Review

Not peer-reviewed version

Composite Electrolytes for Supercapacitors

Lijun Fu , Qunting Qu , Lili Liu , Rudolf Holze [*]

Posted Date: 27 January 2025

doi: 10.20944/preprints202501.1926.v1

Keywords: supercapacitors; electrolytes; electrolyte solutions; solid electrolytes; polymer electrolytes; composites; hybrid materials doi:10.20944/preprints202501.1926.v1

Review

Composite Electrolytes for Supercapacitors †

Lijun Fu [1], Qunting Qu [2], Lili Liu [1] and Rudolf Holze [1,3,4,5,*]

[1] State Key Laboratory of Materials-oriented Chemical Engineering, School of Energy Science and Engineering, Nanjing Tech University, Nanjing, 211816, Jiangsu, China
[2] College of Energy, Soochow University, Suzhou, Jiangsu 215006, China
[3] Confucius Energy Storage Lab, School of Energy and Environment, Southeast University, Nanjing 210096, China
[4] Department of Electrochemistry, Institute of Chemistry, Saint Petersburg State University 7/9 Universitetskaya nab., St. Petersburg, 199034, Russian Federation
[5] Chemnitz University of Technology, D-09107 Chemnitz, Germany
* Correspondence: rudolf.holze@chemie.tu-chemnitz.de

† Dedicated to the memory of H.-J. Schäfer, an inspiring organic (electro)chemist and driver of electrochemistry in organic chemistry.

Abstract: Composite electrolytes for applications in electrochemical energy technology, i.e. in batteries and supercapacitors, are gaining increasing attention. In the absence of a commonly accepted definition a ternary combination of materials, e.g. a polymer with an electrolyte salt or electrolyte salt solution and a third conductivity-enhancing constituent, is assumed as a definition of a composite electrolyte in the following review. Relevant fundamentals and reported research results up to explanations of the observed effects and improvements are reviewed. Future perspectives and directions of further research are indicated.

Keywords: supercapacitors; electrolytes; electrolyte solutions; solid electrolytes; polymer electrolytes; composites; hybrid materials

1. Introduction

The ionically conducting phase between the electrodes of a battery or a supercapacitor is frequently and rather imprecisely called the electrolyte. By definition an electrolyte is composed of ions (a true electrolyte according to standard textbooks [i], e.g. NaCl) or of molecules, which dissociate into ions upon interaction with a suitable solvent (potential electrolytes, e.g. HCl in water), accordingly in most cases electrolyte solutions are actually employed [ii - iv]. Ionic liquids composed of ions only and liquid already at room temperature (room temperature ionic liquids RTIL) are the rare exemption. In this text, the distinction between electrolyte and electrolyte solution is ignored for the sake of simplicity only. Mostly because of safety concerns and of risks associated with leakage of devices the use of liquid electrolyte (solution)s is not welcome in most applications [v]. Consequently, numerous attempts to replace them with non-liquid or even solid materials have been proposed and examined. The absence of any non-liquid electrolyte in a most recent wide-ranging review on supercapacitors appears to be an aberration and not representative of the current research trend [vi]. These attempts started with the general "wishing list" for an electrolyte system in mind [v, vii]:

- Wide available electrode potential window
- high ionic conductivity
- sufficient chemical and electrochemical stability
- thermal stability
- compatibility with electrode and separator materials
- environmental compatibility
- low price

- sustainable resources

Given the stated flaws, limitations and challenges of liquid electrolytes reported attempts to improve in particular solid electrolytes have addressed implicitly or explicitly these aspects:

- Enhanced ionic conductivity
- wider range of operating temperatures
- improved mechanical stability
- better long-term stability
- increased thermal stability

Further aspects like improved electrode/electrolyte interaction, lower prices, flexibility and bendability [viii] etc. may also have come into play; they are mostly of minor importance only. For an example wherein cotton added into a hydrogel of sodium alginate and starch improved flexibility of a supercapacitor see [ix].

Added or improved catalytic properties of a further constituent may be relevant for selected applications as with separators in lithium-sulfur batteries. Most frequently improved ionic conductivity is a major aim of composite-formation. The case of membrane-electrode assemblies with mixed conduction (ionic and electronic one) has been examined also [x].

Based on the preceding lists already the combination of poly(ethyleneoxide) PEO with $LiClO_4$ may be called linguistically correct a composite as in [xi], in another case combinations of two ionic liquids with a lithium salt [xii] or of clay with an ionic liquid [xiii] have been called a composite electrolyte. The definition of a composite as a two-phase combination formed by distributing a small fraction of a filler into a solid or gel electrolyte seems to cover only part of the material presented below [xiv].

Nevertheless, in this report the result of addition of a further performance-enhancing ingredient to an electrolyte will be called a composite electrolyte only. Thus all presented examples below may be classified as ternary composites. A slightly different classification of composite electrolytes as always being a combination of organic and inorganic material classified into layered composite electrolytes and polymer electrolytes with inorganic fillers appears to be less suitable and is not followed here [xv]. In a very rare example of the first class a laminated electrolyte has been proposed [xvi]. A layered electrolyte structure (not laminated) of PEO and MoO_3 further handled in a rather complicated procedure has been proposed [xvii]. To call graphene or CNTs a composite may be a bit of a stretch [xviii]. The sometimes-encountered eye-catcher “nano” like in “nanocomposite” or “nanofiller” is ignored as being meaningless in the present content. The “good charge storage capacity” requested from an electrolyte [xviii] will certainly not by discussed below, instead it seems to suggest a fundamental misunderstanding – which can be found elsewhere again [xix]. The meaning of “composite nature” invoked frequently in a report [xx] could not be identified. Dimensionalities of the added ceramic material have been considered in a review of ceramic material/polymer composite electrolytes [xxi].

Composite electrolytes in the meaning assumed in this reports have also attracted attention for polymer electrolyte membrane fuel cells in particular with respect to opening up avenues to higher operating temperatures [xxii]. Already addition of highly thermally conductive nanoparticles can yield an ink-jet printable composite electrolyte liquid [xxiii].

Following a first mentioning of composite electrolytes in a conference proceeding in 1985 [xxiv] the report on *in situ* formation of a solid/liquid composite electrolyte for a lithium-iodine battery in 1986 may be considered as the starting point of the development reviewed here. This report addresses an early and until today successful application of a solid electrolyte in a lithium battery: In pacemakers, which have been using a solid layer of LiI formed between the lithium metal negative electrode and the positive electrode of iodine and poly-2-vinylpyridin as solid electrolyte successfully for years [xxv]. This is a very low current application, the already mentioned flaw of poor ionic conductivity is barely relevant, whereas the very low self-discharge is a remarkable advantage. A report on a solid polymer electrolyte modified with an inert filler for lithium batteries in 1982 may be considered as a starting point for that field [xxvi], for an overview see [xxvii].

Early reports on composites, mostly on solid/solid composites, were few, and only around 2018 the rate of publications quickly increased as depicted in Figure 1.

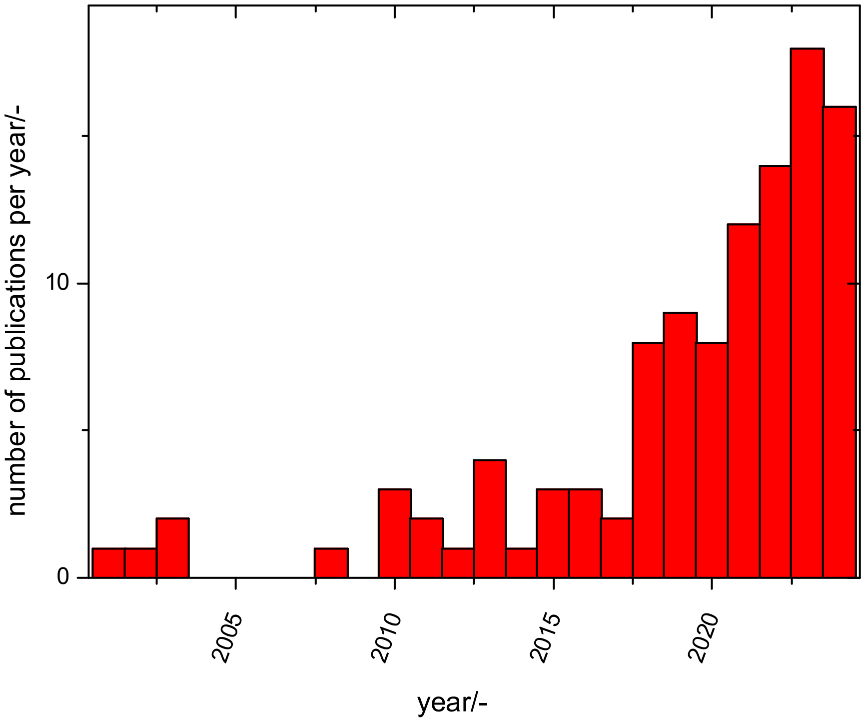

Figure 1. A search with the string “composite AND electrolyte AND (supercapacitor OR battery)” found anywhere in the title, keywords or abstract (Data from Scopus® and Web of Science® retrieved on December 16th, 2024 yielded 16059 hits. Upon closer inspection it turned out, that a large number of research reports were not dealing with composite electrolytes at all. Given the later detected inspired phantasy of many authors manifested in the creation of terms like “electrolyte composite” or “polymer electrolyte composites” [xxviii] the apparently logical search string "*composite* *electrolyte*" AND (supercapacitor OR battery) yielded only 1591 hits missing many products of said inspired creativity. For this report finally the search string “composite AND electrolyte AND supercapacitor” was used yielding 4178 hits, irrelevant reports were removed manually. Searches using various AI-based tools were rather similar in terms of results. The results are depicted above as annual publication numbers of reports. Further publications with these keywords somewhere in the text could initially not be counted; but when noticed and considered relevant in the present context they were included below. A particularly noteworthy example reports on polyvinylidenefluoride-co-hexafluoropropylene co(PVDF-HFP) (or simply PVDF-HFP, see below for figure) plasticized with DMF (not even mentioned) and added zinc acetate providing mobile ions but called a dopant [xxix]. The result is called a composite electrolyte! Elsewhere authors could not decide whether to call a solution of two magnesium salts in water a composite or a compound electrolyte [xxx].

