The recent advances on potential solid electrolytes for all-solid-state supercapacitors: A short review

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Abstract. The increasing demand to develop renewable energy has increased drastically due to limited resources and environmental problems of fossil fuel. The most widely used energy storage devices are batteries and capacitors. Supercapacitors, on the other hand, can induce higher power density by fast charging/discharging rate which results in higher power density and longer cycle life compared to batteries and fuel cells. To fulfil the demand for safer energy sources, the use of highly flammable organic liquid electrolytes and polymer separators must be replaced by solid electrolytes. Therefore, supercapacitors with solid electrolytes can be alternative renewable energy. Commercially, there are three types of electrolytes of supercapacitors: aqueous electrolytes, organic electrolytes, and ionic liquids. In this paper, there is selective review on solid electrolytes of supercapacitors including chitosan, polyacrylamide, poly(aryl ether ketone), and polyethylene glycol. Overall, this paper aims to provide comprehensive reviews on recent advances in potential solid electrolytes of supercapacitors and the remaining challenges.

1. Introduction
The consumption of fossil fuel to be applied in many aspects of life seems unstoppable. Figure 1 illustrates global fossil fuel consumption ranges from 1800 – 2017. It shows that global fossil fuel consumption reaches its highest plateau in 2017 with more than 120,00 TWh [1].

Figure 1. Global fossil fuel consumption measured in terawatt-hours [1].
Recent data for 2018 from IEA of global fossil fuel consumption subsidies by energy source [2]. It shows that the estimated value to be more than $400 billion which is understandable since the rising demand for fossil fuel inversely proportional to the availability of fossil fuel resources. Therefore, the limited resources and environmental problems caused by the use of fossil fuels are the major reasons why renewable energy is being highly developed [3].

However, the focus has been shifted to energy storage devices which contain electrical energy to smooth the intermittency of the energy sources. The most widely used energy storage devices are batteries and capacitors. The latest research of battery has demonstrated better battery with higher energy density and longer life cycle but struggles with power densities. While the limited application of capacitors caused by the small amount of energy thus can be charged and discharged easily and deliver pulses of energy [4].

Supercapacitors, on the other hand, which is one of the words that is used to describe capacitors [6]. Supercapacitors have developed extensively since the first patents of capacitors back in 1957 [7] and first attempts to introduce it to market in 1969 [8]. There are several advantages of supercapacitors
making it superior to the rest of energy storage devices. Supercapacitors demonstrate higher power density and longer life cycle ( >100,000 cycles) [9]. To fulfil the demand for safer energy sources, the use of highly flammable organic liquid electrolytes and polymer separators must be replaced by solid electrolytes. Therefore, supercapacitors with solid electrolytes can be alternative renewable energy.

Commercially, there are three types of electrolytes of supercapacitors: aqueous electrolytes, organic electrolytes, and ionic liquids. In this paper, there is a selective review on solid electrolytes of supercapacitors including chitosan, polyacrylamide, poly(aryl ether ketone), and polyethylene glycol. Overall, this paper aims to provide comprehensive reviews on recent advances in potential solid electrolytes of supercapacitors and the remaining challenges.

2. A selective review of solid electrolytes of all-solid-state supercapacitors

There are several recent researches on solid electrolytes including chitosan, polyacrylamide, poly(aryl ether ketone), and polyethylene glycol. The advantages and future improvements of these researches are discussed in this section

2.1. Chitosan

Chitosan is a biopolymer composed of glucosamine and N-acetyl glucosamine units glucosidic bonds [10][11]. Chitosan has been a hot research topic due to its advantages including safer (non-toxic), water-soluble, and biodegradable which are important to solve the environmental issues caused by the use of fossil fuel [12]. Chitosan is chosen as an electrolyte due to its excellent mechanical properties and high film-forming capability. Material to be applied as an electrolyte must exhibit high ionic conductivity in the order \(-10^{-3}\) S/cm at room temperature. However, chitosan has low conductivity [13]. Therefore, various attempts have been made to increase the conductivity of chitosan [14].

