



Short communication

# High rate all-solid electrochemical capacitors using proton conducting polymer electrolytes

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## ABSTRACT

All-solid electrochemical capacitors (EC) utilizing a proton conducting polymer electrolyte and graphite electrodes have demonstrated exceptionally high rate capability. The solid polymer electrolyte-based ECs charge and discharge at sweep rate over  $20 \text{ V s}^{-1}$  and exhibit a time constant of 10 ms. This high rate performance is enabled by a proton conducting ternary solid thin film electrolyte composed of silicotungstic acid, orthophosphoric acid, and polyvinyl alcohol. This work shows that solid polymer electrolytes can support high power and high rate energy storage applications.

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## 1. Introduction

Rate and power capabilities are key characteristics of electrochemical capacitors (EC). Recent advances demonstrating up to  $200 \text{ V s}^{-1}$  rate capability as reported by Pech et al. [1] and 120 Hz filtering as reported by Miller et al. [2] have further broadened their application area in electronics. Both reports attributed the achieved ultrahigh rates to novel electrode materials such as onion-like nanocarbon (OLC) [1] and graphene [2], while relying on conventional liquid electrolytes, such as organic tetraethylammonium tetrafluoroborate ( $\text{Et}_4\text{NBF}_4$ ) in propylene carbonate [1] or aqueous KOH [2]. Supplementing superior electrodes, advanced electrolytes could also play an important role in enhancing energy and power density of EC devices. For example, high performance polymer electrolytes, acting as a separator and ionic conductor, could not only improve energy and power density, but also enable light, flexible form factors and multi-cell/single-package EC devices. Polymer electrolytes, such as polyvinyl alcohol (PVA)–KOH [3], (PVA)– $\text{H}_3\text{PO}_4$  gel electrolyte [4], polyacrylate (PAAK)–KCl [5], poly(ethylene oxide)–tetra ethyl ammonium tetrafluoroborate (PEO– $\text{Et}_4\text{NBF}_4$ ) [6], Nafion [7], or ionic liquids with poly(ethylene oxide) [8] have been used in EC systems. While otherwise showing many promising results, devices leveraging these electrolytes deliver only low rates with voltage cycling at less than  $100 \text{ mV s}^{-1}$ . We have reported proton conducting polymer electrolytes with heteropoly acids (HPA) for symmetric and asymmetric EC devices

[9,10] at rates up to  $1 \text{ V s}^{-1}$ , as well as a 10-cell PVA– $\text{H}_3\text{PO}_4$  device operating at  $10 \text{ V s}^{-1}$  [4] on pseudocapacitive electrodes.

Proton conducting polymer electrolytes are promising electrolyte systems for both double layer and pseudocapacitors. Based on our earlier results [9,10], we have further optimized HPA–PVA systems with various additives. While there are many excellent electrode materials available, for these experiments we selected graphite ink as electrodes to minimize the influence of pores, in order to focus on the impact of the electrolyte on system behavior. In this paper, we report preliminary results achieved for all-solid double layer ECs using a silicotungstic acid (SiWA) based HPA– $\text{H}_3\text{PO}_4$ –PVA polymer electrolyte (referred to subsequently as SiWA– $\text{H}_3\text{PO}_4$ –PVA), specifically focusing on high rate behavior.

## 2. Experimental

The polymer electrolyte was prepared by mixing a polyvinyl alcohol (PVA, Aldrich MW = 85,000–124,000) solution with  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  (SiWA, Alfa Aesar) and orthophosphoric acid ( $\text{H}_3\text{PO}_4$ , Alfa Aesar) to form a precursor solution, composed of 10% SiWA, 3%  $\text{H}_3\text{PO}_4$ , 2.5% PVA, and 84.5% de-ionized water (all in wt%).

For the electrodes, an aqueous based graphite conductive ink (Alfa Aesar) was coated on  $50 \mu\text{m}$  thick stainless steel foils and dried in air. The thickness of the graphite ink coating was about  $25 \mu\text{m}$ . The solid-state EC devices were then fabricated in the following two steps (see Fig. 1):

- 1) Electrodes were first coated with the precursor solution via brush painting and dried under ambient conditions.