Organization of the material aiming at optimized accessibility for the reader and at keeping a systematic overview enabling identification of details and trends of particular interest to the reader follows a scheme primarily determined by the chemical identity of the host or major material. Although the fields “batteries” and “supercapacitors” appear to be in some merger as reviewed elsewhere [xxxi, xxxii] the traditional separation is kept here given the vast difference in the number of reports (56 on supercapacitors, 1187 on batteries. A corresponding overview dealing with batteries will be provided elsewhere, a first general overview is available [xxxiii]. Obviously the arrangement electrolyte/electrolyte (solution)/electrode in a supercapacitors is very similar to that in a secondary battery; actually a supercapacitor may be called an extreme version of a high power battery whereas a secondary battery may be considered as a high-energy version of a supercapacitor. Not surprisingly some of the problems faced with secondary batteries show up with supercapacitors again. The assumed merger of both fields and the congruence of principles of operation as highlighted in [xxxi, xxxii] should not be confused with hybridization of components addressed elsewhere [xxxiv]. The term hybrid may actually also be applied to some of the composite electrolytes discussed below because apparently one condition for the proper application of this term of Greek origin ὕβϱις (hybris) meaning arrogance or presumptuous in the common usage but meaning in the present context something bundled, mixed or interbreeded with interactions going beyond plain addition is met in many cases. The terms and overlaps are illustrated in Figure 2.

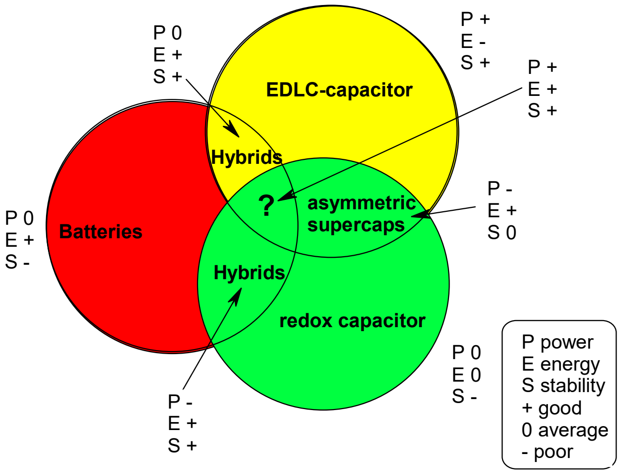

Figure 2. The merger of batteries and various types of supercapacitors, for details see text.

As shown combinations of electrodes from two different “families” yields hybrids, from two similar “families” yields asymmetric devices. When looking for advantages of the combinations power P, energy E and stability S are major criteria. Realized or at least expected advantages are tentatively marked in the figure, the “holy grail” frequently placed in the top right corner of Ragone-plots [xxxv] is marked in the center.

Nevertheless the term composite has prevailed so far on the materials level. Apparently the term mixture may have been correct in many examples where the reason for combining specific constituents remains as mysterious as the reason for the particular mixing ratio. Presumably the term “composite or hybrid supercapacitors” found in [xxxvi] will hardly help.

Given the obvious differences between batteries and supercapacitors first the slightly different tasks of electrolytes (although the distinction between electrolyte and electrolyte solution has been stated above and the need to keep this distinction is obvious for the sake of brevity in the following text electrolyte and electrolyte solution (the latter are not in the focus of attention anyway) will be used as synonyms) in both devices will be briefly laid out. The main part of this report is finally dedicated to studied examples organized as described above. Particular attention is paid to the function and role of the constituents, this will initially help to understand the operation of the electrolyte, in addition, data pertaining to stability are mentioned because stability will finally decide about the practical value of a battery or supercapacitor component. This has been stressed before [xxxvii], more attention to unified reporting has been requested elsewhere again [xxxviii].

2. Electrolyte tasks and challenges

In conventional electrolytes as well as electrolyte solutions the roles played by the ingredients is perfectly obvious in almost every case [ii - iv]. Once a further ingredient is added into an electrolyte, e.g. another ionic liquid or salt into one ionic liquid or a further salt into an electrolyte solution there should be a reason specified together with the suggestion of the addition. Unfortunately, this may not always be the case, the reader is left wondering about conceivable ideas behind the addition.

2.1. Composite electrolytes

Beyond the trivial statement, that any combination of two materials enabling ionic conduction without showing electronic conduction – this may even qualify as the definition of an electrolyte – combining materials is commonly pursued with particular improvements in mind. These may range from obvious improvements in terms of the electrochemical properties listed above in the wishing list to further technical and even economical improvements. When examining composites with a polymer the mechanical scaffold provided by the macromolecular material serving as a welcome stiff material rendering a separator possibly superfluous combined with an improvement of the ionic conductivity of the polymer are in the focus of attention. In case of composites composed of two or more non-polymeric materials the welcome mechanical contribution of a polymeric scaffold remains absent, other advantages beyond improved ionic conductance will be the driving force behind mixing. Use of the sometimes-encountered term filler (see above) appears to be a bit unclear, at least undefined. The distinction between passive (insulting) fillers not providing internal ionic conduction and active (conducting) fillers suggested in [xxxix] has apparently not found widespread use.

2.1.1. Composites with polymer hosts

Overviews on polymer electrolytes are available [xl - xlii], more specific ones on the use of polymer electrolytes in supercapacitors are available also [xliii], a recent review presents the current status [vii]. Starting a composite electrolyte with a polymer or a polymer electrolyte is very rational: The polymer will provide the mechanical support (or backbone) providing the scaffold desired for an application not needing an extra separator. The added (composite) constituent may e.g. reduce crystallinity of a polymer like PEO thus increasing ionic conductivity [xliv, xlv] or may provide particularly transport-accelerating particle/host interfaces as demonstrated in [xlvi]. There is also evidence that effects may depend on particle size with small particles increasing conductivity only and larger ones increasing conductivity and transport number [xlvii]. This applies to all added particular materials. In another highly unsystematic study of several inorganic components with different particle sizes and dielectric constants no coherent conclusions were obtained [xlviii]. Ion-conducting materials may add further ionic conduction pathways inside the particles. Possibilities of enhanced ionic conductivity mechanisms have been reviewed [xlix]. Further advantages may be gained by starting from a polymer blend of e.g. poly(vinylalcohol) PVA (Figure 3) and poly(ethyleneoxide) PEO (Figure 4) with addition of 3 wt.% TiO_2 [l]. Similar beneficial effects were observed upon addition of $BaTiO_3$ to a polymer blend of PVA and poly(ethylenglycol) PEG (Figure 5) [li], of $Li_{0.5}La_{0.5}TiO_3$ to a blend of PEO and PVDF [lii], or of ZrO_2 to PVDF-HFP [liii]. Actual modes of operation of the added ceramic may differ from material to material depending on the exact chemical composition.

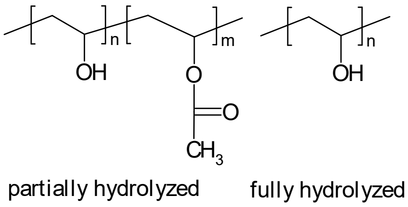

Figure 3. Poly(vinylalcohol)

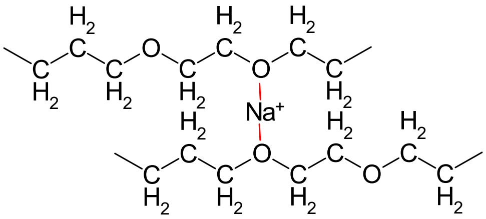

Figure 4. Poly(ethyleneoxide) and a scheme of interactions between a sodium ion and PEO.

