



# Computational modelling of polymer electrolytes: What do 30 years of research efforts provide us today?



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## ABSTRACT

The advent of polymer electrolytes was perfectly timed with the enormous increase in computational power and availability in the early 1980's. Thus we could/should expect a pool of knowledge to be available from all modelling efforts; MD or MC simulations, analytical approaches, FEM, *ab initio*/DFT, etc. This would be especially valuable when (now again) more emphasis is directed towards safer electrolytes in general and all solid-state electrolytes and batteries in particular – where polymer electrolytes has a major role to play. Here the main lines of polymer electrolyte modelling research both historical and current, as well as the balance between fundamentals/materials/applications, and especially what we might be missing to address, are brought forward. As a result the emphasis has historically clearly been on PEO and PPO based polymer electrolytes aimed at Li and Na batteries application. This mini-review is largely based on the plenary lecture delivered at the ISPE-14 conference held in Geelong, Australia during August 2014 and on the ISPE1-13 conference proceedings.

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## 1. Introduction

Computational modelling of polymer electrolytes may at a first swift look seem a very awkward approach as these materials often are highly complex with multiple phases present, their dynamics are slow, and most often they are found out of thermodynamic equilibrium. The research community targeting polymer electrolytes therefore has to be smart and study sub-systems of full polymer electrolytes or address fundamental phenomena by choosing methods that can circumvent these issues. The purpose here is to review the research questions tackled during 30 years of efforts (and by what methods) and how the field in general has progressed – continuously straight-forward or hit by sudden changes in research directions – to finally give some hints on what is done today and perhaps more importantly; what is not done and maybe awaits us tomorrow? The limitations in scope are set to: i) studies with, at least in some respect, batteries in focus, which has been the main track during these 30 years, and ii) mainly, if not strictly, studies reported in the proceedings of the ISPE1-13<sup>1</sup>

conferences, to make the review feasible in scope for the proceedings of ISPE-14 and still highly relevant to the community.

Looking back 30 years the very conditions for performing computational modelling has truly been revolutionized. As for any other characterization technique it is actually the hardware development that sets the fundamental limits and for computers Moore's law has been most effective in this respect. In 1984 there were only a few supercomputers around and available to scientists, the fastest was likely a Cray-X MP in the US at 400 MFlops and 2–4 processors, while in 2014 we find supercomputers in very many countries and many universities. Not too surprising the fastest computer around is currently the Tianhe-2 at the National University of Defense Technology in China at a fantastic 34 PFlops and 3120000 cores [1]. The even larger difference, however, is that today computing can be done more or less everywhere – desktop computers are now extremely wide-spread and typically come with the measures of ca. 8 GB RAM and at 3 GHz – a hardware agreeable for many, even if not all, computational tasks. This also assures a wider user community of the major software (also more abundant today – and often as freeware or shareware under different open licenses) for computational approaches to materials like polymer electrolytes.

Another starting point is to look at how the polymer electrolytes themselves and the properties studied have developed since 1984 (not only regarding simulations). The 1<sup>st</sup> ISPE conference was held in 1987 in St Andrews, but will here represent the first half of

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<sup>1</sup> For ISPE-13 no common conference proceeding in Electrochimica Acta was made, why references are collected based on the programme of oral and poster presentations.

the 1980's. Practically everything in the proceedings of ISPE-1 centered on solid polymer electrolytes (SPEs) based on a few polymers: PEO, PPO, and PEI. Similarly only a few salts were used, with anions such as Tf, SCN, ClO<sub>4</sub>, and AsF<sub>6</sub>. To note is that the TFSI anion, first synthesized in 1984 [2], had not yet entered the field. More or less all studies at the time considered the fundamentals – there were questions on the ion conduction mechanism, the phase-diagrams – many crystal structures were determined, the stabilities vs. Li metal, *etc.* Seen in the recent up-surge for sodium based batteries and their electrolytes [3], it is interesting to note that Na based SPEs were equally popular as study objects as the Li based. One important reason for this was that in 1984 the launch of the lithium-ion battery (LIB) was yet to come, the Li metal batteries with SPEs were still competing against those with liquid organic electrolytes and also Na based batteries alternatives were seen as possible competitors. For many years since then, however, only the LIBs saw commercialization; initially urged for by the need for power of the earlier launched Sony Walkman (1979) and later on powering the portable electronic devices revolution ever since the early 1990's – first the GSM cellular phones and laptops and then the smartphones and tablets *etc.* from *ca.* 2007 and onwards. The LIBs are now at a vast 10<sup>10</sup> cells/year made, but since 2011 also the often quoted polymer electrolyte battery concept by Bolloré in the Bluecar of Autolib' [4] is “commercial”. In 2014 we have *e.g.* seen the advent of ionic liquids (ILs) into the electrolyte field, for polymer electrolytes resulting in ternary polymer electrolytes, and other new materials such as plastic crystals, much more complex polymers as the matrices, many new salts as the dopants, *etc.* At the same time the properties studied are less on the fundamentals and more oriented towards application, especially electrochemical performance under various conditions.

