

Stretchable electrolytes for stretchable/flexible energy storage systems – Recent developments



Jagdeep Mohanta^a, Dong-Won Kang^b, Jung Sang Cho^c, Sang Mun Jeong^{a, **}, Jae-Kwang Kim^{d, *}

^a Department of Chemical Engineering, Chungbuk National University, 1 Chungdae-ro, Seowon-gu, Cheongju, Chungbuk, 28644, Republic of Korea

^b School of Energy Systems Engineering, Chung-Ang University, Seoul, 06974, Republic of Korea

^c Department of Engineering Chemistry, Chungbuk National University, Chungbuk, 361-763, Republic of Korea

^d Department of Solar & Energy Engineering, Cheongju University, Cheongju, Chungbuk, 28503, Republic of Korea

ARTICLE INFO

Keywords:

Stretchable electrolytes
Stretchable electronic devices
Ion transport
Energy storage systems

ABSTRACT

Stretchable/flexible electronic devices such as smart electronics, medical instruments, stretchable skin etc. are indeed necessary to make the life of human beings more comfortable. Viability of fully stretchable/flexible electronic equipment heavily relies on development of stretchable/flexible energy storage system. Since electrolyte plays a key role in ion transport and safety of these energy storage systems, stretchability in electrolyte can generate better scope for stretchable/flexible electronic devices as it will provide the greater mechanical sturdiness to the devices while regulating the ion transport. From last few years stretchable electrolytes has become a booming research topic. Thus, this mini review mainly highlights some of the latest works dealing with categories, synthesis strategies and applications of stretchable electrolytes.

1. Introduction

With rapid progress in the development of electronic devices, the demand for the development of stretchable/flexible devices for healthcare, smart devices and human body sensors is increasing. Stretchable electronics, are emerging electronics that will change the fate of future devices. Stretchable electronics usually consist of circuits, parts, and devices that show stretchability while maintaining the integral characteristics of the devices. As compared to flexibility, stretchability is a broader feature and harder to achieve in a device as stretchable devices have to revert to their original form after deformation while maintaining their properties [1–3]. In contrast to rigid devices, stretchable/flexible devices are sturdier, and thus, more pressure resistant. Stretchability/flexibility in devices such as electric machines, medical apparatus, and robotic skin can make life easier [4,5]. There are three primary ways to realizing stretchable/flexible devices, i) making an inherently rigid conducting substance elastic via patterning, ii) introducing some rigid conductive fillers into an elastomeric composite, and iii) using conducting substances that are inherently stretchable [6–8]. Stretchable/flexible electronics has become a thriving research area because it not only expands the reach of established technologies, but also forms the basis of some novel technologies since stretchability can assist in

transmitting electronics over movable and other devices [9–16]. To realize completely stretchable/flexible devices, amalgamation of novel nanoparticles and molecules with substrates made of stretchable polymers is necessary [17]. There are many reports on stretchable devices such as field-effect transistors, sensors, wearable skin, etc.; however, they still need a wired connection. Therefore, they have to depend on some energy storage systems that are not stretchable/flexible. Hence, there should be well-developed devices for storage and conversion of energy in stretchable/flexible devices [18,19]. To commercialize stretchable/flexible devices, development of safe and efficient stretchable/flexible energy storage systems such as stretchable/flexible supercapacitors or batteries and their production scale up are imperative. Stretchability in stretchable/flexible energy storage systems is of two types i.e. intrinsically and structure dependent. If all the constituent of the device is stretchable then it is acknowledged as intrinsically stretchable whereas in structure dependent stretchability, the stretchability provided to the device is due to that specific structure of the device [20,21]. Stretchability in energy storage systems is much needed to realize fully stretchable wearable devices. These energy storage systems consist of two integral components: electrodes and electrolytes. Electrodes contain active materials that assist in the storage and conversion of energy, whereas electrolytes are a crucial component of energy storage systems

* Corresponding author.

** Corresponding author.

E-mail addresses: smjeong@chungbuk.ac.kr (S.M. Jeong), jaekwang@cju.ac.kr (J.-K. Kim).

<https://doi.org/10.1016/j.ensm.2020.03.009>

Received 1 November 2019; Received in revised form 28 February 2020; Accepted 7 March 2020

Available online 14 March 2020

2405-8297/© 2020 Elsevier B.V. All rights reserved.

that helps in the transportation of ions during the charge–discharge mechanism and in keeping the electrode separate (Fig. 1).

For stretchable devices, primarily stretchable electrodes have been in the limelight as many research groups are working on them [22,23], however, reports on stretchable electrolytes are scarce [24]. When the mesh-type electrode is constructed for the stretchable electrode, it is expected that the stretchability is excellent and the electrons transfer can be improved. Stretchable electrolytes are the electrolytes that can sustain deformation to a large extent without undergoing any significant loss in terms of electrochemical characteristic as shown in Fig. 1. To develop a stretchable/flexible energy storage devices, stretchable electrolytes is very much needed because with aqueous or liquid electrolytes the required stretchability cannot be provided and apart from that there is risk of leakage and short-circuit. Stretchability in electrolyte could provide a safer and sturdy design as stretchable electrolyte is mainly responsible for providing the mechanical support to it. For usage of these stretchable electrolytes in stretchable/flexible devices it should display high ionic conductivity and self-healing properties [24,25]. Polymer as a substrate or an additional component is an integral component in any stretchable electrolyte as it gives the required stretchability. Apart from that incorporation of additives such as plasticizers, nanofillers, ionic liquid, crosslinker etc. into stretchable electrolyte has been done to improve the electrochemical and mechanical performance of the stretchable electrolytes.

As stretchable electrolytes have gained the attention of researchers in the last few years, in this review, we discuss the recent developments in stretchable electrolytes and their implication in stretchable/flexible energy storage systems. First, we discuss the mechanism involved in polymer electrolytes that will enlighten about the ion transportation process within an electrolyte. Next, we highlight the different types of stretchable electrolytes and their preparation techniques, and then concentrate on the application of these electrolytes in stretchable/flexible energy storage systems such as supercapacitor and batteries. The last section is dedicated to the overall summary that includes scope, problem and possible solutions associated with the stretchable electrolytes.

2. Ion transport mechanism in polymer electrolytes

One of the important characteristics of electrolytes is the ionic conductivity, which rely on the movement of ions through the electrolyte. Polymer electrolytes can be broadly classified into nanocomposite polymer electrolyte and gel polymer electrolyte. In case of nanocomposite polymer electrolyte, the nanofiller is mainly responsible for better ion transport whereas plasticizer is the main cause in enhanced ion

transport of gel polymer electrolytes. The transport of ions in a nanocomposite polymer electrolyte depends on the movement of polymer segments in the presence of salt ions [26,27].

One of the celebrated mechanisms of ionic motion in a nanocomposite polymer electrolyte is the Lewis acid-base mechanism in which the surface of nanofillers interacts both with the anions as well as with the polymer chains as indicated in the schematic diagram depicted in Fig. 2. In this mechanism the nanoparticle surface behaves as Lewis acid whereas the polyether oxygen acts as Lewis base, hence resulting in a formation of complex. Structural changes occur within the polymer chains leads to increase in amorphicity of the polymer host due to presence of the dispersed ceramic fillers that highly impacts the recrystallization kinetics of the polymer. Apart from that the additional sites provided by the interaction of the cations and anions with the Lewis acid base-type surface group of fillers, leads to generation of improved conduction pathways around the filler grains for the movement of ions [28]. Facilitation of better ionic transport as a result of Lewis acid-base mechanism has been documented well. Kwon et al. recently demonstrated that Lewis acid-base interaction between Al_2O_3 and LiTFSI leads to ion-dissociation and hence better ion transport [29]. Similarly enhancement of ionic conductivity has also been observed in the PEO-NaBr complex with the introduction of SiO_2 nanoparticles [30].

In gel polymer electrolytes, plasticizers are mainly responsible for conductivity enhancement. Hence, for gel polymer electrolytes, the ionic conduction mechanism is based on the interaction of the plasticizers with the polymers; this mechanism is also known as vehicle mechanism and Fig. 3 display a schematic representing how in vehicle mechanism different moieties in gel polymer electrolytes interact with each other [31].

As like of nanofillers, in gel polymer electrolytes the plasticizers also leads to enhancement of ion conductivity by carrying out ion pair dissociation, but apart from that they also provide great amount of flexibility towards polymer chain segments owing to lowering of the glass transition temperature (T_g) [32]. Das et al. demonstrates the impact of various plasticizers like poly ethylene glycol, propylene carbonate, ethylene carbonate and dimethyl carbonate on PEO-LiClO₄ polymer electrolyte and observed enhancement in ionic conductivity with addition of all plasticizers except dimethyl carbonate which shows anti-plasticization effect owing to lower dielectric constant as compared to the polymer host PEO [33]. In another work, influence of plasticization of succinonitrile towards reduction of glass transition temperature of PEGDA-LiTFSI polymer electrolyte and hence enhancement in ionic conductivity on incorporation of succinonitrile has been described [34].