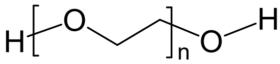

Figure 5. Poly(ethylene glycol)

Some general procedural aspects of polymer and composite polymer electrolytes (preparation and handling) have been summarized in [liv]. (Gel) Electrolytes obtained by plastification (gelling) of a polymer with a suitable solvent (this may be a solvent or a solvent mixture but also an electrolyte solution) have been called composite electrolytes infrequently (for an example see [lv]). An overview covering PEO-based composite electrolytes with a major focus on batteries is available [lvi].

2.1.2. Binary composites

Instead of a polymer acting as a host and providing in most cases the major fraction of a composite electrolyte an inorganic material like fumed silica may act as a highly porous host material which is subsequently soaked with an electrolyte solution yielding a solid material which may not possess the mechanical properties enabling its use as separator or similar, for typical examples see [lvii,lviii]. Mixtures of two inorganic compounds have also been suggested and examined as composite electrolyte. Composites based on a ceramic component like in Al_2O_3 with LiI [lix] show a lithium ion conductivity three orders of magnitude larger than that of plain LiI. Possibly microstructural features in the composite are the reason of the major conductivity increase. Procedures towards composite electrolytes based on casting of polymer electrolytes into 3-D ceramic frameworks have been collected and reviewed in [lx].

3. The materials

3.1. Composite electrolytes in supercapacitors

Following the classification suggested above identification of true examples of a composite electrolyte turns out to be difficult because of the generous use of the term composite for whatever material combination as in [lxi]. In this example, none of the ingredients qualifies as an "enhancing" constituent for an already established electrolyte.

3.1.1. Composites with polymer hosts

PEO

Addition of 0.1 wt.% silica nanoparticles to a copolymer of poly(ethylene oxide)-poly(propylene oxide) with an ionic liquid as ion source [lxii]. Increased ionic conductivity and mechanical strength were attributed to cross-linking between "silane groups present in the precursor and the SiO_2 surface". Surprisingly none of the precursors contained silicon. The assembled EDLC-supercapacitor kept 94 % of its initial capacitance after 10000 cycles.

Transport parameters of charge carriers in PEO-LiTf-based polymer electrolyte with added Al_2O_3 have been studied in detail [lxiii].

Addition of an inorganic constituent for enhanced mechanical stability was demonstrated in a study of PEO containing an ionic liquid as ion source reinforced with electrospun silica nanofiber [lxiv].

Increased thermal stability measured as slower thermal decomposition rate of a PEO-based composite has been observed when an inorganic (NASICON-type ceramic) compound like $Li_{1.4}Al_{0.4}Ge_{1.6}(PO_4)_3$ was added at 50 wt.% [lxv], for a further similar example with a stable capacitance of the EDLC-device up to 16000 cycles see [lxvi] and also [lxvii]. The effect was attributed to a lower organic fraction in the electrolyte, in particular of potentially volatile organic solvent. Further influences of the participating organic solvent were noticed [lxviii]. Beneficial effects of this ceramic in PEO have also been identified in [lxix], similar observations were reported after incorporation of nanocrystalline $Na_3Zr_2Si_2P_3O_{12}$ into PEO [xxxix]. An overview of PEO-based composite electrolytes with added ceramic particles is available [lxx]. Advantages of added ceramics instead of plastification with some liquid in particular with respect to stability have been highlighted [lxxi]. Clays as ceramic constituents have been studied in detail [lxxii - lxxiiilxxiv]. By cation exchange the original montmorillonite was modified into "organic clays". Nanosized alumina has been tested as another constituent [lxxv].

PVDF

To ameliorate the inferior mechanical properties of otherwise attractive PVDF it has been reinforced with woven fabrics of polyamide and poly(ethylene terephthalate) [lxxvi]. The major improvement of mechanical properties did not affect ionic conductivity. Incorporation of silica particles into an electrolyte of co(PVDF-HFP) and an electrolyte solution of $TEABF_4$ in a carbonate solvent mixture yielded a composite electrolyte with significantly increased ionic conductivity at 15 wt.% addition of silica [lxxvii]. A similar approach with PVDF only dissolved in DMF with 5 % silica (called nanostructured only in the title of the report) added to the solution has been reported [lxxviii]. Why silica addition resulted in the lowest ESR, highest capacitance, elevated operation temperature and 91 % capacitance retention of the EDLC-device after 2000 cycles remains unclear. Infiltration of co(PVDF-HFP) into alumina nanotubes arrays arranged perpendicularly between the electrodes of an EDLC-device subsequently soaked with a 1 M tetraethylammonium tetrafluoroborate/propylene carbonate electrolyte solution yielded a solid electrolyte [lxxix]. Some general advantages in comparison to commercial separators were claimed.

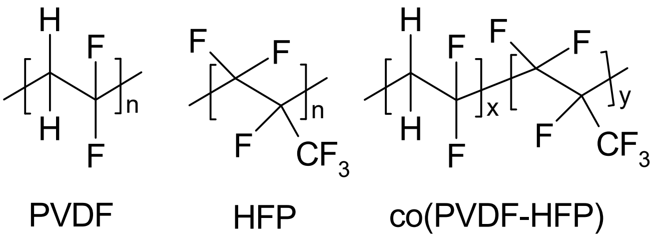

Figure 6. PVDF, HFP and co(PVDF-HFP)

Polyurethane

Addition of 4 wt.% fumed silica to an electrolyte of thermoplastic polyurethane and an ionic liquid yielded a free-standing film with increased ionic conductivity and decreased interfacial resistance between electrodes and electrolyte [lxxx]. The composite also acted as separator.

PVA

PVA grafted with dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride with KOH as electrolyte and added GO for increased ionic conductivity has been suggested for use in an asymmetric supercapacitor [lxxxi]. After 5000 cycles, 87 % of the initial capacitance were retained. Hypergrafted poly(amine-ester) nano silica added to a PVA-KOH electrolyte was used in an EDLC-supercapacitor with improved performance when compared with a device not containing said additive [lxxxii]. The improvement was attributed to the enhanced ionic conductivity of the electrolyte. Silica nanoparticles added to a PVA/H_2SO_4 electrolyte immobilized the sulfate ions shifting ionic conduction to protons for use as electrolyte and separator in a symmetric redox supercapacitor with polyaniline as active material in both electrodes [lxxxiii]. Addition of cellulose dissolved in phosphoric acid added to PVA resulted in crosslinking of the polymer [xix]. Already at a cellulose content of 5 wt.% major improvements of mechanical properties were reported. Addition of $ZnCl_2$ to a PVA/cellulose mixture with added $CaCl_2$ and LiCl as ion source resulted in improved mechanical strength and deep temperature performance [lxxxiv].

Porous montmorillonite with heteroatom-doped graphene-like carbon added to a PVA-based electrolyte sulted in improved mechanical properties and increased conductivity [lxxxv]. The assembled EDLC-device kept a stable capacitance along 500 cycles (!).

PAA

Addition of GO to a polyacrylic acid/H_2SO_4-based electrolyte yielded at an optimum content of 0.5 % of GO a significant increases of mechanical stability and ionic conductance [lxxxvi].

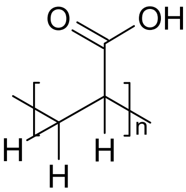

Figure 7. Polyacrylic acid PAA

Enhanced conduction was attributed to hydrogen-bonded networks formed with the help of the oxygen-containing surface groups of the GO. These groups may also contributed to higher mechanical strength by forming hydrogen bonds with the by the polyacrylic acid chain. After 10000 cycles 103 % of the initial capacitance were retained. Poly(methacrylic acid–methyl methacrylate) was added as mechanical reinforcement to a hydrogel lectrolyte of poly(sodium acrylate–vinyl phosphonic acid) [lxxxvii]. Coulombic efficiency of an EDLC-device was stable along 10000 cycles whereas capacity retention was not reported.

Biopolymers

Addition of 9 wt.% of GO to a blend of chitosan and potato starch with $LiClO_4$ as ion source and glycerol as plasticizer yielded a solid electrolyte [lxxxviii]. Increased ionic conductivity was attributed to formation of “ion highways” along polymer/GO particle interfaces. Addition of zwitter ion-bearing nano-hydroxyapatite grafted zwitterionic silane to a carboxylated chitosane-based yielded a solid hydrogel electrolyte with improved mechanical strength and ionic conductivity because of reduced crystallization [lxxxix]. With an optimized addition at 20 % the EDLC-supercapacitor kept 98 % of its initial capacitance after 5000 cycles. Addition of chitosan to an animal gelatin-based hydrogel electrolyte yielded a material with greater mechanical robustness and better performance at low temperatures [xc]. The assembled EDLC-type supercapacitor kept 81 % of its initial capacitance after 2000 cycles.

Addition of 1 wt.% of hierarchical porous carbon HPC to a gel polymer electrolyte yielded an improvement of ionic conductivity by about 116 % [xci]. The macropores in the added HPC serve as electrolyte solution reservoir preventing leakage of solution. How the interconnected microtunnels in the HPC shorten the pathways for ions remains unclear, the wealth of oxygen-containing surface groups in turn may facilitate ion movement by e.g. forming a particularly amorphous interphase on the HPC surface.

