slow concentration change in the core and a fast concentration change in the shell, led to mechanically stable particles while keeping the capacity and stability advantages (45, 46).

$\text{Al}_2\text{O}_3$  coatings as an alternative method for stabilising NMC particles were described by Kuniaki Tatsumi (National Institute of Advanced Industrial Science and Technology (AIST), Japan).  $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]\text{O}_2$  was mechanochemically coated, the  $\text{Al}_2\text{O}_3$  was uniformly distributed on the surface with no migration into the bulk particle. The material showed greatly improved cycling performance, even at elevated temperatures. The  $\text{Al}_2\text{O}_3$  coating suppressed crack formation, reduced degradation of charge transfer sites and increased cycling stability at 1 C. Without coating, carbonates and  $\text{LiF}$  formed on the particle surfaces, concomitant with an increase in the detrimental cubic NMC phase at particle surfaces (47).

A third strategy to increase the stability of NMC based layered compounds is to make a composite of  $\text{Li}_2\text{MnO}_3$  and  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ , also known as Li-rich NMC.  $\text{Li}_2\text{MnO}_3$  is structurally related to  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ; however excess Li resides in the transition metal layers. This results in the presence of electrochemically inactive  $\text{Mn}^{4+}$  which acts as a structural scaffold and prevents collapse of the metal oxide layers. The resulting compound has a reversible capacity as high as  $200 \text{ mAh g}^{-1}$ . However, transition metal cations migrate from the transition metal layers



to the Li layers, leading to voltage fade over time. The cause of this migration is not fully understood, however, Jean-Marie Tarascon shed some light on the problem using simplified compounds like  $\text{Li}_2\text{Ru(IV)}_{1-y}\text{Sn(IV)}_y\text{O}_3$  (as opposed to  $\text{Li}_2\text{MnO}_3$ ). This 3d-metal-free compound could be cycled over 100 times, delivering reasonably high capacity. X-ray diffraction (XRD) was used to show the onset of large disorder on charging which was recovered on discharge. High-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) showed massive cationic migration to the Li layers on charging which returned to the completely ordered state when subsequently discharged. Despite this cationic migration the  $\text{Li}_2\text{Ru(IV)}_{1-y}\text{Sn(IV)}_y\text{O}_3$  structure shows no voltage fade over time. Testing the impact of ion size ( $\text{Sn}^{4+} > \text{Ti}^{4+} > \text{Mn}^{4+}$ ), the titanium compound  $\text{Li}_2\text{Ru}_{0.75}\text{Ti}_{0.25}\text{O}_3$  was synthesised. It showed the worst voltage fade. A combination of X-ray photoelectron spectroscopy (XPS) and electron microscopy showed that upon cycling,  $\text{Ti}^{4+}$  accumulates in tetrahedral sites between the metal oxide and Li layers where it is no longer active. Preventing metals entering these tetrahedral sites will prevent voltage fade in layered-layered compounds.  $\text{Sn}^{4+}$  is therefore attractive to reduce voltage fade, however replacing Mn with Sn has not worked. Compounds with the stoichiometry  $\text{Li}_4(\text{M}^{n+}, \text{M}^{m+})\text{O}_6$  where  $m + n = 8$  are considered best as an answer to the voltage fade issue in Li-rich NMCs (48, 49).

## 6. Anode Materials

Future anode materials are more likely to be conversion or alloying type materials rather than insertion materials like the state-of-the-art graphite anode. Complex reaction mechanisms and high volume changes present challenges for these materials. Nanostructuring and coating with polymers or carbons are two approaches to protect materials against side reactions and ensure good cycling, even at high rates.

$\text{Fe}_3\text{O}_4$  is a conversion material which reacts with  $\text{Li}^+$  to form  $\text{Li}_2\text{O}$  and Fe metal. The Fe metal produced can also alloy with Li as the battery continues to discharge.  $\text{Fe}_3\text{O}_4$  has in the past been doped with Zn to produce  $\text{ZnFe}_2\text{O}_4$ , however this material has poor coulombic efficiency. Stefano Passerini (Helmholtz Institute, Ulm, Germany) presented his group's work in which  $\text{ZnFe}_2\text{O}_4$  was coated with carbon using glucose as precursor. In addition to the particle coating, a carbon matrix was

formed in which many particles were combined to form macroscopically sized particles. These 'carbon coated matrix' particles showed improved performance compared to micron sized particles (50, 51). In a separate piece of work  $\text{TiO}_2$  nanorods were carbon coated using polyacrylonitrile (PAN) as precursor. The block copolymer was anchored to the  $\text{TiO}_2$  surface before carbonising to create an even carbon layer. The performance of these new nanorods was greatly improved with respect to the uncoated sample (52).

Karim Zaghbi (Hydro-Québec, Canada) described the latest advances in trying to stabilise reactive Li metal anodes with polymer coatings. The challenges and opportunities in developing thin Li metal with a stable solid electrolyte interphase (SEI) as the negative electrode were discussed in this presentation. In a unique process, Li metal was extruded to 20  $\mu\text{m}$  thin films at a speed of 30  $\text{m min}^{-1}$ . The surface was treated with a special solution and pressed against a solid polymer electrolyte film (dry polymer and ionic liquid-polymer electrolytes). Due to the surface treatment, the very clean conditions and constant pressure on the stack, long term cycling (3000 cycles at C/3 and 80°C) without major fading and dendrite growth was possible.