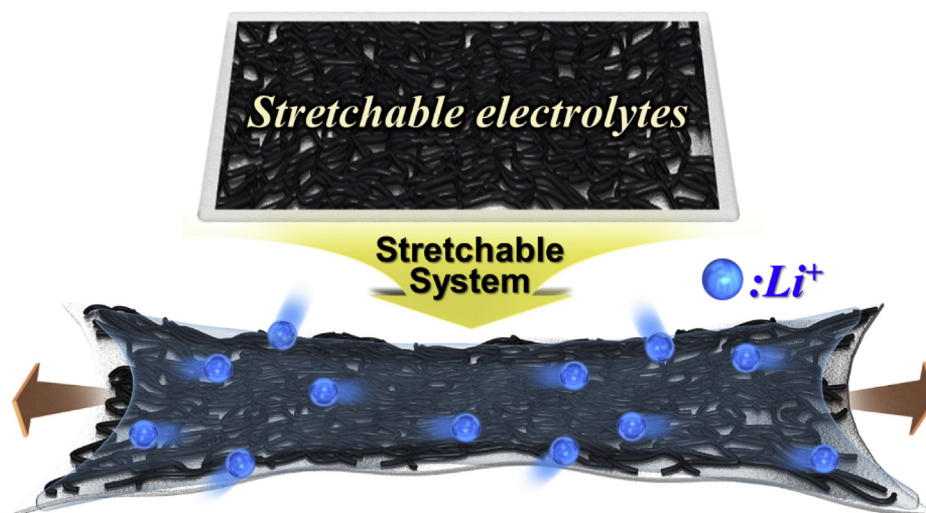


Fig. 1. A stretchable electrolyte.

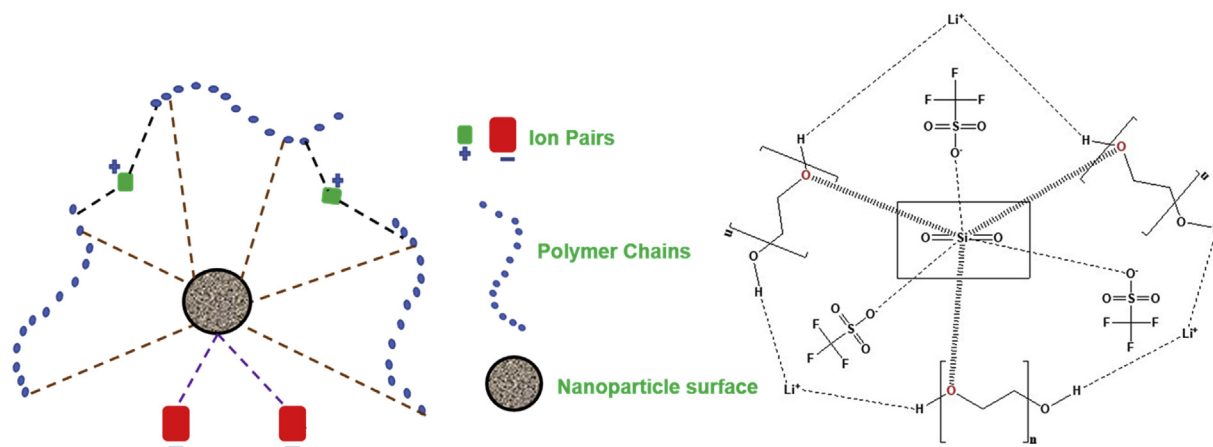


Fig. 2. Schematic for Lewis acid-base mechanism in nanocomposite polymer electrolytes.

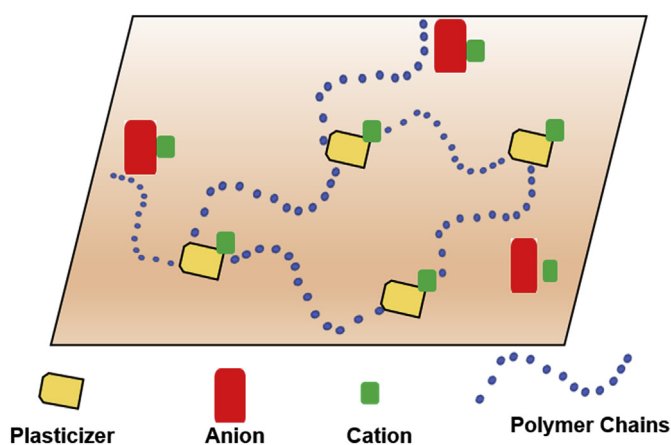


Fig. 3. Schematic for ion transport mechanism in gel polymer electrolytes.

3. Types of stretchable electrolytes

Stretchable electrolytes provide a mechanical support to stretchable energy storage systems [24]. There are two basic types of stretchable electrolytes: hydrogel electrolyte and ionic liquid-based electrolyte or ionogel electrolytes that are mostly used in stretchable devices. Hydrogel electrolyte consist of aqueous/electrolytic solution of polymer composites whereas in case of ionogel electrolytes in addition to polymers, ionic liquids are also incorporated in the mixture which assist in providing better stability and stretchability. Some examples of hydrogel electrolytes and ionogel electrolytes along with their application and resultant properties has been depicted in Table 1.

3.1. Hydrogel electrolyte

Hydrogel electrolytes have a crosslinked polymeric structure owing to which they exhibit a high water uptake, and hence, better flexibility and ionic conductivity. In addition, hydrogel electrolytes are biocompatible, economical (as they do not employ costly organic solvents) and exhibit a high energy density with a broader potential window. Unlike in the case of liquid electrolytes, the gel form avoids the risk of any type of leakage [35–37]. These characteristics of hydrogel electrolytes make them a good choice for electrolytes for stretchable devices.

Hydrogel electrolytes composed of polyvinyl alcohol (PVA) and phosphoric acid (H_3PO_4) are the most commonly used electrolytes in stretchable devices. The solvent casting technique is generally adopted for the synthesis of PVA- H_3PO_4 , in which an aqueous solution of PVA was stirred while heating until a clear solution was obtained followed by

introduction of H_3PO_4 and then stirring continues, after which it is casted on Teflon petri dishes followed by vacuum drying [49]. A similar procedure was used to produce another important hydrogel electrolyte, PVA- H_2SO_4 [41]. In addition to PVA based hydrogel electrolytes, some other kinds of hydrogel electrolytes have also been reported using different polymer host like polyethylene oxide (PEO), biopolymers (Chitosan, Gelatin) etc [43,44,50,51].

3.2. Ionogel electrolytes

Amalgamation of polymer composites or a polymer with an ionic liquid results in the formation of ionogel electrolytes with a three dimensional network [52]. Polymeric substrates render ionogel electrolytes highly stretchable and leakage-proof, whereas the ionic liquid imparts a high ionic conductivity, large potential window, and non-volatility to ionogel electrolytes [47,53–55]. With ionogels, the drawbacks associated with liquid electrolytes and PVA-based hydrogel electrolytes, i.e., the inherent leakage issue and the deterioration of charge-storage ability due to evaporation of water contained in the hydrogel can be avoided [19].

Kim et al. utilized a simple solution casting process to prepare ionogels consisting of PVdF-HFP and 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (EMIM-TFSI) in the presence of acetone. They mixed PVdF-HFP and acetone followed by the incorporation of an ionic liquid, and finally evaporated the acetone to obtain the desired ionogel electrolyte [18]. Apart from better homogeneity of the components, the incorporation of ionic liquid EMIM-TFSI during ionogel synthesis plays a significant role as a plasticizer in enhancing the stretchability as compared to hydrogel electrolytes by reducing the T_g [52]. Sometimes in spite of better homogeneity between components, a hindrance to plasticizer effect occurs that results in reduction of mechanical sturdiness on ionic liquid incorporation. To counteract this issue usage of cross-linkers proved to be a better option. Ha et al. employed 2-hydroxy-2-methylpropiophenone (HOMPP) as an ultraviolet cross-linking initiator to prepare a PEGDA and EMIM-TFSI-based ionogel electrolyte [47]. Recently, Wallace et al. polymerized a methyl methacrylate (MMA) monomer by free radical polymerization using polyethylene glycol diacrylate as a cross-linker in the presence of EMIM-TFSI [24].

3.3. Different preparation strategy of stretchable electrolytes

There are many approaches for design of stretchable electrolytes to impact the stretchability and other vital features. In the following section, the different methods for developing stretchable electrolyte has been discussed. Traditional solvent casting method was used by Jin et al. to prepare hydrogel electrolyte consisting of PVA and H_2SO_4 . In this PVA

Table 1
Few examples of hydrogel and ionogel electrolytes with their application and properties.