Nanofibrillated cellulose of biological origin with its internal structure filled with an aqueous electrolyte solution containing proton-transporting polystyrene sulfonic acid was used as solid electrolyte with two paper-based electrodes in an EDLC-device [xcii]. Although the perfomance data were not overwhelming a proof-of-concept of a cellulose-based supercapacitor was provided.

Miscellaneous polymer host materials

Addition of Bi_2O_3 nanoparticles and nanosheets of graphitic carbon nitride to a polyelectrolyte of polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene yielded a composite membrane electrolyte tested in an EDLC-type supercapacitor [xciii]. Increased water uptake due to the added constituents was claimed as the cause of improved proton conductivity. The device showed 97.8 % capacitance retention after 10000 cycles.

The insufficient mechanical strength of highly sulfonated polyether ether ketone (SPEEK) can be ameliorated by addition of an inorganic components like heteropolyacids [xciv]. This also increases the proton conductivity of the heteropolyacid. Further addition of reduced graphene oxide GO was suggested, the reasons for this remain unclear.

An epoxy matrix soaked with an electrolyte solution of $TEABF_4$ in propylene carbonate has been used in a structural EDLC-type supercapacitor [xcv]. Further examples of solid polymer electrolytes with added silica for use in structural supercapacitors have been reported [xcvi]. Different from most other reports addition of the silica resulted in decreased ionic conductivities. Addition of Al_2O_3 to a mixture prepared for epoxy polymer preparation with an ionic liquid added later for ionic conduction resulted in improved mechanical properties [xcvii]. With a composite electrolyte based

Preprints.org (www.preprints.org) | NOT PEER-REVIEWED | Posted: 27 January 2025 doi:10.20944/preprints202501.1926.v1

on an epoxy matrix with $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ a large capacitance increase of the assembled structural EDLC-supercapacitor was observed after addition of 6.5 wt.% of single wall carbon nanotubes to the composite [xcviii].

A microporous poly(arylene ether ketone)/poly(ethylene glycol)-grafted poly(arylene ether ketone) polymer membrane was soaked with an aqueous electrolyte solution of $LiClO_4$ containing added chitosan for increased solution uptake [xcix]. Capacitance was stable for 5000 cycles, compared with a control cell with the liquid electrolyte only self-discharge was much smaller. How the "excellent electric insulation characteristics of the electrolyte" contributed to this outcome remains unclear.

The poor wetting of polypropylene used as separator by ionic liquids could by overcome by soaking it with a solution containing in addition dissolved PEO in acetone [c]. Whether the added PEO changed the wetting properties of the PP surface was not addressed.

The inherent limitations of poor mechanical strength and narrow operating temperature range of poly dimethyl diallyl ammonium chloride as a potential solid electrolyte could be ameliorated by adding sodium montmorillonite [ci]. With various electrode materials, capacitance rententions above 90 % during 1000 cycles were found.

Establishment of a sufficiently large electrode/electrolyte interface already addressed as a major challenge with both batteries and supercapacitors elsewhere [v, vii] has been reviewed for polymer-based composite electrolytes [cii].

After addition of Na-montmorillonite to poly(2-acrylamide-2-methyl propanesulfonic acid) a composite (hydro)gel with increased ionic conductivity and enhanced tensile strength was obtained [ciii], for a further example see [civ]. Elsewhere Na-montmorillonite was used as a crosslinker in a mixed poly(acrylamide)/poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) electrolyte [cv].

Hollow silica spheres in a polymer matrix as cavities filled with ionic liquid increased ionic conductance by suppressing the braking effect of polymer strands on ionic movement outside of such cavities [cvi].

3.1.2. Binary composites

A proton-conducting $Sn_{0.95}Al_{0.05}H_{0.05}P_2O_7$ powder was pressed into a pellet with PTFE as a binder yielding a solid electrolyte membrane [cvii]. Carbon electrodes used as EDLC-type electrodes were soaked with 105 % H_3PO_4 (called for unknown reasons ionomer) and assembled with this electrolyte membrane into a supercapacitor showing stable cycling behavior for 7000 cycles at 150 °C. Addition of fumed silica (also called a filler) to an ionic liquid resulted in increased ionic conductivity and a significantly higher possible operating temperature [lvii, cviii]. Particles with a diameter of 10 nm showed best improvements. The meaning of "33-time improvement of device performance" remains mysterious.

0.1 wt.% of reduced GO added to an ionic liquid yielded improved performance of an EDLC-type supercapacitor [cix]. Why this electrolyte which even does not escape the drawbacks of liquid electrolytes is called a composite electrolyte remains mysterious.

3.2. Miscellaneous materials and observations

Using an organohydrogel as binder in the electrodes and as electrolyte enabled a supercapacitor with a wider range of operating temperatures and a capacitance stable along 2000 cycles at room temperature [cx].

In a consistently mysterious report a composite of reduced GO and poly(methyl methacrylate) constitutes a supercapacitor [cxi].

Delignified wood was used as a scaffold and filled with a polymer mixture with $LiClO_4$ as ion source yielding a solid electrolyte for an EDLC-supercapacitor [cxii]. The many internal cavities in the wood scaffold accelerated ion transport, the device kept a stable capacitance during 4000 cycles. For similar studies of analogous constituents see [cxiii, cxiv]. The influence of the degree of delignification of wood as additive to a poly(acrylic acid-acrylamide)-based solid electrolyte on supercapacitor performance was examined [cxv]. Significantly, improved ionic conductivity was attributed to the directing effect of the straight pores in the wood. Delignified balsa wood was added to a hydrogel of quaternized gelatin with cross-linked poly(acrylic acid-co-acrylamide) effecting increased ionic conductivity, reduced swelling and enhanced mechanical strength of the obtained electrolyte [cxvi]. 94.6 % of the initial capacitance were retained after 10000 cycles.

Ionic liquids added to various powdered ceramic ion conductors yielded much better conducting electrolytes [cxvii]. The electrolyte discs were mounted between EDLC-type electrodes by applying substantial mechanical pressure. Performance was much improved when compared with a cell having only an ionic liquid electrolyte. Circumstances – details were not revealed – suggest that an unknown separator has been used increasing the internal resistance of the cell considerably.

A solidified mixture of ordinary Portland cement, $K_3Fe(CN)_6$, KOH and polyacrylic acid in water has been suggested as electrolyte for supercapacitors in building engineering [cxviii]. A similar approach with alkali-activated slag and polyacrylamide with KOH for use in a structural supercapacitor has been described [cxix]. Again the high compressional strength of the material has been highlighted with regard to the intended application. In another study improvements were achieved by adding recycled steel slag and waste glass powder [cxx]. Further examples of structural supercapacitors with cement in composite electrolytes have been reported [cxxi - cxxvii]. Further highly complex electrolyte mixtures have been examined with respect to their use in structural supercapacitors [cxxviii], see also [cxxix, cxxx]. Incorporation of water supporting good ionic conduction without compromising mechanical properties of composite electrolytes for structural supercapacitors has been achieved [cxxxi].

4. Concluding remarks and conclusions

A wide variety of material combinations has been studied as solid composite electrolyte materials for supercapacitors. Substantial progress in terms of performance data has been reached. Stability data are reported only infrequently and mostly up to rather low cycle numbers. Further progress up to commercialization seems to require much more rigorous stability testing of materials and devices.

Understanding of the beneficial effects of the added material making up the composite finally in the terminology stated in the introduction appears to be developing. Interactions at the interface between the host material and the added (mostly nanoparticular) additive play a major role, actually sometimes the material may even be called a hybrid material. On a more fundamental-practical level, the establishment of a sufficiently large contact interface area between a solid electrolyte and an electrode is of outmost importance. The application of high mechanical pressure on electrode/electrolyte/electrode-assemblies sometimes tried hardly seems to be a practically useful solution. The pressure may damage the porous structure of the electrolyte; penetration of electrolyte material into the porous electrode body may be insufficient. An attempt mentioned a few times and mostly only in passing is soaking of the electrode with an ion-containing liquid component of the electrolyte. This may sound like a contradiction to the "all-solid-state" concept strenuously advertised (and may be the reason for not mentioning this detail), but actually there will be no free liquid around posing any of the risks deplored when critically examining the use of liquid electrolyte (solutions).

Author Contributions: All authors have contributed, read and agreed to the published version of the manuscript equally.

Funding: This research received no external funding.

Data Availability Statement: Data is contained within the article.

Acknowledgments: Preparation of this review has been supported in various ways by National Key R & D Program of China (2021YFB2400400), by the Alexander von Humboldt-Foundation, Deutscher Akademischer Austauschdienst, Fonds der Chemischen Industrie, Deutsche Forschungsgemeinschaft, National Basic Research Program of China, Natural Science Foundation of China (Grant # 52131306), Project on Carbon Emission Peak and Neutrality of Jiangsu Province (BE2022031-4), and by grants № 26455158 and № 70037840 within research projects at St. Petersburg State University.

Conflicts of Interest: The authors declare no conflicts of interest.