Nanostructuring has become a key requirement for the utilisation of high capacity silicon anodes. Whilst these anodes have very high capacities they can be difficult to utilise, due to a large volume change of around 300% occurring on lithiation. Fei Luo (Chinese Academy of Sciences) described how the volume variation in Si/C composites is very anisotropic. Si/C particles were synthesised as nanorods attached to the substrate which allowed for the large volume expansion. There was a complex evolution of particle shape caused by amorphous to amorphous diffusion-controlled phase transitions; however porous films did not prevent cracking. Isolated Si column structures showed much less cracking than dense films (53).

## 7. Electrolytes

Increasing the operational potential of the cathodes brings new challenges for the electrolyte. Jeff Dahn and Laura Downie (Dalhousie University, Canada) described their approach to tackle increased side reactions originating from electrolyte oxidation on high voltage material surfaces. Commonly used carbonate based electrolyte solutions show increasing reaction rates above 4.2 V vs.  $\text{Li}^+/\text{Li}$ . Additives such as vinylidene carbonate (VC), tris(trimethylsilyl)phosphite

(TTSPi) and methylene methanedisulfonate (MMDS) (54) can be used to increase this maximum operating potential (55). NMC pouch cells were cycled at C/10 with low temperature impedance measurements made every 10 cycles. The results of this study showed that there was a very large increase in charge transfer resistance when cells are cycled above 4.4 V. Increased electrolyte oxidation is correlated to increased parasitic heat flow, detected *via* isothermal microcalorimetry. When more than 100  $\mu\text{V}$  of heat is generated during cycling, the entire electrolyte of an A5 pouch cell would be consumed within one year (56–58). Jeff Dahn carefully summarised that the electrolyte stability usually increases with the number of additives.

Ceramic solid state electrolytes as a safe high-voltage solution were presented by Chihiro Yada (Toyota Motor Europe). A main problem is the huge charge-transfer resistance at the interfaces due to fast Li-ion depletion upon load. Dielectric modification of these layers using  $\text{BaTiO}_3$  could decrease this resistance and increase the quantity of Li at the interface.  $\text{Li}_{1.1}(\text{Nb}_{0.5}\text{Ta}_{0.5})_{0.9}\text{O}_{3-\delta}$  was identified as a promising material with high permeation and Li-ion mobility (59). Flexible solid state electrolytes which can be printed in any shape were presented as a key component for future electronic devices (wearable technology, flexible devices) by Sang-Young Lee (Ulsan National Institute of Science and Technology (UNIST), Korea). The plastic crystal electrolyte (PCE) consists of alumina/silica ceramic nanoparticles, ethylene carbonate, succinonitrile and an ultraviolet (UV) cross linker. The electrolyte ink has no additional processing solvents and shows thixotropic behaviour. Addition of ethoxylated trimethylolpropane triacrylate (ETPTA) successfully suppresses dendrite growth. Cells can be stretched and bent during operation (60, 61). Maria Forsyth (Deakin University, Australia) presented organic ionic plastic crystals (OIPCs, solidified ionic liquids), which show good electrochemical behaviour. Phosphonium based OIPCs incorporating Na salts show electrochemical properties similar to Li containing analogues (62–64). However, the presence of multiple phases, high viscosity and high-temperature eutectics remain issues which can be altered by a careful choice of ion combination (65).

The fact that polymer electrolytes are still solid, after 30 years of research, was no cause for concern for Michel Armand (CIC EnergiGUNE, Spain). Poly(ethylene oxide) (PEO) suffers from increasing glass transition

temperature ( $T_g$ ) (and therefore decreased conductivity) with increasing salt concentration. In poly(ethylene carbonate) (PEC) it is the other way around and this might be an interesting solution for the problem of low conductivity at sub-ambient temperatures (66). Polyelectrolytes have the anion attached to the backbone and the Li transport number should therefore be 1, since  $\text{Li}^+$  is the only mobile species. However, the overall conductivity remains low for these systems so far. Armand's group linked TFSI anions and PEO elements to a polystyrene backbone which could achieve conductivities around  $10^{-5} \text{ S cm}^{-1}$  at  $60^\circ\text{C}$  (67, 68). The question of whether PEO based systems can successfully suppress Li dendrite formation was investigated by the group of Nobuyuki Imanishi (Mie University, Japan). A  $\text{PEO}_{18}\text{LiTFSI}$  with 10 wt%  $\text{BaTiO}_3$  system was swollen with ionic liquid which reduced the bulk resistance of the battery and increased the cycle performance. *In situ* scanning electron microscopy investigations showed that dendrite growth could be retarded.

## 8. Conclusions

This conference was loaded with excellent talks and an enormous number of interesting poster contributions. It was a very well organised event and the beautiful weather underlined the lovely venue. It was obvious that the research on post Li-ion systems is a quickly growing field, which already generate dedicated conferences. One can happily look forward to the next IMLB meeting in 2016 which will be held in Chicago, USA.

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