All of the above has affected the community at large, the new materials and the proposed commercial targets not the least, and therefore also the subjects of computational studies of polymer electrolytes – to different degrees. Several cross-sections are of course possible in order to review the efforts and results over 30 years, and below this is performed in a set of time-slots for each of the main simulation techniques used and properties targeted, all based on the ISPE proceedings. Prior to that, however, it is instructive to remind ourselves the very reasons as to why apply computational modelling to polymer electrolytes first place.

## 2. The purpose of computational modelling

Often two distinctly different stances are taken on the main purpose of performing computational modelling – although not necessarily totally orthogonal or exclusive. One is that testing theories and determine fundamental limitations is the prime aim of modelling. For polymer electrolytes this can for example be concretized as elucidating the conduction mechanism at the most fundamental level and relate it to theories like the dynamic bond percolation theory (DBPT) [5] or free volume theory, rationally design the materials based on proper knowledge of optimal choices of inter-spacings, chain lengths, salt concentrations, *etc.*, or determine the behavior of properties in ranges difficult to access experimentally *e.g.* very high/low pressures and temperatures. It can also concern the fundamental limitations of various concepts *e.g.* comparing the intrinsic problems/promises of the standard salt + polymer SPEs with those of gel polymer electrolytes (GPEs), single-ion conductors (SICs), nano-particle containing composite polymer electrolytes (CPEs), and ternary polymer electrolytes based on including ILs, *etc.* The second stance is that the purpose of simulations is mainly to assist and support the interpretation of experiments. Here the typical examples are structure determination by X-ray and neutron diffraction (XRD and ND) supported by reverse Monte-Carlo (RMC) or molecular dynamics (MD)

simulations, the probing of local structure and interactions by various spectroscopies (NMR, IR, Raman) supported by *ab initio* and density functional theory (DFT) calculations or MD simulations, the many various properties or a more dynamic origin like diffusion from NMR, conductivity and relaxation data from dielectric spectroscopy (DS) or electrochemical impedance spectroscopy data, all supported by MC or MD simulations or analysis via sets of differential equations. There is no need to build any firm borders between these two main stances, but an understanding of their very existence is nevertheless needed to be able to encompass the development of the field of computational modelling of polymer electrolytes.

## 3. Simulation techniques and properties targeted

Reviewing all the proceedings of ISPE some simulation techniques are clearly used much more frequently than others and also persist over time, while others appear and disappear as they are strongly connected to more special concepts or properties. There is also the factor that the number of groups and scientists focusing on computational modelling of polymer electrolytes are few, so large fluctuations frequently occur in the intensity of the reported studies. Nevertheless, from all the proceedings there are *ca.* 35 publications that can be classified as completely or mainly computational studies and scientists from no less than 11 different countries have been active. Below there will be not complete coverage of the simulation techniques qualifications as such, nor any attempt to necessarily include all work performed, but the focus is on creating a time and simulation technique dependent picture of the development of the field of computational modelling of polymer electrolytes and the scientific issues targeted.

### 3.1. Molecular dynamics simulations

The prime advantage of molecular dynamics (MD) simulations is the possibility to treat the full polymer electrolyte system, and MD can thus be made to target the mobility of ions via hopping as well as via the segmental motion of the polymer chains, or the mobility of any included solvents such as for GPEs. Thus MD data are excellent to compare with dynamics data; diffusion of ions, relaxation times, *etc.*) obtained from NMR or QENS measurements [6–13]. It can also be used for overall structural studies including the stability of electrolyte/electrode surfaces and reconstruction, comparable to XRD or ND data [14,15], as well as to elucidate local structure via radial distribution functions (rdfs) and thereby reveal the speciation and coordination in detail including also very SPE specific phenomena like salting out – hence providing comparisons also to local ion coordination sensitive experimental techniques such as IR or Raman spectroscopies [7,11–13,16,17]. MD is thus a truly versatile tool and has clearly been amongst the most popular tools for computational modelling of polymer electrolytes.

Starting from the fourth ISPE meeting MD simulations have been used frequently – but initially targeted a single SPE system: NaI in PEO [6,7,14]. The NaIPEO<sub>3</sub> crystal structure was one target to reproduce, primarily to assess whether or not the MD potentials developed for pure PEO could be re-used for PEO in Na based SPEs. This was made by comparing rdfs obtained from MD to XRD derived structural data. Simultaneously the dynamics of both NaIPEO<sub>n</sub> SPEs and the liquid analogue NaI in G1/monoglyme (CH<sub>3</sub>O–(CH<sub>2</sub>CH<sub>2</sub>O)<sub>1</sub>–CH<sub>3</sub>) were studied as functions of concentration and temperature. While all simulations by necessity used long time-steps and rather short simulation times, the papers all provide qualitative reasoning vs. theories like DBPT – for instance the local conditions determining if and how ion “hopping” is likely

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