References

---

i Kortüm, G. *Lehrbuch der Elektrochemie*. 4th ed., Verlag Chemie, Weinheim, Germany 1966.

ii Robinson, R.A.; Stokes, R.H. *Electrolyte Solutions*. Academic Press Inc., New York, USA 1955.

iii Harned, H.S.; Owen, B.B. *Physical Chemistry of Electrolyte Solutions.* 3rd ed, Reinhold Publ.Corp, New York, USA 1957.

iv Wright, M.R. *An Introduction to Aqueous Electrolyte Solutions*. WILEY, Chichester, UK 2007.

v Holze, R. Between the Electrodes of a Supercapacitor: An Update on Electrolytes. *Adv. Mater. Sci. Technol*. **2024**, *6*, 0627771.

vi Shuja, A.; Khan, H.R.; Murtaza, I.; Ashraf, S.; Abid, Y.; Farid, F.; Sajid, F. Supercapacitors for energy storage applications: Materials, devices and future directions: A comprehensive review. *J. Alloy. Compd.* **2024**, 1009, 176924.

vii Chen, X.; Holze, R. Polymer Electrolytes for Supercapacitors. *Polymers* **2024**, 16, 3164.

viii Lin, L.; Ning, H.; Song, S.; Xu, C.; Hu, N. Flexible electrochemical energy storage: The role of composite materials. *Compos. Sci. Technol*. **2020**, 192, 108102.

ix Mohammed, N.B.; Batoo, K.M.; Hussain, S.; Subramaniam, R.; Kasi, R.; Bhuyan, M.; Imran, A.; Muthuramamoorthy, M. Natural Solid-State Hydrogel Electrolytes Based on 3D Pure Cotton/Graphene for Supercapacitor Application. *Micromachines* **2023**, 14, 1379.

x Casado, N., Zendegi, S.; Olmo, R.D.; Dominguez-Alfaro, A.; Forsyth, M. Tuning Electronic and Ionic Conductivities in Composite Materials for Electrochemical Devices. *ACS Appl. Polym. Mater*. **2021**, *3*, 1777-1784.

xi Wang, W.M. Study on all solid-state composite polymer electrolyte. *Adv. Mater. Res*. **2012**, *571*, 13-16.

xii Wang, Z.F.; Zhang, X.X.; Li, C.H.; Liu, J.H.; Zhang, Q.L. Composite electrolyte containing binary ionic liquids and LiDFOB additive on the performance of graphite anode in Li-ion battery. *Adv. Mater. Res*. **2014**, *986-987*, 34-37.

xiii Borges, R.S.; Reddy, A.L.M.; Rodrigues, M.T.F.; Gullapalli, H.; Balakrishnan, K.; Silva, G.G.; Ajayan, P.M. Supercapacitor Operating at 200 Degrees Celsius. *Sci. Rep*. **2013**, *3*, 2572.

xiv Fang, X.; Yao, D. An overview of solid-like electrolytes for supercapacitors. ASME International Mechanical Engineering Congress and Exposition, November 15-21, 2013, San Diego, California, USA, Proceedings (IMECE) 2013, 6A, IMECE2013-64069.

xv Ye, T.; Li, L.; Zhang, Y. Recent Progress in Solid Electrolytes for Energy Storage Devices. *Adv. Funct. Mater*. **2020**, *30*, 2000077.

xvi Yu, X.; Xue, L.; Goodenough, J.B.; Manthiram, A. Ambient-Temperature All-Solid-State Sodium Batteries with a Laminated Composite Electrolyte. *Adv. Funct. Mater*. **2021**, *31*, 2002144.

xvii Wang, X.; Huang, S.; Guo, K.; Min, Y.; Xu, Q. Directed and Continuous Interfacial Channels for Optimized Ion Transport in Solid-State Electrolytes. *Adv. Funct. Mater*. **2022**, *32*, 2206976.

xviii Kumar, Y.; Gupta, A.; Thakur, A.K.; Uke, S.J.; Khatri, V.; Kumar, A.; Gupta, M.; Kumar, Y. Advancement and current scenario of engineering and design in transparent supercapacitors: electrodes and electrolyte. *J. Nanopart. Res*. **2021**, *23*, 119.

xix Zhang, R.; Wu, C.; Yao, C.; Yang, W.; Jing, Y.; Zhang, X.; Yu, N.; Su, S.; Zhu, J. Preparation of PVA based multifunctional hydrogel electrolyte reinforced by phosphoric acid-dissolved-cellulose and its application in quasi-solid supercapacitors. *Cellulose* **2024**, *31*, 1071-1087.

xx Singh, D.; Gupta, M.; Singh, R.C.; Pandey, S.P.; Karn, R.K.; Singh, P.K. Polyvinylpyrrolidone (PVP) with Ammonium Iodide (NH_4I) and 1-Hexyl-3-Methylimidazolium Iodide Ionic Liquid Doped Solid Polymer Electrolyte for Efficient Supercapacitors. *Macromol.Symp*. **2019**, *388*, 1900036.

xxi Qian, S.; Chen, H.; Wu, Z.; Li, D.; Liu, X.; Tang, Y.; Zhang, S. Designing Ceramic/Polymer Composite as Highly Ionic Conductive Solid-State Electrolytes. *Batteries&Supercaps* **2021**, *4*, 39-59.

xxii Hibino, T.; Kobayashi, K.; Nagao, M.; Yamamoto, Y. Design of a rechargeable fuel-cell battery with enhanced performance and cyclability. *J. Electrochem. Soc*. **2016**, *163*, A1420-A1428.

xxiii Cheng, M.; Ramasubramanian, A.; Rasul, M.G.; Jiang, Y.; Yuan, Y.; Foroozan, T.; Deivanayagam, R.; Tamadoni Saray, M.; Rojaee, R.; Song, B.; Yurkiv, V.R.; Pan, Y.; Mashayek, F.; Shahbazian-Yassar, R. Direct

---

Ink Writing of Polymer Composite Electrolytes with Enhanced Thermal Conductivities. *Adv. Funct. Mater.* **2021**, *31*, 2006683.

xxiv TRANSPORT-STRUCTURE RELATIONS IN FAST ION AND MIXED CONDUCTORS, PROCEEDINGS OF THE 6TH RISO INTERNATIONAL SYMPOSIUM ON METALLURGY AND MATERIALS SCIENCE. Proceedings of the Riso International Symposium on Metallurgy and Materials Science 1985

xxv Mallela, V.S.; Ilankumaran, V.; Rao, N.S. Trends in cardiac pacemaker batteries. *Ind. Pac. Electrophysiol. J.* **2004**, *4*, 201-212.

xxvi Weston, J.E.; Steele, B.H. Effects of inert fillers on the mechanical and electrochemical properties of lithium salt-poly(ethylene oxide) polymer electrolytes. *Solid State Ionics* **1982**, *7*, 75-79.

xxvii Agrawal, R.C.; Pandey, G.P. Solid polymer electrolytes: Materials designing and all-solid-state battery applications: An overview. *J. Phys. D: Appl. Phys.* **2008**, *41*, 223001.

xxviii Lee, S.J.; Yang, H.M.; Cho, K.G.; Seol, K.H.; Kim, S.; Hong, K.; Lee, K.H. Highly conductive and mechanically robust nanocomposite polymer electrolytes for solid-state electrochemical thin-film devices. *Organ. Electr*. **2019**, *65*, 426-433.

xxix Yohans, M.; Singh, M.; Singh, R.C.; Shukla, P.K.; Singh, V.; Singh, P.K. Poly(vinylidine fluoride-co-hexafluoropropylene)-doped zinc acetate polymer electrolyte for supercapacitor application. *High Perf. Polym*. **202**0, *32*, 151-157.

xxx Chen, L.; Zhong, F.; Zan, J. Discharge property and voltage delay of AZ31B Mg alloy in $Mg(NO_3)_2/Mg(ClO_4)_2$ composite electrolyte. *J. Chin. Soc. Corros. Prot*. **2018**, *38*, 197-202.

xxxi Wu, Y.; Holze, R. Batterie oder Superkondensator oder Beides? Die Verschmelzung zweier elektrochemischer Speicheroptionen. *Bunsen-Magazin* **2022**, *24*, 100-102.

xxxii Wu, Y.; Holze, R. Battery and/or supercapacitor?-On the merger of two electrochemical storage system families. *Energy Stor. Convers*. **2024**, *2*, 491.

xxxiii Thomas, F.; Mahdi, L.; Lemaire, J.; Santos, D.M.F. Technological Advances and Market Developments of Solid-State Batteries: A Review. *Materials* **2024**, *17*, 239.

xxxiv Cericola, D.; Kötz, R. Hybridization of rechargeable batteries and electrochemical capacitors: Principles and limits. *Electrochim. Acta* **2012**; *72*, 1-17.

xxxv Ragone, D. Review of Battery Systems for Electrically Powered Vehicles. SAE Technical Paper **1968**, 680453.

xxxvi Afif, A.; Rahman, S.M.; Tasfiah Azad, A.; Zaini, J.; Islam, M.A.; Azad, A.K. Advanced materials and technologies for hybrid supercapacitors for energy storage - A review. *J. Energy Stor*. **2019**, *25*, 100852.