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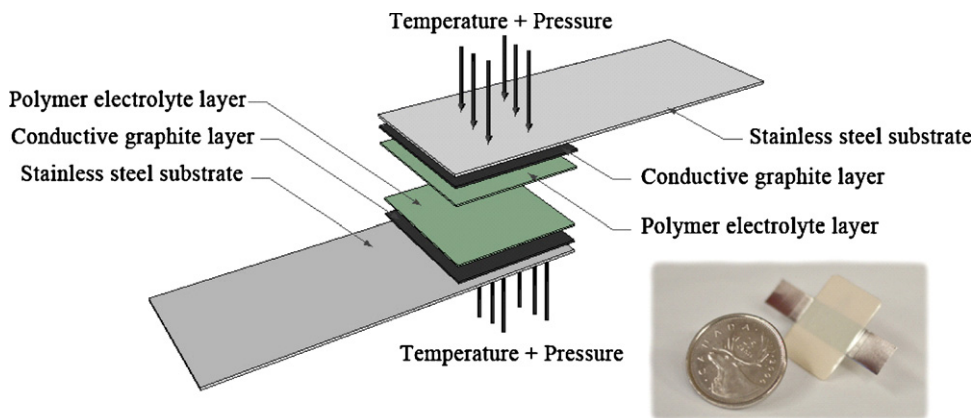


Fig. 1. Schematic diagram of assembly process for a solid EC and assembled device (inset).

2) Cells were fabricated by hot pressing two electrolyte-coated electrodes together for 20 min under 10–12 psi pressure at a temperature of 90 °C, and allowing them to cool down in ambient temperature.

The hot pressing process leaves the electrolyte as a solid film containing mostly SiWA with crystallized water in a polymer matrix [11] rather than in gel form. The thickness of the processed solid polymer electrolyte film was in the range of 45–50  $\mu\text{m}$ . Consequentially, each individual cell was roughly 200  $\mu\text{m}$  thick. A fabricated device is shown in the inset of Fig. 1.

The solid-state EC devices were characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV and EIS were performed on a CHI 760D bipotentiostat. All electrochemical tests were conducted under ambient conditions, at around 25 °C temperature and 10–30% relative humidity. The reported cell resistance is based on an average of 6 devices.

### 3. Results and discussion

Cyclic voltammetric studies were conducted on the solid ECs. The EC devices were scanned incrementally from 1  $\text{V s}^{-1}$  to 20  $\text{V s}^{-1}$ . Fig. 2 shows overlaid CVs of a device at sweep rates of 1, 5, 10, and 20  $\text{V s}^{-1}$ . All CVs showed near rectangular shape indicating capacitive behavior. To our knowledge, this is the first time that a solid EC device has been shown to exhibit such rectangular CV profiles at such high rates. In addition, as shown in the voltammograms in Fig. 2, the current increased linearly with the sweep rate, further suggesting good rate capability at high charge/discharge

rates. Capacitance at 1  $\text{V s}^{-1}$  was about 1  $\text{mF cm}^{-2}$  and decreased to 0.7  $\text{mF cm}^{-2}$  at 20  $\text{V s}^{-1}$ . An EC with similar electrodes but totally immersed in an aqueous HPA electrolyte was reported to have a capacitance of 7  $\text{mF cm}^{-2}$  at 0.1  $\text{V s}^{-1}$  [12]. Comparing to the liquid electrolyte, the capacitance obtained in this solid device was about 2  $\text{mF cm}^{-2}$  at the same rate, and was most likely contributed from the surface rather than the bulk of the graphite ink layer. The behavior of this solid EC is similar to that reported for onion-like nano carbon in a liquid electrolyte [1], where the high rate capability was also attributed to the effect of the electrode surface.

Further investigation of the solid polymer electrolyte-based capacitor was performed through EIS. For capacitance analyses, we relied on the approach by Teberna et al. [13] to separate the real part of the capacitance ( $C'$ ) from its imaginary part ( $C''$ ) and to plot them as a function of frequency as depicted in Fig. 3.  $C'$  represents the accessible capacitance per area of the device at the corresponding frequency, which approaches the capacitance obtained from dc methods at low frequencies. On the other hand,  $C''$  corresponds to energy dissipation by an irreversible process. The maximum of the  $C''$  vs. frequency curve represents an RC time constant, where the phase angle of the impedance of the cell reaches 45° and the energy of the device is discharged at 50% efficiency [13,14]. This time constant is used as “factor of merit” to compare the rate capability of EC devices [14]. Examining the curves in Fig. 3,  $C'$  was approaching 0.9  $\text{mF cm}^{-2}$  at low frequency (1 Hz). The capacitance decreased gradually over 3 decades of frequency agreeing with the capacitance obtained in Fig. 2. This gradual decrease in capacitance is desirable and was also reported for OLC in liquid electrolytes [1].

