



Polyacrylamide-lithium chloride polymer electrolyte and its applications in electrochemical capacitors



Alvin Virya, Keryn Lian *

Department of Materials Science and Engineering, University of Toronto, Toronto M5S 3E4, Ontario, Canada

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ABSTRACT

A neutral polymer electrolyte containing lithium chloride (LiCl) and polyacrylamide (PAM) was developed. The LiCl-PAM electrolyte film had an amorphous structure and an ionic conductivity $> 10 \text{ mS cm}^{-1}$. The addition of LiCl to the polyacrylamide did not alter the chemical bonding of PAM. Symmetric double layer capacitors (EDLC) were constructed using CNT-graphite electrodes. The solid EDLC retained approximately 85% of the capacitance achieved with a baseline cell in a LiCl aqueous solution. The solid EDLC devices demonstrated a wide voltage window (1.5 V), good cycle life ($> 10,000$ cycles), and excellent rate capability (up to 5 V s^{-1}).

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1. Introduction

Solid, thin, and flexible energy storage devices are required to power flexible and wearable technologies which are rapidly growing in importance. One of the key components for solid-state energy storage is a polymer electrolyte which eliminates liquid electrolyte leakage and minimizes bulky packaging. Among the various types of polymer electrolytes, aqueous-based electrolytes have the advantage of simplified manufacturing process under ambient conditions and without relying on volatile or flammable solvents.

Among aqueous-based polymer electrolytes, proton- and alkaline-conducting polymer electrolytes have been widely reported [1–5]. Neutral pH polymer electrolytes, however, have not been systematically investigated due to its perceived lower ionic conductivities demonstrated in liquid system ($\text{H}^+ > \text{OH}^- > \text{neutral ions}$, from the ion mobility and degree of dissociation [6]). Whenever a neutral polymer electrolyte is required, lithium chloride (LiCl)-polyvinyl alcohol (PVA) electrolytes have been commonly utilized [7–15]. However, the LiCl-PVA electrolyte has not been properly characterized for its material and electrochemical properties. While the ionic conductivities of H_2SO_4 - and KOH -based polymer electrolytes are commonly reported in the range of 10 mS cm^{-1} [1,2,5], only a single study reported the ionic conductivity of LiCl-PVA as 5.5 mS cm^{-1} [12]. Moreover, reported LiCl-PVA electrolytes were in gel form due to the high composition of hygroscopic LiCl salt (ca. 68 wt%) and therefore still required the use of a separator. The use of a separator not only increases device thickness and

resistance, but also prevents manufacturing of such devices through printing.

Albeit being the least studied, neutral pH polymer electrolytes can be highly advantageous due to their less-corrosive nature; high compatibility with many electrodes and current collectors materials; and wide potential window from its higher overpotential for both hydrogen and oxygen evolution [16]. Symmetric cells with carbon-based electrodes in various kinds of neutral pH electrolyte, both aqueous solution and gel polymer, were reported to exhibit a voltage window $> 1.5 \text{ V}$ [10,17–19]; a significant improvement from the typical $\leq 1 \text{ V}$ window in acid-based electrolytes [19,20]. As the energy density correlates to the voltage window squared ($E = \frac{1}{2} CV^2$), the aqueous-based neutral polymer electrolyte is a promising enabler towards high energy density, safe, and printable solid-state supercapacitor devices.

In this work, we investigated LiCl-polyacrylamide (PAM) as an alternative aqueous-based neutral polymer electrolyte. PAM was chosen for its amorphous structure [21] and great affinity to water [22], both are desirable attributes to facilitate ion conduction in aqueous-based solid polymer electrolytes. Due to the hygroscopic nature of LiCl, a low salt content is preferable to maintain a solid film integrity. With respect to material characteristics of the electrolyte, film crystallinity and chemical bonding were assessed, while the electrochemical performance was characterized in terms of ionic conductivity in a solid metallic cell and voltage window with carbon nanotube (CNT)-graphite double layer capacitor (EDLC) electrodes. The developed solid cells were analysed and compared with a LiCl aqueous electrolyte baseline. CNT-graphite electrodes, despite having lower surface area than activated carbon, are suitable for high rate capability and have been demonstrated with both acid solution electrolyte and alkaline polymer electrolyte [23,24].

* Corresponding author.

E-mail address: keryn.lian@utoronto.ca (K. Lian).

2. Experimental

The LiCl-PAM electrolyte was prepared by mixing a 3% PAM solution (Scientific Polymer, Mw: 5–6,000,000) with LiCl powder (Alfa Aesar) to form a precursor solution. Both PAM and LiCl were used as-received assuming no crystallized water. Two compositions with a LiCl:PAM molar ratio of 5000:1 and 10,000:1 were investigated (hereafter referred to as LiCl-PAM(5000) and LiCl-PAM(10000), respectively). The LiCl-PAM(5000) film corresponds to 96.3 wt% PAM + 3.7 wt% LiCl, whereas LiCl-PAM(10000) corresponds to 92.8 wt% PAM + 7.2 wt% LiCl.