xxxvii Fu, L.; Qu, Q.; Holze, R.; Kondratiev, V.V.; Wu, Y. Composites of metal oxides and intrinsically conducting polymers as supercapacitor electrode materials: The best of both worlds? *J. Mater. Chem. A* **2019**, *7*, 14937-14970.

xxxviii Wu, Q.; He, T.; Zhang, Y.; Zhang, J.; Wang, Z.; Liu, Y.; Zhao, L.; Wu, Y.; Ran, F. Cyclic stability of supercapacitors: materials, energy storage mechanism, test methods, and device. *J. Mater. Chem. A* **2021**, *9*, 24094-24147.

xxxix Neha, Dalvi, A. Fast ionic PEO-$NaCF_3SO_3$-$Na_3Zr_2Si_2P_3O_{12}$ membranes for all-solid-state energy storage devices. *Mater. Sci. Eng. B* **2023**, *289*, 116252.

xl Bruce, P.G.; Vincent, C.A. Polymer electrolytes. *J. Chem. Soc. Farad. Trans*. **1993**, *89*, 3187-3203.

xli Polymers in Energy Conversion and Storage (Inamuddin, M.I. Ahamed, R. Boddula, T. Altalhi Eds.) CRC Press, Boca Raton 2022.

xlii Xi, G.; Xiao, M.; Wang, S.; Han, D.; Li, Y.; Meng, Y. Polymer-Based Solid Electrolytes: Material Selection, Design, and Application. *Adv. Funct. Mater*. **2021**, *31*, 2007598.

xliii Majumdar, D.; Bhattacharya, S.K. Polymer Electrolytes for Supercapacitor Applications. in: *Polymers in Energy Conversion and Storage* (Inamuddin, M.I. Ahamed, R. Boddula, T. Altalhi Eds.) CRC Press, Boca Raton 2022, p. 13-61.

xliv Bakar, R.; Darvishi, S.; Senses, E. Enhanced ionic conductivity and mechanical strength in nanocomposite electrolytes with nonlinear polymer architectures. *Turk. J. Chem*. **2023**, *47*, 242-252.

xlv Lee, S.; Park, S.J.; Kim, S. Thermal and electrical conducting property of sodium polymer electrolyte containing barium titanate filler. *J. Nanosci. Nanotechnol*. **2017**, *17*, 5768-5770.

xlvi Croce, F.; Persi, L.; Scrosati, B.; Serraino-Fiory, F.; Plichta, E.; Hendrickso, M.A. Role of the ceramic fillers in enhancing the transport properties of composite polymer electrolytes. *Electrochim. Acta* **2001**, *46*, 2457-2461.

xlvii Capiglia, C.; Yang, J.; Imanishi, N.; Hirano, A.; Takeda, Y.; Yamamoto, O. Composite polymer electrolyte: The role of filler grain size. *Solid State Ionics* **2002**, *154-155*, 7-14.

xlviii Arya, A.; Sadiq, M.; Sharma, A.L. Effect of variation of different nanofillers on structural, electrical, dielectric, and transport properties of blend polymer nanocomposites. *Ionics* **2018**, *24*, 2295-2319.

xlix Khan, S.; Ullah, I.; Ur Rahman, M.; Khan, H.; Shah, A.B.; Althomali, R.H.; Rahman, M.M. Inorganic-polymer composite electrolytes: basics, fabrications, challenges and future perspectives. *Rev. Inorg. Chem*. **2024**, *44*, 347-375.

l Koduru, H.K.; Kondamareddy, K.K.; Iliev, M.T.; Marinov, Y.G.; Hadjichristov, G.B.; Karashanova, D.; Scaramuzza, N. Synergetic effect of TiO_2 nano filler additives on conductivity and dielectric properties of

PEO/PVP nanocomposite electrolytes for electrochemical cell applications. *J. Phys. Conf. Ser*. **2017**, *780*, 012006.

li Sadiq, M.; Tanwar, S.; Raza, M.M.H.; Aalam, S.M.; Sarvar, M.; Zulfequar, M.; Sharma, A.L.; Ali, J. High performance of the sodium-ion conducting flexible polymer blend composite electrolytes for electrochemical double-layer supercapacitor applications. *Energy Storage* **2022**, *4*, e345.

lii Gurusamy, R.; Lakshmanan, A.; Srinivasan, N.; Venkatachalam, S. Incorporating LLTO ceramic into PVDF/PEO polymer electrolyte for lithium-ion capacitor. *J. Electroanal. Chem.* **2024**, *957*, 118135.

liii Yadav, N.; Mishra, K.; Hashmi, S.A. Nanozirconia polymer composite porous membrane prepared by sustainable immersion precipitation method for use as electrolyte in flexible supercapacitors. *Mater.Today Commun*. **2020**, *25*, 101506.

liv Wang, W.M. Preparation and characterization of composite polymer electrolyte. *Adv.Mater.Res*. **2012**, *571*, 17-21.

lv Teramoto, D.; Yokoyama, R.; Kagawa, H.; Sada, T.; Ogata, N. A Novel Ionic Liquid-Polymer Electrolyte for the Advanced Lithium Ion Polymer Battery in: *Molten Salts and Ionic Liquids: Never the Twain?* M. Gaune-Escard, K.R. Seddon Eds. WILEY Hoboken USA 2012, 367-388.

lvi Xi, J.; Qiu, X.; Zhu, W.; Tang, X. Enhanced electrochemical properties of poly(ethylene oxide)-based composite polymer electrolyte with ordered mesoporous materials for lithium polymer battery. *Micropor. Mesopor. Mater*. **2006**, *88*, 1-7.

lvii Kim, D.W.; Jung, S.M.; Jung, H.Y. A super-thermostable, flexible supercapacitor for ultralight and high performance devices. *J. Mater. Chem. A* **2020**, *8*, 532-542.

lviii Kim, D.W.; Jung, S.M.; Jung, H.Y. Long term thermostable supercapacitor using in-situ SnO_2 doped porous graphene aerogel. *J.Power Sources* **2020**, *448*, 227422.

lix Kumar, B.; Scanlon, L.G. Solid electrolyte development for lithium batteries. SAE Technical Papers 1997, 971228.

lx Cui, L.F.; Ju, J.W.; Cui, G.L. Three-dimensional porous ceramic framework reinforcing composite electrolyte. *Acta Phys.Sin*. **2020**, *69*, 228203.

lxi Yin, C.; Liu, X.; Wei, J.; Tan, R.; Zhou, J.; Ouyang, M.; Wang, H.; Cooper, S.J.; Wu, B.; George, C.; Wang, Q. "all-in-Gel" design for supercapacitors towards solid-state energy devices with thermal and mechanical compliance. *J. Mater. Chem. A* **2019**, *7*, 8826-8831.

lxii Kim, S.; Kim, J.H.; Han, J.H.; Lee, J.Y.; So, S.; Yoon, S.J.; Kim, H.J.; Lee, K.T.; Kim, T.H. Cross-Linked Composite Gel Polymer Electrolyte Based on an H-Shaped Poly(ethylene oxide)-Poly(propylene oxide) Tetrablock Copolymer with SiO_2 Nanoparticles for Solid-State Supercapacitor Applications. *ACS Omega* **2021**, *6*, 16924-16933.

lxiii Bandara; T.M.W.J.; Gunasekara, L.B.E.; Gunathilake, S.M.S.; Mellander, B.E. Transport parameters of charge carriers in PEO-LiTf-based, plasticized, composite, and plasticized-composite electrolytes intended for Li-ion batteries. *Ionics* **2022**, *28*, 2701-2714.

lxiv Kimura, K.; Tominaga, Y. Ionic liquid-containing composite poly(ethylene oxide) electrolyte reinforced by electrospun silica nanofiber. *J. Electrochem. Soc*. **2017**, *164*, A3357-A3361.

lxv Denney, J.; Huang, H. Thermal Decomposition Characteristics of PEO/$LiBF_4$ /LAGP Composite Electrolytes. *J. Compos. Sci*. **2022**, *6*, 117.

lxvi Sharma, S.; Singh, M.D.; Dalvi, A. All-solid-state electric double layer supercapacitors using $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ reinforced solid polymer electrolyte. *J. Energy Stor*. **2022**, *49*, 104178.

lxvii Sharma, S.; Dalvi, A. Solid polymer electrolyte membranes using the "polymer-in-ceramic" approach for all-solid-state supercapacitor applications. *Solid State Ionics* **2022**, *387*, 116063.

lxviii Lee, J.; Rottmayer, M.; Huang, H. Impacts of Lithium Salts on the Thermal and Mechanical Characteristics in the Lithiated PEO/LAGP Composite Electrolytes. *J. Compos. Sci*. **2022**, *6*, 12.

lxix Méry, A.; Rousselot, S.; Lepage, D.; Aymé-Perrot, D.; Dollé, M. Limiting Factors Affecting the Ionic Conductivities of LATP/Polymer Hybrid Electrolytes. *Batteries* **202**3, *9*, 87.