Stretchable Electrolytes	Components	Application	Properties	Reference
Hydrogel electrolytes	PVA + H ₃ PO ₄	Flexible supercapacitor	Provides mechanical stability to the device	[38]
		Stretchable supercapacitor	No significant decrease in capacitance of the device on bending upto 180° Hydrogel electrolyte plays dual role of electrolyte as well as separator	[39]
		Stretchable electrochemical capacitors	Sustain a strain upto 350% Enhanced capacitance of 30.7 Fg ⁻¹ Delivers lofty stretchability and stability	[40]
	PVA + H ₂ SO ₄	Stretchable supercapacitor	After 100 stretching cycles with 100% strain in every cycle, still maintains capacity upto 70%	[41]
		Stretchable supercapacitor	Improved properties displayed after 20 cycles of stretching and releasing upto 100% Display stretchability of 200% in every direction Enhanced energy density and lofty specific capacity	[42]
	PEO + PVA + KOH	Flexible and stretchable battery	Hydrogel electrolyte act both as electrolyte as well as separator avoids any leakage or short-circuit	[43]
	PEO + LiClO ₄ PAM	Stretchable lithium ion battery	At 2Ag ⁻¹ improved electrochemical properties displayed	[44]
		Stretchable zinc ion battery	Ion conductivity enhances with tensile strain Stretchability is found to be around 300%	[45]
	PAM + Nanofibrillated cellulose	Stretchable zinc ion battery	Capacity preservation upto 96.5% even after immersing in water for 12 hours Stretchability enhanced up to 1400%	[46]
	PVdF-HFP + EMIM-TFSI	Stretchable Supercapacitor	Mechanical stability even after stitching 120 times with 88.5% of initial capacity Ionogel electrolyte also behaves as a supporting layer for the stretchable supercapacitor	[18]
Ionogel Electrolytes	PEGDA + EMIM-TFSI + HOMPP	Flexible microsupercapacitors	Stretchable in every direction while providing large cell voltage of around 3 V Better cycling ability even after undergoing 30 000 cycles of charge and discharge	[47]
		Flexible lithium ion batteries	Superior mechanical sturdiness Enhanced Ionic Conductivity of 1.4 mS/cm Excellent tensile strength of 10.6 MPa and complete strain retrieval after 100% stretch	[48]

was dispersed in a solution containing H₂SO₄ and distilled water by stirring it at a temperature of 80 °C. Appearance of a transparent solution indicates the formation of PVA/H₂SO₄ hydrogel electrolyte [56]. Physically crosslinked PVA-H₂SO₄ hydrogel film were fabricated by Guo et al. by employing freezing/thawing procedure. This hydrogel film acts as both electrolyte and separator for the healable all-in-one configured supercapacitor. For this first a solution mixture of concentrated H₂SO₄ and water was prepared. Then PVA was introduced into the solution mixture and stirred vigorously at a high temperature of 90 °C till a clear solution was obtained. Then the solution was transferred to a mould and allowed for freezing at -15 °C up to 1 h. After that thawing of the solution was carried out at room temperature approximately up to 12 h that results in the formation of PVA-H₂SO₄ film which was well physically crosslinked [57]. Liu et al. created a hydrogel electrolyte with sodium polyacrylate (PANA). For this first of all an ice bath maintained at a temperature of 273 K was taken in which a solution of acrylic acid was prepared with water. To this NaOH solution (prepared with NaOH and water) was introduced sluggishly to neutralize the monomer. Afterwards addition of ammonium sulfate into the mixture and its half an hour stirring was carried out. Then degassing followed by nitrogen sealing was carried out. After that in an oven the free radical polymerization was carried out for 30 h while sustaining a temperature of around 40 °C. At last complete removal of solvent from the membrane was carried out by exposing the membrane in an oven for 2 h with a temperature of 100 °C. Then, it was kept immersed in a solution mixture of KOH and ZnCH₃COOH for 2 days [58]. Wang et al. utilize Agar and hydrophobically associated polyacrylamide (HPAAm) to synthesize a double network (DN) hydrogel by a one-pot technique. In this all the constituents like Agar, AAm etc were dispersed in a solution containing SDS and NaCl in a reactor, followed by degassing of the reactor in an inert N₂ atmosphere. After that the reactor was heated at 90 °C for complete solubility of the constituents. Then to form the first network it was cooled for 30 min while maintaining a temperature of 4 °C. Subsequently, in

presence of UV light photo polymerization was carried out for 1 h to prepare the DN hydrogel electrolyte [59]. Yun et al. also applied UV treatment for fabrication of polyacrylamide (PAAm) centered hydrogel electrolyte. For this first of all deionised water was used for dissolution of a lithium salt i.e. LiCl of higher concentration. Then the monomer acrylamide was incorporated into the solution followed by the introduction of cross-linker and photoinitiator i.e. N,N-methylenebisacrylamide and ammonium persulfate respectively. Finally the cross-linking accelerator i.e. N,N,N',N'-tetramethylethylenediamine was poured into the mixture and then the mixture was cured for 30 min with the aid of UV light that leads to preparation of the transparent and stretchable hydrogel electrolyte. To retain moisture for extended period and to endure excessive temperature by hydrogel electrolyte, Mo et al. developed a biomimetic organohydrogel (BM-gel) electrolyte. The whole process of preparation of BM-gel electrolyte i.e. alginate/PAM organohydrogel is almost same as above except the addition of alginate and a coupling agent viz. 3-(trimethoxysilyl) propyl methacrylate. Typically the monomer, initiator, crosslinking agent, coupling agent and alginate were mixed properly and after that free radical polymerization was carried out through the UV treatment for around 2 h resulting in the formation of alginate/PAM organohydrogel [60]. Hu et al. design an extremely stretchable and self-healable hydrogel electrolyte comprising of polyvinyl alcohol (PVA) and phytic acid through a hot pressing technique. In this process the two constituents are mixed through stirring at a higher temperature of around 85 °C. Then it was transferred to a mould and of a pressing unit and pressure was applied for 20 min and the temperature being maintained at 85 °C. Then freezing of the mould was carried out for half an hour at a temperature of -15 °C. Then by usage of ethanol the PVA/PA gel was taken out and kept at room temperature for 12 h [61]. A new and unique Nanofibrillated cellulose (NFC) based hydrogel electrolytes have been prepared by Wang et al. by carrying out the polymerization of acryl amide in presence of NFC. In this first dissolution of acryl amide in cellulose nanofibrils dispersion were carried out. Then

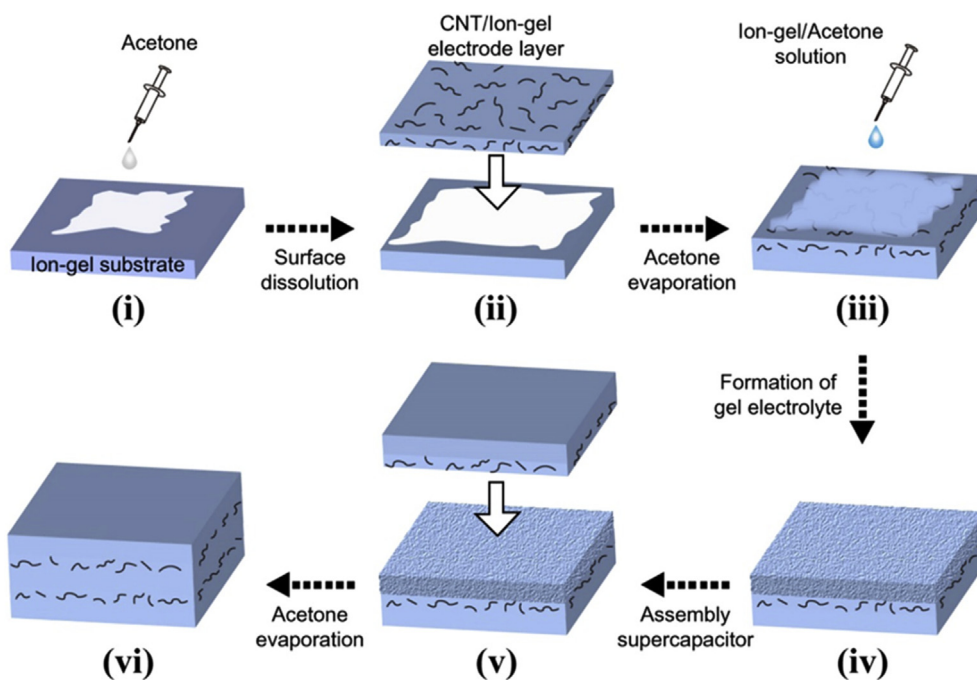


Fig. 4. Preparation method of stretchable supercapacitor consisting of a single matrix. Reprinted with permission from Ref. 18, Copyright 2016, IOP publishing Ltd.

incorporation of $K_2S_2O_8$ and N,N' -methylenebisacrylamide was done and it was stirred for homogenous mixing. After that the mixture was placed between two glass plates divided with rubber spacers and exposed to a temperature of $60\text{ }^\circ\text{C}$ for 2–3 h that leads to formation of the polymer film. To attain a state of equilibrium the polymer film was dipped overnight in a mixture of solution containing $MnSO_4$ and $ZnSO_4$ [62].

For fabrication of stretchable ionogel electrolytes, Kim et al. first dissolved the host polymer P(VdF-HFP) into acetone with the aid of magnetic stirring, followed by incorporation and mixing of ionic liquid EMIM-TFSI. On evaporation of solvent, the solution turns into gel electrolyte [18]. For attaining the enhanced aerial capacity of micro supercapacitors (MSCs), Kim et al. prepared a patterned ionogel electrolyte. For preparation of ionogel electrolyte, poly (ethylene glycol) diacrylate, EMIM-TFSI and UV cross linking initiator i.e. 2-hydroxy-2-methylpropionophenone (HOMPP) were all blended in a definite weight ratio and then stirred to obtain the ionogel electrolyte [47]. Angelo et al. fabricate fully zwitterionic (f-ZI) polymer scaffold-supported solvate ionogel electrolyte that possess good self healing competency as well as better stretchability.

First, they take two zwitterionic monomers viz. sulfobetainevinyimidazole (SBVI) and 2-methacryloyloxyethyl phosphorylcholine (MPC), then their free radical copolymerisation mediated through UV irradiation was carried out in situ inside the solvate ionic liquid [Li (G4)] [TFSI], consisting of tetraglyme (G4) and lithium bis(trifluoromethylsulfonyl) imide. As the above work here also HOMPP is employed as the cross linking initiator [63]. Sun et al. developed a novel ionogel electrolyte comprising of ionic liquid and dynamic covalent bond that results in an ionogel electrolyte that display good self healability. For this they adopted one-pot polymerization technique. First of all, an ionic liquid i.e. 3-(1, 2-dihydroxypropyl)-1-methylimidazole chloride (DDPMIMCl). Then for doing the copolymerisation, different components like 4-vinylphenylboric acid (4-VPBA), lithium salt, lithium 2-acrylamido-2-propane-1-sulfonate (AMPSLi) and AIBN dissolved in anhydrous ethyl alcohol and stirred while keeping a temperature of $70\text{ }^\circ\text{C}$, resulting in the formation of gel. To eliminate the excess ethyl alcohol the ionogel was subjected to vacuum drying [64].