A titanium foil (McMaster Carr, 50 μm thick) was used as electrode in the electrolyte performance study, while CNT-graphite electrodes coated on a titanium foil current collector were used for the solid EDLC devices. The preparation of the CNT-graphite electrodes was described in a previous report [19]. Carbon loading was *ca.* 1.5–2 mg cm^{-2} , containing 60 wt% CNT, 20 wt% graphite, and 20 wt% cross-linked PVA binder. The apparent area of the electrode was 1 cm^2 . The solid cells were assembled by casting the precursor solution onto each electrode followed by sandwiching the electrolyte between two electrodes and protecting it with tape. The thicknesses of the test cells were measured using Mitutoyo digital micrometer and the average value was 0.55 mm, resulting an electrolyte thickness of *ca.* 0.1 mm. All solid cells were stored at room temperature in a 45% RH desiccator. For comparison with the polymer electrolyte, a liquid cell was constructed using the same CNT-graphite electrodes. The electrolyte was a Whatman™ 2.5 μm porosity filter paper soaked in a 0.5 M LiCl solution and sandwiched between two CNT-graphite electrodes.

To investigate the full potential range of the solid LiCl-PAM electrolyte, a modified Zensor™ screen-printed electrode was employed where both the working and counter electrode was coated with a layer of CNT-graphite ink and the Ag/AgCl reference electrode was left as-is.

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge cycling were performed

using a CHI760C bipotentiostat. EIS spectra were recorded from 100 kHz to 1 Hz (for metallic cells) or 0.01 Hz (for CNT-graphite cells) with a 5 mV amplitude and 0 V DC bias. The capacitance from CV was calculated by dividing the charge by the voltage window ($C = \frac{Q}{V}$) whereas the capacitance from galvanostatic charge/discharge cycling was calculated by dividing the current with slope of voltage-time curve ($C = \frac{j}{dV/dt}$). Ionic conductivity σ was calculated from the equivalent series resistance (ESR) obtained from EIS measurements ($\sigma = \frac{t}{A \times \text{ESR}}$ A: apparent area and t: electrolyte thickness).

X-ray diffraction (XRD) was utilized to characterize film crystallinity and the chemical bonding structure was investigated through Raman spectroscopy. All films were conditioned at 45% RH for 7 days. XRD patterns were obtained with a Phillips XRD system. The analysis was carried out with a monochromatized copper K- α anode source at 40 kV/40 mA. The XRD pattern was acquired from 5° to 50° 2 θ with a step scan of 0.02°. The Raman spectra were recorded on a Horiba XploRA™ PLUS Raman microscope system with a 532 nm laser and diffraction grating of 1800 g/mm. The spectra were recorded between 15 cm^{-1} and 4000 cm^{-1} wavenumbers.

3. Results and discussion

The structure and chemical compatibility of LiCl and PAM were first investigated in terms of the resulting film crystallinity and chemical bonding structure. The performance of the polymer electrolyte was characterized in metallic cells to study the environmental stability of the ionic conductivity. The optimized electrolyte was further demonstrated in a solid carbon-based EDLC configuration.

3.1. Material characterizations

The LiCl-PAM mixture formed a homogenous precursor solution with no apparent interaction or side reaction. As the precursor solutions were cast and dried under ambient conditions, both LiCl-PAM(5000) and LiCl-PAM(10000) formed transparent films. Comparing the mass

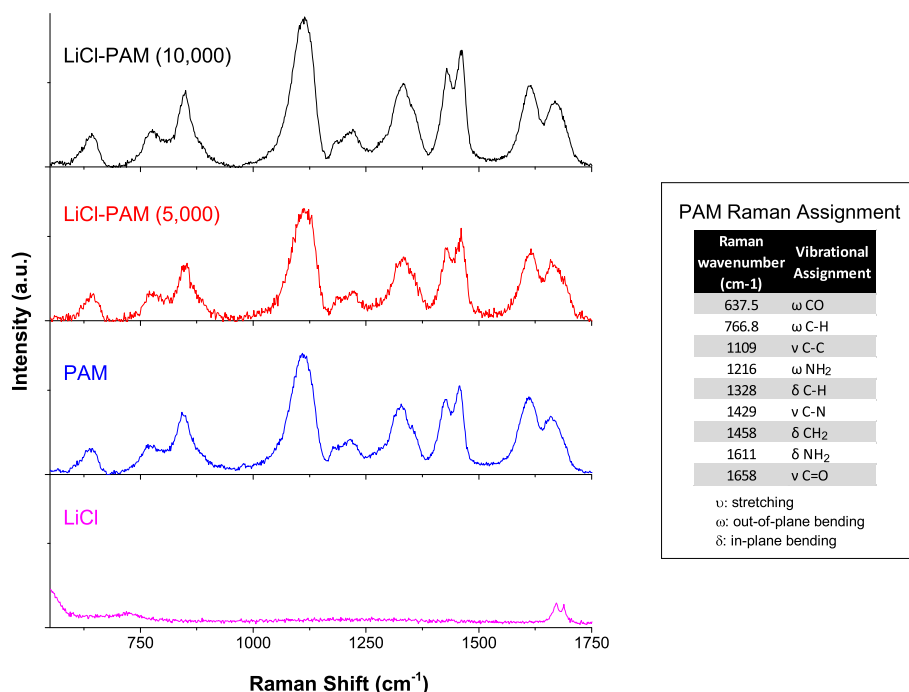


Fig. 1. Raman spectra of LiCl-PAM film vs. its components along with PAM functional group peak assignment.

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