lxx Croce, F.; Curini, R.; Martinelli, A.; Persi, L.; Ronci, F.; Scrosati, B.; Caminiti, R. Physical and chemical properties of nanocomposite polymer electrolytes. *J. Phys. Chem. B* **1999**, *103*, 10632-10638.

lxxi Croce, F.; Appetecchi, G.B.; Persi, L.; Scrosati, B. Nanocomposite polymer electrolytes for lithium batteries. *Nature* **1998**, *394*, 456-458.

lxxii Kim, S.;. Hwang, E.J.; Jung, Y.; Han, M.; Park, S.J. Ionic conductivity of polymeric nanocomposite electrolytes based on poly(ethylene oxide) and organo-clay materials. *Coll. Surf. A: Physicochem. Engin. Asp.* **2008**, *313-314*, 216-219.

lxxiii Chen, H.W.; Chang, F.C. The novel polymer electrolyte nanocomposite composed of poly(ethylene oxide), lithium triflate and mineral clay. *Polymer* **2001**, *42*, 9763-9769.

lxxiv Kim, S.; Park, S.J. Interlayer spacing effect of alkylammonium-modified montmorillonite on conducting and mechanical behaviors of polymer composite electrolytes. *J. Coll. Interf. Sci.* **2009**, *332*, 145-150.

lxxv Nookala, M.; Kumar, B.; Rodrigues, S. Ionic conductivity and ambient temperature Li electrode reaction in composite polymer electrolytes containing nanosize alumina. *J. Power Sources* **2002**, *111*, 165-172.

---

lxxvi Karabelli, D.; Leprêtre, J.C.; Cointeaux, L.; Sanchez, J.Y. Preparation and characterization of poly(vinylidene fluoride) based composite electrolytes for electrochemical devices. *Electrochim. Acta* **2013**, 109, 741-749.

lxxvii Tripathi, M.; Kumar Dwivedi, B.; Kumar, Y.; Bobade, S.M.; Kumar, A. Synthesis and performance assessment of silica dispersed nano-composite polymer gel electrolyte for high-performance solid-state supercapacitors. *J. Electroanal. Chem.* **2023**, *948*, 117797.

lxxviii Ortega, P.F.R.; Trigueiro, J.P.C.; Silva, G.G.; Lavall, R.L. Improving supercapacitor capacitance by using a novel gel nanocomposite polymer electrolyte based on nanostructured SiO_2, PVDF and imidazolium ionic liquid. *Electrochim. Acta* **2016**, *188*, 809-817.

lxxix Acauan, L.H.; Zhou, Y.; Kalfon-Cohen, E.; Fritz, N.K.; Wardle, B.L. Multifunctional nanocomposite structural separators for energy storage. *Nanoscale* **2019**, *11*, 21964-21973.

lxxx Kim, D.W.; Jung, H. High temperature supercapacitor with free standing quasi-solid composite electrolytes. *Kor. J. Mater. Res.* **2019**, *29*, 121-128.

lxxxi Chen, Z.; Yang, Y.; Ma, Z.; Zhu, T.; Liu, L.; Zheng, J.; Gong, X. All-Solid-State Asymmetric Supercapacitors with Metal Selenides Electrodes and Ionic Conductive Composites Electrolytes. *Adv.Funct.Mater*. **2019**, *29*, 1904182.

lxxxii Hou, G.M.; Huang, Y.F.; Ruan, W.H.; Zhang, M.Q.; Rong, M.Z. Hypergrafted nano-silica modified polymer gel electrolyte for high-performance solid-state supercapacitor. *J.Solid State Electr.* **2016**, *20*, 1903-1911.

lxxxiii Yadav, N.; Mishra, K.; Hashmi, S.A. Nanozirconia polymer composite porous membrane prepared by sustainable immersion precipitation method for use as electrolyte in flexible supercapacitors. *Mater. Today Commun.* **2020**, *25*, 101506.

lxxxiv Zhang, R.; Wu, C.; Liao, X.; Luo, A.; Jing, Y.; Yu, N.; Su, S.; Zhang, X.; Zhu, J.; Deng, G. Preparation of PVA/cellulose composite hydrogel electrolytes based on zinc chloride-dissolved cellulose for flexible solid-state capacitors, *J. Mater. Chem. C* **2024**, *12*, 2063-2072.

lxxxv Yang, Y.; Xiao, R.; Sun, X.; Lu, L.; Chen, Y. Constructing two dimensional composite nanosheets with montmorillonite and graphene-like carbon: Towards high-rate-performance PVA based gel polymer electrolytes for quasi-solid-state supercapacitors, *Mater. Chem. Phys.* **2022**, 287, 126333.

lxxxvi Xin, Y.; Yu, Z.; Soomro, R.A.; Sun, N. Facile Synthesis of Polyacrylic Acid/Graphene Oxide Composite Hydrogel Electrolyte for High-Performance Flexible Supercapacitors. *Coatings* **2023**, *13*, 382.

lxxxvii Agrawal, R.C.; Pandey, G.P. Solid polymer electrolytes: Materials designing and all-solid-state battery applications: An overview. *J.Phys.D: Appl. Phys.* **2008**, *41*, 223001.

lxxxviii Majumdar, S.; Sen, P.; Ray, R. High-performance graphene oxide-grafted chitosan-starch solid biopolymer electrolytes for flexible hybrid supercapacitors. *J. Solid State Electr.* **2022**, *26*, 527-547.

lxxxix Li, W.C.; Chen, R.K.; Wen, T.C. The role of nano-hydroxyapatite bearing zwitterion within carboxylated chitosan hydrogel electrolyte in improving supercapacitor performance. *Electrochim. Acta* **2023**, *466*, 143064.

xc Zaidi, S.F.A.; Saeed, A.; Ho, V.C.; Heo, J.H.; Cho, H.H.; Sarwar, N.; Lee, N.E.; Mun, J.; Lee, J.H.Chitosan-reinforced gelatin composite hydrogel as a tough, anti-freezing, and flame-retardant gel polymer electrolyte for flexible supercapacitors, *Int. J. Biol. Macromol.* **2023**, *234*, 123725.

xci Tang, J.; Yuan, P.; Cai, C.; Fu, Y.; Ma, X. Combining Nature-Inspired, Graphene-Wrapped Flexible Electrodes with Nanocomposite Polymer Electrolyte for Asymmetric Capacitive Energy Storage. *Adv. Energy Mater.* **2016**, *6*, 1600813.

xcii Jiao, F.; Edberg, J.; Zhao, D.; Puzinas, S.; Khan, Z.U.; Mäkie, P.; Naderi, A.; Lindström, T.; Odén, M.; Engquist, I.; Berggren, M.; Crispin, X. Nanofibrillated Cellulose-Based Electrolyte and Electrode for Paper-Based Supercapacitors. *Adv. Sust. Syst*. **2018**, *2*, 1700121.

xciii Maria Mahimai, B.; Moorthy, S.; Sivasubramanian, G.; Deivanayagam, P. Selective Proton-Conducting Polystyrene-Based Polyelectrolyte Membrane Containing Bi_2O_3 Nanoparticles and Graphitic Carbon Nitride Nanosheets for Fuel Cells and Supercapacitors. *ACS Appl. Nano Mater*. **2023**, *6*, 18139-18149.

xciv Wu, H.; Cai, H.; Xu, Y.; Wu, Q.; Yan, W. Hybrid electrolyte SiW_9MoV_2/rGO/SPEEK for solid supercapacitors with enhanced conductive performance. *Mater. Chem. Phys.* **2018**, *215*, 163-167.

xcv Reece, R.; Lekakou, C.; Smith, P.A. A structural supercapacitor based on activated carbon fabric and a solid electrolyte. Materials Science and Technology (United Kingdom) **2019**, *35*, 368-375.

xcvi Hwang, M.; Jeong, J.S.; Lee, J.C.; Yu, S.; Jung, H.S.; Cho, B.S.; Kim, K.Y. Composite solid polymer electrolyte with silica filler for structural supercapacitor applications. *Kor .J. Chem. Eng*. **2021**, *38*, 454-460.

xcvii Kwon, S.J.; Kim, T.; Jung, B.M.; Lee, S.B.; Choi, U.H. Multifunctional Epoxy-Based Solid Polymer Electrolytes for Solid-State Supercapacitors. *ACS Appl. Mater. Interfaces* **2018**, *10*, 35108-35117.

xcviii Liao, G.Y.; Geier, S.; Mahrholz, T.; Wierach, P.; Wiedemann, M. Temperature influence on electrical properties of carbon nanotubes modified solid electrolyte-based structural supercapacitor, ASME 2017 Conference on Smart Materials, Adaptive Structures and Intelligent Systems, SMASIS 2017 1 (2017) 3908.

xcix Hu, F.; Liu, Y.; Shao, W.; Zhang, T.; Liu, S.; Liu, D.; Zhang, S.; Jian, X. Novel poly(arylene ether ketone)/poly(ethylene glycol)-grafted poly(arylene ether ketone) composite microporous polymer