Chen et al. developed composite solid state electrolytes by grafting

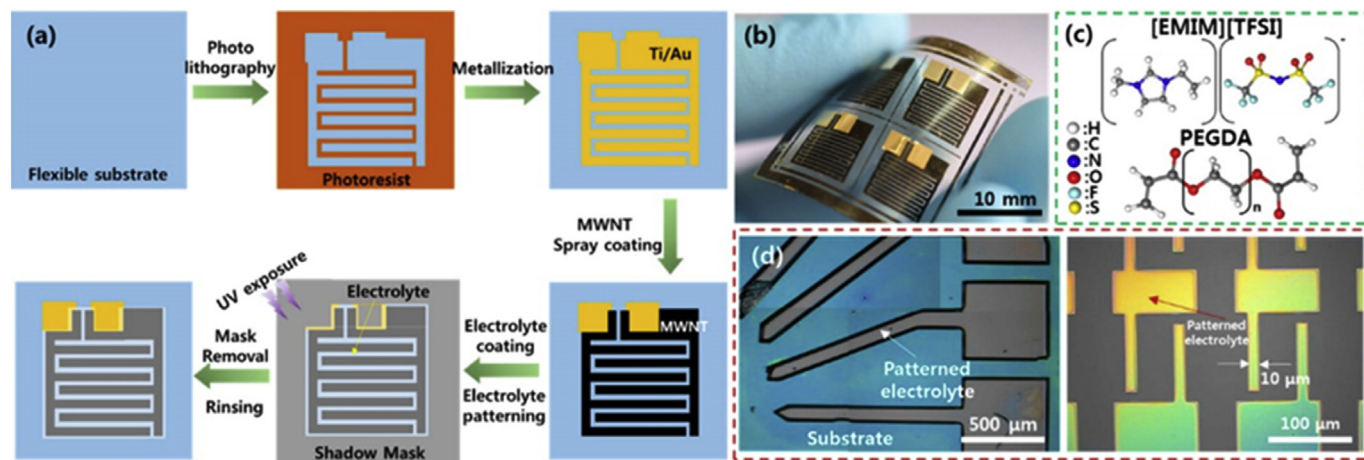


Fig. 5. Schematic diagram of fabrication of a flexible MSC with a patterned solid electrolyte on a PET substrate. Reprinted with permission from Ref. [36], Copyright 2015, American Chemical Society.

polymers on graphene oxide (GO). These electrolytes display enhanced ionic conductivity while maintaining good stretchability. To get a well-mixed solution of PVA, it was first dissolved in deionised water and swelled at ambient temperature followed by robust stirring at temperature of 85 °C. Then a calculated amount of GO was introduced into the solution and stirred for some time for mixing. After that dimethyloctadecyl [3-(trimethoxysilyl)propyl]ammonium chloride (DMAOP) was slowly introduced maintaining a mass ratio of PVA:DMAOP (1:1) Then magnetic stirring of the solution for 12 h at 70 °C was done for the grafting procedure. Afterwards to the prepared solution KOH was incorporated and for formation of membrane it was poured into a plate and collected after the solvent was evaporated thoroughly. Finally it was kept soaked in KOH solution for one day to obtain the composite solid-state electrolyte [65].

4. Applications of stretchable electrolytes

Many research groups worldwide have reported the usage of stretchable electrolytes towards stretchable/flexible energy storage systems, such as batteries and supercapacitors, to realize completely stretchable/flexible devices. Following section describes how stretchable electrolyte impregnated into these devices and performances of the devices are discussed.

4.1. Stretchable supercapacitors

Fast charging and discharging, safety, and extended cycle life are some of the key features that make stretchable supercapacitors a strong candidate for application in stretchable devices. Therefore, stretchable supercapacitors can be considered a boon to modern-day stretchable devices [23]. Many research efforts are being made to develop stretchable components for stretchable supercapacitors. Ionogel electrolytes are suitable for stretchable supercapacitors owing to their significant features, as described in the earlier section. Some of the recent works on stretchable ionogel-based supercapacitors are as follows.

Kim et al. used a single composition of poly (vinylidene fluoride-hexafluoropropylene) and 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide to prepare all the components of a stretchable supercapacitor, i.e., electrodes and stretchable electrolytes. This stretchable supercapacitor found to be stretched in every direction without any delamination. The entire preparation method for the stretchable supercapacitor comprising a single matrix is displayed in Fig. 4. Here, the polymer and ionic liquid matrix acts as an electrolyte as well as a supporting layer. This is an intrinsically stretchable supercapacitor where both the winding carbon nanotubes (CNT) as electrode and the ionic liquid contained electrolyte are stretchable which leads to display of omni directional stretching. Also, Easy blending of every layer provides a strong cohesiveness that results in improved cell voltage of 3 V [18].

In another work by the same group utilized PVdF-HFP and EMIM-TFSI as stretchable ionogel electrolytes, but here they employed deposited CNT on metal coated PDMS as electrodes that assist in achieve a better adhesion between all the layers of the components. This leads to display of better stretchability as well as enhanced electrochemical features. After 3000 cycles with 20% strain, the stretchable supercapacitor demonstrated remarkable capacity retention of approximately 96.6% [19].

Wallace et al. prepared a stretchable ionogel electrolyte through free radical polymerization of polymerization of MMA using a crosslinker that could resist large strains and can be employed to design stretchable supercapacitor for wearable devices. For the supercapacitor, they used carbon nanotubes (CNTs) dispersed in dimethylformamide as electrodes with the stretchable ionogel electrolyte. The supercapacitor exhibited over 1.5 MPa of tensile breaking strength with the electrolyte and an optimal ionic conductivity of approximately $7 \times 10^{-5} \text{ S cm}^{-1}$. Moreover, around 30% prestraining was applied to the electrodes to obtain a highly

stretchable supercapacitor that demonstrated a stretching capacity of more than 500% and an excellent reversible electric double layer charge–discharge response. The enhanced features of the stretchable supercapacitor can be devoted to the excellent mechanical stability and volatility resistant ionogel electrolyte [24]. Ramprabhu et al. designed a stretchable supercapacitor with hydrogen-exfoliated graphene (HEG) as the electrodes and an ionic liquid-containing PMMA as the electrolyte. Here, the ionogel electrolyte also serves as a stretchable support for the HEG electrodes. As depicted through molecular vibrations, there is lesser interaction within the polymer chains due to the absence of chemical bonds between [BMIM][TFSI] and PMMA. Excellent electrochemical properties with an improved ionic conductivity of $7.8 \times 10^{-4} \text{ S cm}^{-1}$ is demonstrated by the electrolyte. Apart from that the electrolyte can be stretched up to four times of its initial condition [66]. Rana et al. designed high-temperature flexible supercapacitors (hfSCs) by using double network (DN) ionogel electrolyte comprising of soft and hard polymers among which ionic liquid has been infused. These DN ionogel electrolytes display some very interesting characteristics such as extremely stretchable, high durability, and improved ionic conductivity. Owing to the DN structure the hfSCs still sustain the mechanical and electrochemical sturdiness at elevated temperatures. The hfSCs can be stretched up to as high as 500% and can retain an ionic conductivity value of 36.8 mS cm^{-1} still at a temperature of 100 °C. Among all the reported solid state supercapacitors, this hfSCs consisting of DN ionogel electrolyte describes the maximum energy density at an increased temperature of 180 °C i.e. 51 Wh Kg^{-1} . Apart from that it also display greatest durability even after 100,000 cycles [67].

Apart from supercapacitors, many researchers employed stretchable electrolytes towards micro-supercapacitors (MSCs) as they can smoothly assimilate within stretchable micro- or nano-electronic equipment. Ha et al. designed flexible/stretchable MSCs by employing a photolithographic technique for patterning a stretchable ionogel electrolyte (consisting of PEGDA/EMIM-TFSI and HOMPP) to as low as $10 \mu\text{m}$ (as shown in Fig. 5) and used the patterned ionogel electrolyte with MWCNTs over a polyethylene terephthalate (PET) substrate. Owing to the presence of the UV-cross linking agent i.e. HOMPP, the MSC displayed excellent electrochemical properties and only 20% reduction in initial capacitance was observe dafter 30,000 cycles. In addition, these MSCs exhibited impressive aerial stability [47].

The same group also prepared MSC array for a gas sensor based on graphene using the same ionogel electrolyte as mentioned above but here the MSC was designed over an ecolex substrate. These MSC arrays displayed impressive electrochemical behaviors and could withstand 50% and 40% of uniaxial and biaxial strains, respectively. Moreover, at a uniaxial stretching of 50%, a gas sensor prepared with the MSC array could sense nitrogen dioxide for more than 50 min [68].