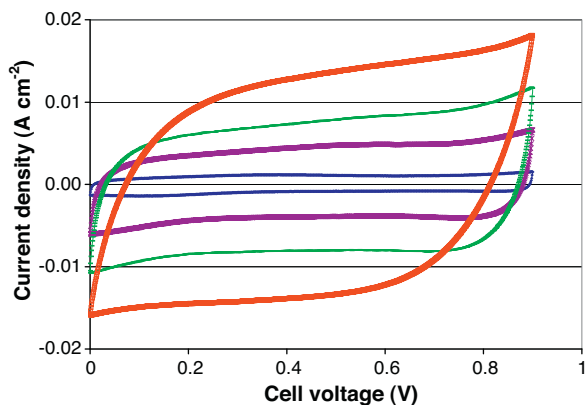


Fig. 2. CVs of a graphite electrode with SiWA- $\text{H}_3\text{PO}_4$ -PVA electrolyte EC cell at sweep rates of 1  $\text{V s}^{-1}$  (inner-most), 5  $\text{V s}^{-1}$ , 10  $\text{V s}^{-1}$ , and 20  $\text{V s}^{-1}$  (outer-most).

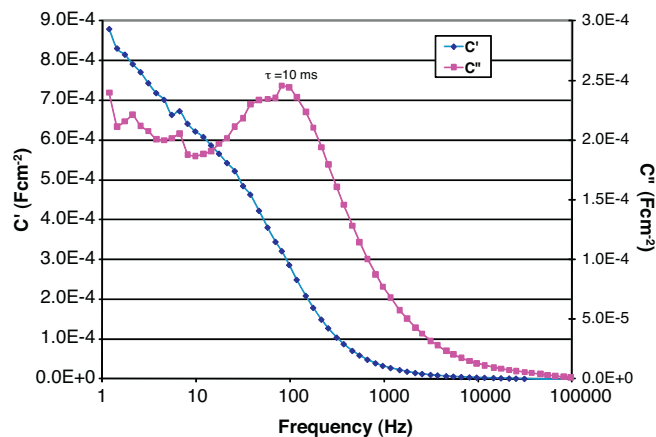


Fig. 3. Evolution of the real part ( $\blacklozenge$ ) and the imaginary part ( $\blacksquare$ ) of capacitance vs. frequency from a graphite/SiWA- $\text{H}_3\text{PO}_4$ -PVA cell.

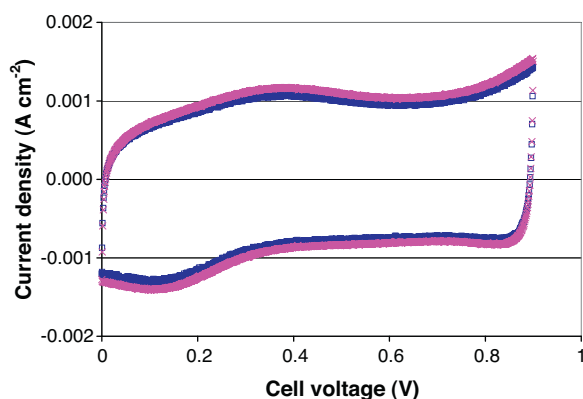


Fig. 4. CVs of a graphite electrode with SiWA–H<sub>3</sub>PO<sub>4</sub>–PVA electrolyte EC cell at 10th (symbol – x) and 7000th (symbol – □) cycle (sweep rates = 1 V s<sup>-1</sup>).

The  $C''$ /frequency curve in Fig. 3 exhibited its maximum at around 100 Hz. This maximum translates to a time constant of 10 ms for the solid electrolyte-based EC, even smaller than that of high performance OLC in organic electrolytes [1], providing additional strong evidence that the SiWA–H<sub>3</sub>PO<sub>4</sub>–PVA polymer electrolyte is capable of transporting protons at very high speed.