---

electrolyte for electrical double-layer capacitors with efficient ionic transport, *RSC Adv*. **2021**, *11*, 14814-14823.

c Liu, W.; Li, Z.; Pan, F.; He, Q.; Zhang, Q. Solid polymer electrolytes reinforced with porous polypropylene separators for all-solid-state supercapacitors. *RSC Adv*. **2023**, *13*, 34652-34659.

ci Huang, B.; Wu, X. Multi-adaptability supercapacitor electrolyte based on Na-MMT/PDADMAC and application in wide temperature range. *Mater. Lett*. **2020**, *269*, 127657.

cii Vedhanarayanan, B.; Lakshmi, K.C.S.; Lin, T.W. Interfacial Tuning of Polymeric Composite Materials for High-Performance Energy Devices. *Batteries* **2023**, *9*, 487.

ciii Wang, J.; Yu, X.; Wang, C.; Xiang, K.; Deng, M.; Yin, H. PAMPS/MMT composite hydrogel electrolyte for solid-state supercapacitors. *J. Alloy. Compd*. **2017**, *709*, 596-601.

civ Hu, Q.; Cui, S.; Sun, K.; Shi, X.; Zhang, M.; Peng, H.; Ma, G. An antifreezing and thermally stable hydrogel electrolyte for high-performance all-in-one flexible supercapacitor. *J. Energy Stor*. **2022**, *50*, 104231.

cv Hina, M.; Bashir, S.; Kamran, K.; Iqbal, J.; Ramesh, S.; Ramesh, K. Fabrication of aqueous solid-state symmetric supercapacitors based on self-healable poly (acrylamide)/PEDOT:PSS composite hydrogel electrolytes. *Mater. Chem. Phys*. **2021**, *273*, 125125.

cvi Thapaliya, B.P.; Do-Thanh, C.L.; Jafta, C.J.; Tao, R.; Lyu, H.; Borisevich, A.Y.; Yang, S.Z.; Sun, X.G.; Dai, S. Simultaneously Boosting the Ionic Conductivity and Mechanical Strength of Polymer Gel Electrolyte Membranes by Confining Ionic Liquids into Hollow Silica Nanocavities, *Batteries&Supercaps* **2019**, *2*, 985-991.

cvii Hibino, T.; Kobayashi, K.; Nagao, M.; Kawasaki, S. High-temperature supercapacitor with a proton-conducting metal pyrophosphate electrolyte. *Sci. Rep*. **2015**, *5*, 7903.

cviii Kim, D.W.; Jung, H. Useful effects of fumed silica nanoparticles in an ionic liquid electrolyte for high temperature supercapacitor. *Kor. J. Mater. Res*. **2018**, *28*, 43-49.

cix Pereira, N.D.M.; Trigueiro, J.P.C.; Monteiro, I.D.F.; Montoro, L.A.; Silva; G.G. Graphene oxide - Ionic liquid composite electrolytes for safe and high-performance supercapacitors. *Electrochim. Acta* **2018**, *259*, 783-792.

cx Qian, Y.; Yu, Y.; Wu, W.; Fan, Q.; Chai, C.; Hao, J. Wide-Temperature Flexible Supercapacitor from an Organohydrogel Electrolyte and Its Combined Electrode. *Chem. Eur. J*. **2023**, *29*, e202300123.

cxi Zabihi, Z.; Rodriguez, P.E.D.S.; Boujakhrout, A.; Viera, J.C.; del Valle, J.A.; Araghi, H.; Villalonga, R. Reduced graphene oxide-poly(methyl methacrylate) nanocomposite as a supercapacitor. *J. Appl. Polym. Sci*. **2018**, *135*, 46685.

cxii Hou, P.; Gao, C.; Wang, J.; Zhang, J.; Liu, Y.; Gu, J.; Huo, P. A semi-transparent polyurethane/porous wood composite gel polymer electrolyte for solid-state supercapacitor with high energy density and cycling stability. *Chem. Eng. J*. **2023**, *454*, 139954.

cxiii Zhang, R.; Wu, C.; Yang, W.; Yao, C.; Jing, Y.; Yu, N.; Su, S.; Mahmud, S.; Zhang, X.; Zhu, J. Design of delignified wood-based high-performance composite hydrogel electrolyte with double crosslinking of sodium alginate and PAM for flexible supercapacitors, *Ind. Crops Prod*. **2024**, *210*, 118187.

cxiv Hou, P.; Liu, Y.; Gao, Z.; Liu, Y.; Gu, J.; Dong, J.; Huo, P. Porous Wood Composite as a Green Approach for Enhancing Electrochemical Performance of Gel Polymer Electrolytes for Supercapacitors. *ChemSusChem* **2024**, *17*, e202400883.

cxv Gao, C.; Liu, Y.; Zhang, J.; Li, H.; Liu, Y.; Gu, J.; Ma, T.; Huo, P. Wood-inspired High Ionic Conductivity Hydrogel Electrolytes for Flexible Supercapacitors. *Batteries&Supercaps* **2024**, *7*, e202400630.

cxvi Gao, Z.; Gao, Z.; Wei, Y.; Luo, N.; Liu, Y.; Huo, P. Flexible Wood Enhanced Poly(acrylic acid-co-acrylamide)/Quaternized Gelatin Hydrogel Electrolytes for High-Energy-Density Supercapacitors. *ACS Appl. Mater. Interfaces* **2022**, 15, 2951-2960.

cxvii Kaur, G.; Sivasubramanian, S.C.; Dalvi, A. Solid-state supercapacitors using ionic liquid dispersed Li^+-NASICONs as electrolytes. *Electrochim. Acta* **2022**, 434, 141311.

cxviii Wang, J.; Zhan, P.; Zhang, D.; Tang, L. Nickel cobalt sulfide composite nanosheet anchored on rGO as effective electrode for quasi-solid supercapacitor. *J. Energy Storage* **2023**, 70, 107938.

cxix Ran, M.; Wang, J.; Zhang, D. A superior electrolyte composite with high conductivity and strength based on alkali-activated slag and polyacrylamide for structural supercapacitor. *J. Energy Storage* **2024**, 79, 110169.

cxx Zhan, P.; Xu, J.; Wang, J.; Zuo, J.; He, Z. Structural supercapacitor electrolytes based on cementitious composites containing recycled steel slag and waste glass powders. *Cement Concrete Compos*. **2023**, 137, 104924.

cxxi Zhang, Y.; Zhang, D. Polymer/cement composite electrolyte with high strength and high ionic conductivity for structural supercapacitors. *Cement ConcreteCompos*. **2024**, 149, 105512.

cxxii Fang, C.; Zhang, D. Enhanced Electrochemical Matching between $NiCo_2O_4$/Reduced Graphene Oxide and Polymer Cement Electrolyte for Structural Supercapacitor. *J. Electrochem. Soc*. **2022**, 169, 060528.

cxxiii Shi, N.; Zhang, D. Inorganic-organic composite solid electrolyte based on cement and Polyacrylamide prepared by a synchronous reaction method. *Electrochim. Acta* **2021**, 391, 138998.

cxxiv Xu, C.; Zhang, D. Multifunctional structural supercapacitor based on cement/PVA-KOH composite and graphene. *J. Compos. Mater*. **2021**, 55, 1359-1369.

doi:10.20944/preprints202501.1926.v1

---

cxxv Wang, J.; Zhan, P.; Zhang, D. Redox active cement-based electrolyte towards high-voltage asymmetric solid supercapacitor. *Cement Concrete Compos.* **2023**, *138*, 104987.

cxxvi Fang, C.; Zhang, D. Portland cement electrolyte for structural supercapacitor in building application. *Constr. Build. Mater.* **2021**, *285*, 122897.

cxxvii Shi, N.; Zhang, D. Inorganic-organic composite solid electrolyte based on cement and Polyacrylamide prepared by a synchronous reaction method. *Electrochim. Acta* **2021**, *391*, 138998.

cxxviii Muñoz, B.K.; Lozano, J.; Sánchez, M.; Ureña, A. Hybrid Solid Polymer Electrolytes Based on Epoxy Resins, Ionic Liquid, and Ceramic Nanoparticles for Structural Applications. *Polymers* **2024**, *16*, 2048.

cxxix Gienger, E.B.; Nguyen, P.A.T.; Chin, W.; Behler, K.D.; Snyder, J.F.; Wetzel, E.D. Microstructure and multifunctional properties of liquid + polymer bicomponent structural electrolytes: Epoxy gels and porous monoliths. *J. Appl. Polym. Sci.* **2015**, *132*, 42681.

cxxx Gallagher, T.M.; Ciocanel, C.; Browder, C. Structural load bearing supercapacitors using a pegdge based solid polymer electrolyte matrix, ASME 2011 Conference on Smart Materials, Adaptive Structures and Intelligent Systems, SMASIS 2011 1 (2011) 141-148.

cxxxi Chang, Y.C.; Teymoory, P.; Shen, C. High-Toughness Hydrated Polymer Electrolytes for Advanced Structural Supercapacitors. *Adv. Mater. Technol.* **2024**, *9*, 2400033.