Hydrogel-based electrolytes are also commonly used for stretchable supercapacitors. A PVA- H_3PO_4 hydrogel electrolyte has been extensively applied for stretchable supercapacitors. Peng et al. coated a fiber on an elastic substrate by a layer-by-layer coating of the hydrogel electrolyte (PVA- H_3PO_4) and electrodes (aligned CNTs and CNT/PEDOT-PSS). For better adhesion, they applied a vacuum treatment. Here the hydrogel electrolyte behaves both as stretchable electrolyte. The supercapacitor displayed an enhanced specific capacitance of 19.2 Fg^{-1} , which further increased upon incorporation of organic modified clay, and high stretchability owing to presence stretchable electrolytes as well as due to its wire shape [39]. The same group fabricated a new stretchable supercapacitor with a pyramidal structure, which demonstrated stretchability as well as excellent dimensional stability in all the three dimensions. For this, they used the same hydrogel as before; however, as electrodes, they used CNT films, which have a pyramidal structure. An enhanced specific capacitance of 162.4 mF cm^{-2} was achieved, which increased upon incorporation of PANI into the electrodes. After 3000 cycles of stretching in three dimensions, only a slight reduction in specific capacitance was observed. In addition, the supercapacitor displayed an enhanced energy density of 19.9 mWh cm^{-3} and a power density of 3.3 W

cm^{-3} . The pyramidal structure can open new avenues for newer applications such as wearable devices [69]. Wallace et al. designed a symmetrical electrochemical capacitor (EC), in which they employed a stretchable PVA- H_3PO_4 electrolyte and reduced graphene oxide (rGO)/single-walled carbon nanotube (SWNT) composite electrodes. Even after repeated stretching cycles, the EC displayed good electrochemical properties [36]. Jeong et al. designed a polyurethane (PU) based stretchable supercapacitor by employing stretchable PVA- H_3PO_4 electrolyte. For the electrode first of all stretchable polyurethane substrate was prepared. Then by utilizing sputter coating method gold was coated over it. After this spray coating technique was adopted to prepare the rGO-SWNT composite electrodes on stretchable gold coated PU substrates. Even after undergoing recurring stretching cycles, there is no alteration in the electrical double layer capacitance as revealed from the rectangular curves displayed in the cyclic voltammetry studies. The capacitive nature remains intact even the supercapacitor is exposed to stretching with 100% strain for longer period. Well reversibility and facile kinetics of supercapacitor was reported through the symmetrical charge discharge cycles throughout the 100 cycles. A little amount of approximately 28% reduction was observed in the capacitance value of the supercapacitor after 100 cycles of stretching, whereas 100% elongation of the stretchable PU supercapacitor only reduces 10% of the initial capacitance value [40]. In another interesting work, Wang et al. prepare a supercapacitor comprising of pristine polypyrrole electrode and agar based double network (DN) hydrogel electrolyte. Improved mechanical features such as no significant difference in length even after stretching various times up to 500% can be attributed to the usage DN hydrogel electrolyte. There are very minimum lasting changes in the supercapacitor even on stretching full 100% for around 1000 times. Also, a capacitance of as high as 79.7 mF cm^{-2} was maintained even after undergoing stretching for 1000 times [59]. To realize the enhanced features of the supercapacitor in large scale, a prominent self-healing ability of the supercapacitor is also essential in addition to good stretchability and enhanced capacity. To develop a supercapacitor with these intrinsic properties Chen et al. employs both hydrogel electrode as well as hydrogel electrolyte. The hydrogel electrode consists of polypyrrole-incorporated gold nanoparticle/carbon nanotube (CNT)/poly (acrylamide) (GCP@PPy) hydrogel electrodes whereas CNT-free GCP (GP) hydrogel was used as the electrolyte for the stretchable supercapacitors. An enhanced energy density of $123 \mu\text{Whcm}^{-2}$ and at the same time a supreme areal capacity of 885 mF cm^{-2} was achieved by the constructed supercapacitor. In spite of having such great

electrochemical features this supercapacitor constituting of hydrogel electrode and electrolyte display extreme stretching ability up to 800% with substantial self-healing feature [70].

Besides PVA- H_3PO_4 , another hydrogel electrolyte, PVA- H_2SO_4 , is currently employed in stretchable supercapacitors. Using PVA- H_2SO_4 as an electrolyte and PANI-coated CNT composite films as the electrodes, Chou et al. fabricated a stretchable supercapacitor having a buckled structure, which can be stretched in all directions. The supercapacitor displayed 200% stretchability in all directions while maintaining a specific capacitance of 9.52 mF cm^{-2} . It has been observed that acid treatment induces high stretchability as well as better electrochemical properties [42]. For high-temperature operating flexible supercapacitor, Ho-Seok et al. used H_3PO_4 -doped PBI (poly [2,2'-(*m*-phenylene)-5,5'-(biphenyl-2,6-diyl)] electrolyte with reduced graphene oxide (RGO) electrode. The H_3PO_4 -doped PBI electrolyte-based flexible supercapacitor showed extreme long-term stability of 100,000 cycles and mechanical durability after hundreds of bending cycles at 100°C [71]. To fabricate a transparent and stretchable supercapacitor (TSS), Nasibulin et al. employed PVA- H_2SO_4 as the stretchable electrolyte and a PDMS/SWNT composite as the electrode. This combination of electrodes and electrolyte imparted 75% transparency to the supercapacitor. In addition, the TSS displayed 120% stretchability and maintained its electrochemical performance even under 1000 stretching and charge-discharge cycles [72]. For carrying out a performance comparison between hydrogel and ionogel electrolytes Zhu et al. developed graphene based MSC utilizing PVA/ H_2SO_4 and fumed silica nanopowder/EMI-TFSI ionic liquid (FS/IL) as hydrogel and ionogel electrolyte respectively. Both ionogel and hydrogel assist in improving the characteristics of the MSC but ionogel is proved to be better than hydrogel electrolytes. A power density of 1860 W cm^{-3} is displayed with ionogel whereas it is 1714 W cm^{-3} for hydrogel electrolyte. Enhanced properties of ionogel electrolytes with respect to hydrogel electrolytes can be ascribed to the presence of ionic liquid as described earlier [73].

4.2. Stretchable batteries

Batteries convert the chemical energy stored in them into electrical energy. In case of batteries, only a few reports exist on stretchable electrolytes, as most work has been dedicated to stretchable electrodes only. Peng et al. fabricated stretchable and flexible zinc-air battery that is rechargeable using a stretchable hydrogel electrolyte comprising PVA, polyethylene oxide (PEO), and potassium hydroxide (KOH). Here the

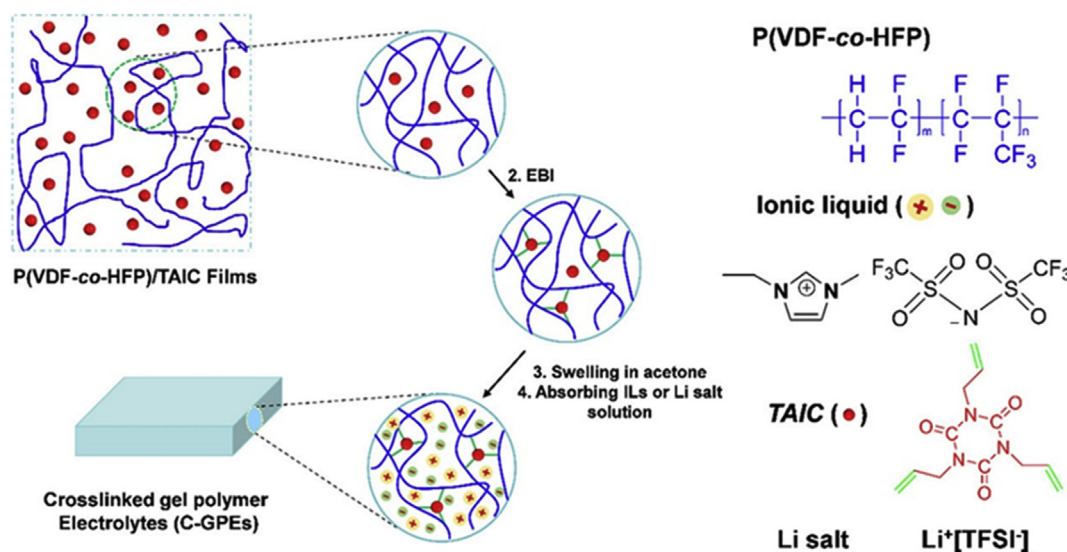


Fig. 6. Fabrication process of PVDF-co-HFP-based crosslinked gel polymer electrolytes (CGPEs). Reprinted with permission from Refs. [44], Copyright 2017, American Chemical Society.

PEO was responsible for enhancing the mechanical stability of the hydrogel electrolyte whereas KOH influence improved ionic conductivity as well as mechanical strength. Aligned CNTs as electrodes imparted good electrochemical characteristics to the zinc–air battery at an enhanced current density. Due to the usage of stretchable electrolyte the battery can be bent up to 150° without affecting the electrochemical properties [43]. Ardebili et al. conducted an in-situ study to examine the effect of tensile strain on a stretchable PEO-based electrolyte that can be used in emerging stretchable devices. PEO and LiClO_4 are the components of the stretchable polymer electrolyte. The through-plane and in-plane study demonstrated linear and steady growths, and the coefficients of strain-dependent ion conductivity enhancement (CSDICE) were calculated as 27.2 and 28.5, respectively that makes this stretchable hydrogel electrolyte an ideal candidate for preparation of stretchable lithium ion batteries [44].

To achieve better properties such as higher stability and enhanced ionic conductivity in lithium-ion batteries, the same group incorporated graphene oxide (GO) inside a PEO– LiClO_4 matrix. The stretchable battery fabricated with this composition was spiral in nature and displayed enhanced mechanical and electrochemical properties. Besides, 1300% out-of-plane deformation was observed for the thin spiral lithium-ion battery [74].