Solid-state electrolytes have three types including solid electrolyte, gel polymer electrolyte, and polyelectrolyte. One of the major drawbacks which limit the application of solid electrolyte is its low conductivity \(10^{-8}\) and \(10^{-7}\) S/cm). Many efforts have been tried to overcome the low conductivity of solid electrolytes. For example, Shujahadeen et al. synthesized chitosan-ammonium triflate (CS-NH4Tf) polymer electrolyte films to see the role of TiO2 filler [15]. However, the obtained dc conductivity was in the order of \(10^{-7}\) S/cm at ambient temperature which is considerably low to be applied as an electrolyte.

Cao et al., on the other side, chose to synthesis a biopolymer-chitosan based supramolecular hydrogel solid-state electrolyte via a simple and fast cross-linking between chitosan and Li+/Ag+. The electrolyte was flexible and high cyclic stability. SEM characterization shows that MnO2 and KBC particles are evenly distributed among the CNTs which is an important characteristic since it makes the adsorption and desorption of the Li+ ion easier. EIS characterization shows that chitosan-based hydrogel solid-state electrolyte has high ionic conductivity of \(1.6 \times 10^{-3}\) S/cm to \(4.6 \times 10^{-3}\) S/cm with temperature ranges from 313 K and 353 K. Their work successfully fulfilled the requirements of a material to be applied as an electrolyte in general [13].

2.2. Polyacrylamide

Polyacrylamide is a synthetic polymer known for its high hydrophilicity formed by polymerization of acrylamide monomer by a catalyst with bifunctional cross-linking agents [16]. Polyacrylamide has considerably high ionic conductivity of \(1.7 \times 10^{-2}\) S/cm but still considered to be lower than commercialized PVA/H2SO4 [17].

Tabanli et al. Focused their research on rectification of current by synthesizing polyacrylamide hydrogel as an electrolyte. Their work showed that the maximum rectification ratio to be around 850 at 6-7 V for Al/PHE/Pt configuration. While recent research from Li et. al. proposed to synthesis polyacrylamide hydrogels as a solid-state electrolyte by cross-linking methacrylated graphene oxide (MGO-PAM). The results showed that polyacrylamide as solid-state electrolyte of supercapacitor could exhibit high specific capacitance, long self-discharge time, and low leakage [18].
2.3. **Poly(aryl ether ketone) and Polyethylene Glycol**

Poly(aryl ether ketone) is one of semicrystalline polymer with a crystalline melting point around 335°C and a glass transition at around 145°C, possesses excellent mechanical properties, good environmental resistance, thermo-oxidative stability, chemical and radiation resistance [19][20]. While polyethylene glycol is a biocompatible poly(ether) which low cost production and highly soluble in aqueous solutions and organic solvents [21].

Li et al. Synthesized hybrid membranes of branched sulfonated poly (aryl ether ketone) with 1,3,5-tris(4-fluorobenzoyl) benzene as the branching agent to improve the properties of mechanical strength, excellent dimensional stability, and low methanol permeability. The work showed that the highest value of proton conductivity value was $8.2 \times 10^{-1} \text{ S/cm}$ [22].

Na et al. Suggested solid-state polymer electrolyte by combining poly(aryl ether ketone)-polyethylene glycol copolymer as a polymer host and LiClO$_4$ as an electrolyte salt aiming to provide alternative to make a flexible solid-state supercapacitor. The results showed that the solid-state supercapacitor has excellent electrochemical performance especially at high temperature, high specific capacitance, and high energy density [23].

3. **Conclusion**

The recent advances of solid-state electrolytes to produce a solid-state supercapacitors have showed that there are several methods and approaches which are needed in order to come up with better solid-state supercapacitors as energy storage thus yet still needs to be improved and developed by tuning either the electrode mass ratios, increasing the ionic conductivity, energy density, and capacitance.

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