The equivalent series resistance (ESR) of the solid EC was extracted from the EIS spectra to calculate the ionic conductivity of the SiWA–H<sub>3</sub>PO<sub>4</sub>–PVA polymer electrolyte [13,14]. The average ESR of the cells was around  $0.85 \pm 0.05 \Omega \text{ cm}^2$ , reflecting the contributions of metal, graphite, and electrolyte. Subtracting the resistance from graphite (roughly  $0.2 \Omega \text{ cm}^2$ ) leaves an ionic conductivity of the solid SiWA–H<sub>3</sub>PO<sub>4</sub>–PVA film of  $8.0 \pm 0.1 \text{ mS cm}^{-1}$ . Compared to the ionic conductivity of solid SiWA ( $27 \text{ mS cm}^{-1}$  [15]), the conductivity of the solid polymer electrolyte was reasonable, as the electrolyte was primarily comprised of solid SiWA and an insulating polymer matrix with H<sub>3</sub>PO<sub>4</sub> as additive. Compared with other proton conductors such as Nafion at the same temperature and humidity [16], the  $8 \text{ mS cm}^{-1}$  conductivity of the solid SiWA–H<sub>3</sub>PO<sub>4</sub>–PVA electrolyte was at least 4 times better, although Nafion can achieve higher conductivity at high temperature and humidity. Further optimization of the solid SiWA–H<sub>3</sub>PO<sub>4</sub>–PVA film for increased conductivity is possible and is under way.

The solid EC was subjected to cycle life tests in order to evaluate the stability of the solid device. Fig. 4 shows two CV profiles obtained from such a capacitor at the 10th and 7000th cycle, respectively, using a voltage scan rate of  $1 \text{ V s}^{-1}$ . The almost overlapping voltammograms suggest good stability of the solid EC device, even with limited packaging (only sealed with tapes as shown in Fig. 1).

Thin and highly conductive electrodes with a readily accessible surface were described as a key for high rate delivery for OLC [1] and graphene [2], and this holds also true for this solid EC. At  $50 \mu\text{m}$  thickness, the proton conducting paths are relatively short and consistent within the polymer framework, which enabled the solid SiWA–H<sub>3</sub>PO<sub>4</sub>–PVA film to deliver charge at such high rates. Previous work on SiWA–PVA polymer electrolytes suggested proton hopping as the conduction mechanism [17]. This might also be the case in the SiWA–H<sub>3</sub>PO<sub>4</sub>–PVA polymer electrolyte, but further confirmation is needed. Traditionally, polymer

electrolytes are developed as free-standing membranes first and sandwiched between electrodes. This process makes it difficult to achieve good interfacial contact. We therefore reversed the manufacturing sequence; by applying the polymer precursor solution onto the electrodes first and then fusing these together, we ensured intimate contact with the electrodes so that interfacial resistance was relatively small [9]. The minimized interfacial contact resistance of the thin electrolyte could be key to achieving high rates and the small time constant of these solid EC devices.

The SiWA–H<sub>3</sub>PO<sub>4</sub>–PVA polymer electrolyte has shown very promising performance and properties as electrolyte for high-rate electrochemical capacitors. Even relying on mediocre electrodes such as graphite, we have achieved exceptional performance in terms of rate capability and frequency response that, to our knowledge, has never been demonstrated before for a solid polymer electrolyte. It will be very interesting to further push the envelope by (a) optimizing the electrolyte material compositions, and (b) incorporating high performance electrodes, in order to achieve high rate, high power density ECs with thin and flexible form factors that can potentially replace electrolytic capacitors.

#### 4. Conclusions

All-solid ECs with a SiWA–H<sub>3</sub>PO<sub>4</sub>–PVA polymer electrolyte on graphite electrodes have shown exceptionally high rate capability. The devices were able to charge and discharge at very high rate ( $20 \text{ V s}^{-1}$ ) and had a time constant of 10 ms. The performance of the solid EC devices was comparable to other reported high-rate devices in liquid electrolytes. A  $50 \mu\text{m}$  thin solid electrolyte cast on the electrodes which achieved an ionic conductivity of  $8 \text{ mS cm}^{-1}$  is believed to be the enabler of the demonstrated high-rate capability. This work suggests that solid polymer electrolytes can enable high rate and high power energy storage devices.

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