Recently, there are also some reports on usage of polyacrylamide (PAM) as polymer host for stretchable electrolytes of batteries. Li et al. demonstrates synthesis of a cross-linked PAM hydrogel electrolyte and their application towards zinc ion battery. Here acrylamide, potassium persulfate and N,N' -methylenebis (acrylamide) were utilized as monomer, initiator and cross-linker respectively. Manganese oxide (MnO_2) and zinc electrodes prepared on carbon nanotubes yarn has been employed for the zinc ion battery. Owing to the presence of PAM hydrogel electrolyte the battery can sustain a strain up to 300% that indicates PAM hydrogel electrolytes assist in enhancing the stretchability of the battery. Superior electrochemical features such as increased volumetric energy density, improved specific capacity etc. has also been displayed by the battery and 96.5% of capacity was still maintained even after keeping it for 12 h in water, which supports its waterproof characteristics [45]. The same group have further enhanced the stretchability of the zinc ion battery by utilizing a nanofibrillated cellulose/PAM based hydrogel electrolyte. A strain of as high as 1400% was observed. Apart from that even after 120 stitches the battery display a great shear force amounting to 43 N while maintaining a capacity 88.5% [46]. Zhong et al. utilized wax emulsion method to develop an interesting gum like electrolyte. In this method they added the liquid electrolyte into the wax solution followed by its blending with PEO solution. It can be deformed to any position and return back without losing its properties. An enhanced room temperature conductivity of 3×10^{-4} S/cm and better mechanical strength has been displayed by the gum-like electrolyte. Besides a 4.5V of electrochemical stability window is depicted through the linear sweep voltammetry of the stretchable gummy electrolyte. These remarkable properties displayed great promise for stretchable lithium ion batteries [75].

To explore the influence of hydrogel electrolytes towards zinc air batteries, Tran et al. designed three different hydrogel electrolyte i.e. poly (vinyl alcohol) (PVA) based, poly (acrylic acid) (PAA) based and poly(4-vinylbenzenesulfonate-co-[3-(methacryloylamino)propyl] trimethylammonium chloride) (PAM) based. For assessing the efficiency of the hydrogel electrolytes towards zinc air batteries, CR2032 coin cells were prepared in which the electrodes are catalyst loaded gas diffusion layer and zinc foil as electrodes. All the three gel polymer electrolytes (GPE) display a good electrochemical stability with stability up to 2V. The ionic conductivity with different electrolytes follows the following trend PAA > PVA > PAM. The PAA based electrolyte display highest zinc ionic conductivity of 204 mS cm^{-1} and it was observed to enhance further with increment of temperature. The electrolyte display higher bulk resistance but it was circumvented by the small charge transfer and interfacial resistance values. An extraordinary cyclic stability has been depicted by

PAA and PVA based hydrogel electrolytes as compared to tradition aqueous electrolytes whereas poor cycling ability was displayed by PAM based hydrogel electrolyte. The charge–discharge study reveals all the three electrolytes display an enhanced efficiency of >65% [76]. Liu et al. develop a novel NiCo//Zn battery which is inherently stretchable and compressible. For this they use hydrogel electrolyte based on sodium polyacrylate (PANA). For making electrodes first they take Au@CNT papers and then place nickel cobalt hydroxide and zinc nanosheets over it to prepare wavy structured electrodes. The high stretchability can be shown by the battery by undergoing 400% strain while 50% strain well indicate its great compressibility. After 1500 cycles of compression only 3% of initial discharge capacity was lost, whereas minimal decrease of 13% was noticed in the capacity after 500 cycles of stretching. The high retention of capacity can be dedicate to employment of wavy structures electrodes and usage PANA hydrogel electrolytes that provides enhanced electrochemical and mechanical sturdiness [58]. Keeping in view of the shortcomings of typical hydrogel electrolytes, Mo et al. designed bio-mimetic organohydrogel (BM-gel) and employ them towards the preparation of Zn– MnO_2 batteries. The rechargeable Zn– MnO_2 batteries was subjected to a varying temperature in between 80°C and -20°C . The coulombic efficiency of the rechargeable Zn– MnO_2 batteries was approximately equals to 100% throughout the temperature deviation whereas 70% of initial discharge capacity was also sustained. To assess the shelf life of the batteries, the batteries were stored at room temperature for 30 days. Only 15% degradation was spotted after 30 days. This enhanced feature can be ascribed to the thin elastomer coating [60].

Guan et al. designed a stretchable ionic liquid based gel polymer electrolytes for its application towards lithium ion batteries. The electrolyte comprises poly (vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP)), triallyl isocyanurate (TAIC), and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm] [TFSI]). Electron beam irradiation, absorption of the ionic liquid, and crosslinking of the polymer were carried out to obtain the stretchable crosslinked gel polymer electrolyte (C-GPE). Fig. 6 shows the schematic of the fabrication of crosslinked gel polymer electrolytes. The presence of a cross-linker leads to the formation of porous nanostructures that are interconnected, as indicated through FE-SEM analysis. Because of this, the ionic conductivity of the prepared C-GPE is twice that of the polymeric ionic liquid matrix. The C-GPE can undergo 100% stretching and recovery without any strain and exhibits enhanced electrochemical stability. The half cells with LiFePO_4 electrode and lithium foil display a first discharge capacity of around 69 mAhg^{-1} and after undergoing 30 cycles of charge and discharge 43% of initial capacity was maintained. Better cyclic stability was also observed for the cells [48]. Angelo et al. design a fully zwitterionic (f-ZI) polymer scaffold-supported solvate ionogel for application towards lithium ion battery. For this they employed free radical polymerization of two zwitterionic monomers carried out through the usage of UV irradiation. There is hardly any variation in ionic conductivity, but the mechanical sturdiness of the ionogels are enhanced remarkably when the ratio between two monomers are kept at 3:1. This can be attributed to the f-ZI polymer network. The f-ZI based ionogel display an improved Li ion transference number of 0.60 and it can sustain a mechanical strain up to 200%. This also leads to high electrochemical stability and enhanced galvanostatic cycling stability to the lithium ion battery employing this f-ZI based ionogel [63].

5. Summary and future outlook

Stretchable energy storage systems such as batteries and supercapacitors are the need of the hour to realize completely stretchable devices that can make our life much easier. This mini-review emphasized some latest research findings on stretchable electrolytes, which is an integral component of stretchable energy storage systems since they not only function as an electrolyte, but also support the electrodes, enabling complete assembly of energy storage systems. A variety of polymer matrix components with novel materials and structures has been reported

for stretchable devices. Hydrogel and ionogel electrolytes have their own merits as stretchable electrolytes and display improved characteristics when applied in supercapacitors and batteries; however, ionogels show superior features compared to hydrogels due to the presence of an ionic liquid. Different types of supercapacitors with stretchable electrolytes (both ionogel and hydrogel) have been fabricated with omni-directional stretchability and pyramidal structures along with good electrochemical properties. MSCs having stretchable electrolytes, which can be easily integrated within wearable devices and gas sensors due to their small size, display significant properties. The use of stretchable electrolytes in batteries especially lithium-ion batteries has also been reported. Hydrogel electrolytes are mostly employed in stretchable battery research. Moreover, although stretchable electrolytes for supercapacitors have been extensively explored, there is a wider opportunity to conduct more research toward completely stretchable lithium-ion batteries (comprising a stretchable electrolyte), which are immensely efficient energy storage systems as compared to supercapacitors.

The recent findings open new possibilities for stretchable electrolytes for next generation devices which can provide the required stretchability/flexibility to the devices. Nevertheless, many issues still remain in the commercialization of stretchable electrolytes like the electrochemical parameters or the ionic conductivity are not as high as that of liquid electrolytes. Apart from that to scale up the preparation method of stretchable electrolyte with the same improved properties that is obtained at lab scale is quite challenging. The compatibility of the stretchable electrolytes with newly improved electrodes is also an issue of concern. The cost of some electrolytes also high. For creating improved stretchable electrolytes that can be employed in stretchable/flexible devices in large scale following things may be considered:

First and foremost thing that is to be considered is to have a more thorough perspective of the charging and discharging behavior in the energy storage systems and the role of electrolytes. It can be achieved if both theoretical and experimental expertise are followed.

To counteract the issue of compatibility between electrolytes and electrodes, efforts should be done towards designing of electrodes with varied structures that can help in better compatibility between electrodes and electrolytes and hence better energy density can be achieved. Also the thickness and density of stretchable electrolytes must be optimized as it will highly impact towards the energy density.

Improved and highly calibrated methods are very much essential to analyse the performance of some latest developed electrolytes faster and with more precision.

To deal with increasing cost it will be helpful if we consider to use some natural occurring components like cellulose etc. to prepare electrolytes.

Fabricating new nanomaterials with whose incorporation could provide an inbuilt stretchability to the electrolytes.

Synthesizing new polymer and ionic liquids and try their combination to prepare stretchable electrolytes.

Developing some new and easy methods of preparing stretchable electrolytes that can be easily expanded to a pilot scale.

If researchers from different fields collaborate on the stretchable electrolyte research and come up with exciting new ideas and strategies, then completely stretchable devices will be a reality in the near future, which can make the life of present and future generations comfortable.

Declaration of competing interest

The authors declare no conflicts of interest.

Acknowledgements

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2017M1A2A2087577 and 2018R1A4A1024691).

References

- [1] D.H. Kim, J. Xiao, J. Song, Y. Huang, J.A. Rogers, Stretchable, curvilinear electronics based on inorganic materials, *Adv. Mater.* 22 (2010) 2108–2124.
- [2] B. Sun, Y.Z. Long, Z.J. Chen, S.L. Liu, H.D. Zhang, J.C. Zhang, W.P. Han, Recent advances in flexible and stretchable electronic devices via electrospinning, *J. Mater. Chem. C* 2 (2014) 1209–1219.
- [3] C. Yu, C. Masarapu, J. Rong, B. Wei, H. Jiang, Stretchable supercapacitors based on buckled single-walled carbon-nanotube macrofilms, *Adv. Mater.* 21 (2009) 4793–4797.
- [4] T.Q. Trung, N.E. Lee, Recent progress on stretchable electronic devices with intrinsically stretchable components, *Adv. Mater.* 29 (2017) 1603167.
- [5] Z. Yu, X. Niu, Z. Liu, Q. Pei, Intrinsically stretchable polymer light-emitting devices using carbon nanotube-polymer composite electrodes, *Adv. Mater.* 23 (2011) 3989–3994.
- [6] S. Nagels, W. Deferme, Fabrication approaches to interconnect based devices for stretchable electronics: a review, *Materials* 11 (2018) 375.
- [7] A. Chortos, Z. Bao, Skin-inspired electronic devices, *Mater. Today* 17 (2014) 321–331.
- [8] S. Choi, H. Lee, R. Ghaffari, T. Hyeon, D.H. Kim, Recent advances in flexible and stretchable bio-electronic devices integrated with nanomaterials, *Adv. Mater.* 28 (2016) 4203–4218.
- [9] T. Sekitani, Y. Noguchi, K. Hata, T. Fukushima, T. Aida, T. Someya, A rubberlike stretchable active matrix using elastic conductors, *Science* 321 (2008) 1468–1472.
- [10] T. Sekitani, T. Someya, Stretchable, large-area organic electronics, *Adv. Mater.* 22 (2010) 2228–2246.
- [11] D.H. Kim, J.H. Ahn, W.M. Choi, H.S. Kim, T.H. Kim, J. Song, Y.Y. Huang, Z. Liu, C. Lu, J.A. Rogers, Stretchable and foldable silicon integrated circuits, *Science* 320 (2008) 507–511.
- [12] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Najafabadi, D.N. Futaba, K. Hata, A stretchable carbon nanotube strain sensor for human-motion detection, *Nat. Nanotechnol.* 6 (2011) 296–301.
- [13] P. Lee, J. Lee, H. Lee, J. Yeo, S. Hong, K.H. Nam, D. Lee, S.S. Lee, S.H. Ko, Highly stretchable and highly conductive metal electrode by very long metal nanowire percolation network, *Adv. Mater.* 24 (2012) 3326–3332.
- [14] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya, Stretchable active-matrix organic light-emitting diode display using printable elastic conductors, *Nat. Mater.* 8 (2009) 494–499.
- [15] D.J. Lipomi, J.A. Lee, M. Vosgueritchian, B.C.K. Tee, J.A. Bolander, Z. Bao, Electronic properties of transparent conductive films of PEDOT: PSS on stretchable substrates, *Chem. Mater.* 24 (2012) 373–382.
- [16] T. Sekitani, T. Someya, Stretchable organic integrated circuits for large-area electronic skin surfaces, *MRS Bull.* 37 (2012) 236–245.
- [17] Z. Bao, X. Chen, Flexible and stretchable devices, *Adv. Mater.* 28 (2016) 4177–4179.
- [18] W. Kim, W. Kim, 3 V omni-directionally stretchable one-body supercapacitors based on a single ion-gel matrix and carbon nanotubes, *Nanotechnology* 27 (2016) 225402.
- [19] J. Lee, W. Kim, W. Kim, Stretchable carbon nanotube/ion-gel supercapacitors with high durability realized through interfacial microroughness, *ACS Appl. Mater. Interfaces* 6 (2014) 13578–13586.
- [20] C. Zhao, C. Wang, Z. Yue, K. Shu, G.G. Wallace, Intrinsically stretchable supercapacitors composed of polypyrrole electrodes and highly stretchable gel electrolyte, *ACS Appl. Mater. Interfaces* 5 (2013) 9008–9014.
- [21] S. He, J. Cao, S. Xie, J. Deng, Q. Gao, L. Qiu, J. Zhang, L. Wang, Y. Hu, H. Peng, Stretchable supercapacitor based on a cellular structure, *J. Mater. Chem.* 4 (2016) 10124–10129.
- [22] W. Liu, Z. Chen, G. Zhou, Y. Sun, H.R. Lee, C. Liu, H. Yao, Z. Bao, Y. Cui, 3D porous sponge-inspired electrode for stretchable lithium-ion batteries, *Adv. Mater.* 28 (2016) 3578–3583.
- [23] X. Wang, C. Yang, J. Jin, X. Li, Q. Cheng, G. Wang, High-performance stretchable supercapacitors based on intrinsically stretchable acrylate rubber/MWCNTs@conductive polymer composite electrodes, *J. Mater. Chem.* 6 (2018) 4432–4442.
- [24] S. Saricilar, D. Antiohos, K. Shu, P.G. Whitten, K. Wagner, C. Wang, G.G. Wallace, High strain stretchable solid electrolytes, *Electrochem. Commun.* 32 (2013) 47–50.
- [25] Y. Shi, Y. Zhang, L. Jia, Q. Zhang, X. Xu, Stretchable and self-healing integrated all-gel-state supercapacitors enabled by a notch-insensitive supramolecular hydrogel electrolyte, *ACS Appl. Mater. Interfaces* 10 (2018) 36028–36036.
- [26] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, Nanocomposite polymer electrolytes for lithium batteries, *Nature* 394 (1998) 456.
- [27] D. Golodnitsky, E. Strauss, E. Peled, S. Greenbaum, On order and disorder in polymer electrolytes, *J. Electrochem. Soc.* 162 (2015) A2551–A2566.
- [28] M. Marcinek, A. Bac, P. Lipka, A. Zalewska, G. Zukowska, R. Borkowska, W. Wieczorek, Effect of filler surface group on ionic interactions in PEG–LiClO₄–Al₂O₃ composite polyether electrolytes, *J. Phys. Chem. B* 104 (2000) 11088–11093.
- [29] S.J. Kwon, B.M. Jung, T. Kim, J. Byun, J. Lee, S.B. Lee, U.H. Choi, Influence of Al₂O₃ nanowires on ion transport in nanocomposite solid polymer electrolytes, *Macromolecules* 51 (2018) 10194–10201.
- [30] A. Chandra, Ion conduction behavior of hot-pressed nanocomposite polymer electrolytes: (1–x) [70PEO: 30NaBr]+ xSiO₂, *Polym. Bull.* 76 (2019) 785–796.
- [31] J.H. Park, M. Kim, Development of an Organic/Inorganic Nano-Composite Separator for Lithium Ion Batteries Using an Irradiation, Republic of Korea, 2010.
- [32] D.K. Pradhan, B.K. Samantaray, R.N.P. Choudhary, A.K. Thakur, Effect of plasticizer on structure–property relationship in composite polymer electrolytes, *J. Power Sources* 139 (2005) 384–393.

- [33] S. Das, A. Ghosh, Effect of plasticizers on ionic conductivity and dielectric relaxation of PEO-LiClO₄ polymer electrolyte, *Electrochim. Acta* 171 (2015) 59–65.
- [34] R. He, T. Kyu, Effect of plasticization on ionic conductivity enhancement in relation to glass transition temperature of crosslinked polymer electrolyte membranes, *Macromolecules* 49 (2016) 5637–5648.
- [35] S.K. Gulrez, S. Al-Assaf, G.O. Phillips, *Hydrogels: methods of preparation, characterisation and applications*, in: A. Carpi (Ed.), *Progress in Molecular and Environmental Bioengineering-From Analysis and Modeling to Technology Applications*, IntechOpen, 2011.
- [36] B.C. Kim, H.T. Jeong, M.J. Higgins, K.H. Yu, G.G. Wallace, Dynamic electrochemical properties of extremely stretchable electrochemical capacitor using reduced graphene oxide/single-wall carbon nanotubes composite, *J. Electrochem. Soc.* 162 (2015) A2351–A2355.
- [37] N.A. Choudhury, S. Sampath, A.K. Shukla, Hydrogel-polymer electrolytes for electrochemical capacitors: an overview, *Energy Environ. Sci.* 2 (2009) 55–67.
- [38] D. He, A.J. Marsden, Z. Li, R. Zhao, W. Xue, M.A. Bissett, Fabrication of a graphene-based paper-like electrode for flexible solid-state supercapacitor devices, *J. Electrochem. Soc.* 165 (2018) A3481–A3486.
- [39] T. Chen, R. Hao, H. Peng, L. Dai, High-performance, stretchable, wire-shaped supercapacitors, *Angew. Chem. Int. Ed. Engl.* 54 (2015) 618–622.
- [40] H.T. Jeong, J.F. Du, Y.R. Kim, C.J. Raj, B.C. Kim, Electrochemical performances of highly stretchable polyurethane (PU) supercapacitors based on nanocarbon materials composites, *J. Alloys Compd.* 777 (2019) 67–72.
- [41] P. Xu, T. Gu, Z. Cao, B. Wei, J. Yu, F. Li, J.H. Byun, W. Lu, Q. Li, T.W. Chou, Carbon nanotube fiber based stretchable wire-shaped supercapacitors, *Adv. Energy Mater.* 4 (2014) 1300759.
- [42] J. Yu, W. Lu, S. Pei, K. Gong, L. Wang, L. Meng, Y. Huang, J.P. Smith, K.S. Booksh, Q. Li, J.H. Byun, Y. Oh, Y. Yan, T.W. Chou, Omnidirectionally stretchable high-performance supercapacitor based on isotropic buckled carbon nanotube films, *ACS Nano* 10 (2016) 5204–5211.
- [43] Y. Xu, Y. Zhang, Z. Guo, J. Ren, Y. Wang, H. Peng, Flexible, stretchable, and rechargeable fiber-shaped zinc–air battery based on cross-stacked carbon nanotube sheets, *Angew. Chem.* 54 (2015) 15390–15394.
- [44] T. Kelly, B.M. Ghadi, S. Berg, H. Ardebili, In situ study of strain-dependent ion conductivity of stretchable polyethylene oxide electrolyte, *Sci. Rep.* 6 (2016) 20128.
- [45] H. Li, Z. Liu, G. Liang, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Tang, Y. Wang, B. Li, C. Zhi, Waterproof and tailorable elastic rechargeable yarn zinc ion batteries by a cross-linked polyacrylamide electrolyte, *ACS Nano* 12 (2018) 3140–3148.
- [46] D. Wang, H. Li, Z. Liu, Z. Tang, G. Liang, F. Mo, Q. Yang, L. Ma, C. Zhi, A nanofibrillated cellulose/polyacrylamide electrolyte-based flexible and sewable high-performance Zn–MnO₂ battery with superior shear resistance, *Small* 14 (2018) 1803978.
- [47] D. Kim, G. Lee, D. Kim, J.S. Ha, Air-stable, high-performance, flexible microsupercapacitor with patterned ionogel electrolyte, *ACS Appl. Mater. Interfaces* 7 (2015) 4608–4615.
- [48] J. Guan, Y. Li, J. Li, Stretchable ionic-liquid-based gel polymer electrolytes for lithium-ion batteries, *Ind. Eng. Chem. Res.* 56 (2017) 12456–12463.
- [49] B.C. Kim, H.T. Jeong, C.J. Raj, Y.R. Kim, B.B. Cho, K.H. Yu, Electrochemical performance of flexible poly (ethylene terephthalate)(PET) supercapacitor based on reduced graphene oxide (rGO)/single-wall carbon nanotubes (SWNTs), *Synth. Met.* 207 (2015) 116–121.
- [50] Y. Wan, K.A. Creber, B. Peppley, V.T. Bui, Chitosan-based electrolyte composite membranes: II. Mechanical properties and ionic conductivity, *J. Membr. Sci.* 284 (2006) 331–338.
- [51] N.A. Choudhury, S. Sampath, A.K. Shukla, Gelatin hydrogel electrolytes and their application to electrochemical supercapacitors, *J. Electrochem. Soc.* 155 (2008) A74–A81.
- [52] J. Le Bideau, L. Viau, A. Vioux, Ionogels, ionic liquid based hybrid materials, *Chem. Soc. Rev.* 40 (2011) 907–925.
- [53] J. Le Bideau, J.B. Ducros, P. Soudan, D. Guyomard, Solid-state electrode materials with ionic-liquid properties for energy storage: the lithium solid-state ionic-liquid concept, *Adv. Funct. Mater.* 21 (2011) 4073–4078.
- [54] M.F. El-Kady, R.B. Kaner, Scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage, *Nat. Commun.* 4 (2013) 1475.
- [55] B. Hsia, J. Marschewski, S. Wang, J.B. In, C. Carraro, D. Poulikakos, C.P. Grigoropoulos, R. Maboudian, Highly flexible, all solid-state micro-supercapacitors from vertically aligned carbon nanotubes, *Nanotechnology* 25 (2014), 055401.
- [56] X. Jin, G. Sun, H. Yang, G. Zhang, Y. Xiao, J. Gao, Z. Zhang, L. Qu, A graphene oxide-mediated polyelectrolyte with high ion-conductivity for highly stretchable and self-healing all-solid-state supercapacitors, *J. Mater. Chem.* 6 (2018) 19463–19469.
- [57] Y. Guo, K. Zheng, P. Wan, A flexible stretchable hydrogel electrolyte for healable all in one configured supercapacitors, *Small* 14 (2018) 1704497.
- [58] J. Liu, M. Hu, J. Wang, N. Nie, Y. Wang, Y. Wang, J. Zhang, Y. Huang, An intrinsically 400% stretchable and 50% compressible NiCo//Zn battery, *Nano Energy* 58 (2019) 338–346.
- [59] Y. Wang, F. Chen, Z. Liu, Z. Tang, Q. Yang, Y. Zhao, S. Du, Q. Chen, C. Zhi, A highly elastic and reversibly stretchable all-polymer supercapacitor, *Angew. Chem. Int. Ed.* 58 (2019) 15707–15711.
- [60] F. Mo, G. Liang, D. Wang, Z. Tang, H. Li, C. Zhi, Biomimetic organohydrogel electrolytes for high-environmental adaptive energy storage devices, *EcoMat* 1 (2019), e12008.
- [61] R. Hu, J. Zhao, Y. Wang, Z. Li, J. Zheng, A highly stretchable, self-healing, recyclable and interfacial adhesion gel: preparation, characterization and applications, *Chem. Eng. J.* 360 (2019) 334–341.
- [62] D. Wang, H. Li, Z. Liu, Z. Tang, G. Liang, F. Mo, C. Zhi, A nanofibrillated cellulose-polyacrylamide electrolyte-based flexible and sewable high-performance Zn–MnO₂ battery with superior shear resistance, *Small* 14 (2018) 1803978.
- [63] A.J. D'Angelo, M.J. Panzer, Design of stretchable and self-healing gel electrolytes via fully zwitterionic polymer networks in solvate ionic liquids for Li-based batteries, *Chem. Mater.* 31 (2019) 2913–2922.
- [64] Y. Sun, Y.Y. Ren, Q. Li, R.W. Shi, Y. Hu, J.N. Guo, Z. Sun, F. Yan, Conductive, stretchable, and self-healing ionic gel based on dynamic covalent bonds and electrostatic interaction, *Chin. J. Polym. Sci.* 37 (2019) 1053–1059.
- [65] Z. Chen, Y. Yang, Z. Ma, T. Zhu, L. Liu, J. Zheng, X. Gong, All-solid-state asymmetric supercapacitors with metal selenides electrodes and ionic conductive composites electrolytes, *Adv. Funct. Mater.* 29 (2019) 1904182.
- [66] P. Tamilarasan, S. Ramaprabhu, Stretchable supercapacitors based on highly stretchable ionic liquid incorporated polymer electrolyte, *Mater. Chem. Phys.* 148 (2014) 48–56.
- [67] H.H. Rana, J.H. Park, E. Ducrot, H. Park, M. Kota, T.H. Han, J.Y. Lee, J. Kim, J.H. Kim, P. Howlett, M. Forsyth, D. Macfarlane, H.S. Park, Extreme properties of double networked ionogel electrolytes for flexible and durable energy storage devices, *Energy Storage Mater* 19 (2019) 197–205.
- [68] J. Yun, Y. Lim, G.N. Jang, D. Kim, S.J. Lee, H. Park, S.Y. Hong, G. Lee, G. Zi, J.S. Ha, Stretchable patterned graphene gas sensor driven by integrated micro-supercapacitor array, *Nano Energy* 19 (2016) 401–414.
- [69] S. He, L. Qiu, L. Wang, J. Cao, S. Xie, Q. Gao, Z. Zhang, J. Zhang, B. Wang, H. Peng, A three-dimensionally stretchable high performance supercapacitor, *J. Mater. Chem.* 4 (2016) 14968–14973.
- [70] C.R. Chen, H. Qin, H.P. Cong, S.H. Yu, A Highly stretchable and real-time healable supercapacitor, *Adv. Mater.* 31 (2019) 1900573.
- [71] S.K. Kim, H.J. Kim, J.C. Lee, P.V. Braun, H.S. Park, Extremely durable, flexible supercapacitors with greatly improved performance at high temperature, *ACS Nano* 9 (2015) 8569–8577.
- [72] E.P. Gilshteyn, T. Kallio, P. Kanninen, E.O. Fedorovskaya, A.S. Anisimov, A.G. Nasibulin, Stretchable and transparent supercapacitors based on aerosol synthesized single-walled carbon nanotube films, *RSC Adv.* 6 (2016) 93915–93921.
- [73] J. Ye, H. Tan, S. Wu, K. Ni, F. Pan, J. Liu, Z. Tao, Y. Qu, H. Ji, P. Simon, Y. Zhu, Direct laser writing of graphene made from chemical vapor deposition for flexible, integratable micro-supercapacitors with ultrahigh power output, *Adv. Mater.* 30 (2018) 1801384.
- [74] M. Kammoun, S. Berg, H. Ardebili, Stretchable spiral thin-film battery capable of out-of-plane deformation, *J. Power Sources* 332 (2016) 406–412.
- [75] Y. Wang, B. Li, J. Ji, A. Elyer, W.H. Zhong, A gum-like electrolyte: safety of a solid, performance of a liquid, *Adv. Energy Mater.* 3 (2013) 1557–1562.
- [76] T.N.T. Tran, H.J. Chung, D.G. Ivey, A study of alkaline gel polymer electrolytes for rechargeable zinc–air batteries, *Electrochim. Acta* 327 (2019) 135021.