



## Short communication

## Bipolar porous polymeric frameworks for low-cost, high-power, long-life all-organic energy storage devices

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## HIGHLIGHTS

- Porous polymeric frameworks for affordable all-organic energy storage devices.
- All-organic energy storage devices having high-power density and long cycle life.
- A potential organic electrode towards high-performance organic energy storage device.

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## ABSTRACT

Organic-based energy storage devices are of great interests due to their high potential as affordable, high-performance energy storage devices. Especially, all-organic energy storage devices, where cathode and anode are constituted of organic compounds, could be an extremely affordable device expected to be applied to smart grids. Recent reports on bipolar porous polymeric frameworks (BPPFs) suggest very promising features of this new organic electrode group towards high-performance energy storage devices. Here, we studied an all-organic system using BPPFs for both anode and cathode parts. The formation of BPPFs was confirmed by Raman spectroscopy and N<sub>2</sub> isotherm measurements. The electrochemical properties of this all-organic energy storage device using BPPFs showed a high-power density of 1 kW kg<sup>−1</sup> based on the total mass of the BPPFs and a long cycle life of over 1000 times.

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## 1. Introduction

Electrical energy storage is a key technology for the successful introduction of renewable energy concept into our society [1–3]. Energy storage devices for stationary applications need to become extremely affordable and to have a long charge–discharge cycle life features that are more essential than having a higher energy density and a higher power density like in case of batteries for the use in vehicle [4]. It is an urgent need to develop energy storage devices which can be integrated into a grid combined with wind and solar power sources, and that can manage energy storage systems. From

this point of view, the discovery of organic materials exhibiting promising electrochemical properties are essential for the development of low-cost, and long-life batteries because of their abundance [5–8]. Moreover, lithium-free all-organic electrodes, which are constituted of only abundant materials, would be a leading candidate for an extremely affordable battery. Here, we show an all-organic battery provided by bipolar porous polymeric frameworks (BPPFs) using covalent triazine-based frameworks (CTFs) [9].

Recently, we have found BPPFs, i.e., porous polymeric frameworks constituted of benzene, as electron donor, and triazine rings, as electron acceptor, as a bipolar semiconducting organic material and have proposed a new energy storage principle using BPPFs [10,11]. Redox active organic materials are often categorized in carbonyl, radical, or organosulfur compounds [6]. However, BPPFs are aromatic compounds comparable to porous graphene [11]. Additional studies on redox-active aromatic compounds [12–14] could pave the way for the further development of organic

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energy storage devices. From the perspective of the industry side, BPPFs have potential for affordable and high-performance batteries, since it shows both high specific power and energy [10,11]. Suga et al. demonstrated a simple, symmetric all-organic battery with an intercalation mechanism by using a new bipolar radical polymer [15], and most recently all-organic batteries using bipolar polyparaphenylene were reported [16]. The features of BPPFs are a promising strategy for the further improvement of all-organic batteries. BPPFs have the following advantages for use as electrode material and in cell fabrication: (I) a high specific power due to rapid ion transport promoted by its porous nature, (II) a long battery life due to the high stability of the framework, (III) a simple, safe and low-cost configuration by using the same organic materials for the cathode and the anode. Hence, the BPPFs for both cathode and anode provide a safe, high-performance and long-life all-organic battery.

Here, we show results for developing all-organic Li- and Na-batteries using BPPFs. The all-organic Li-batteries can provide a specific energy of  $34 \text{ Wh kg}^{-1}$  and a specific power of  $1 \text{ kW kg}^{-1}$  based on the total mass of the BPPF with a cycle-life of over 1000 times. The all-organic Na-batteries also showed electrochemical properties which are comparable to the all-organic Li-batteries.

## 2. Experimental

The BPPFs were synthesized by heating a mixture of *p*-dicyanobenzene and zinc chloride in quartz ampules at  $400^\circ\text{C}$  for 40 h [9]. The obtained samples were washed with 1 M HCl and distilled water for several times. After drying, we used this material as BPPFs without further treatments.

The following measurements were performed to characterize BPPFs. Raman spectroscopy measurements were carried out by using a Ventuno (NSR-1000DT, JASCO) with a laser excitation of 632.8 nm from a He–Ne laser. Powder X-ray diffraction (XRD) measurements were done on a PANalytical X'Pert PRO diffractometer using  $\text{Cu K}\alpha_1$  radiation. Nitrogen physisorption measurements were conducted at 77 K up to 1 bar using a Quantachrome Autosorb 1C apparatus.

Electrodes were made by mixing the active material (70 wt.%), carbon (carbon black; 20 wt.%), and a binder (carboxyl methyl cellulose; 10 wt.%) using Al current collectors. We assembled the cells in a purge-type dry glove box filled with high purity Ar gas and tested them on a multichannel potentiostatic–galvanostatic system (SD-8, Hokuto-denko). 1 M  $\text{NaClO}_4$  in propylene carbonate (PC) or 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio 1:1 (Kishida Chemicals) were used as electrolytes in a two-electrode-type Swagelok cell as test cell. The specific energy  $E$  ( $\text{Wh kg}^{-1}$ ) can be calculated by  $E = \int_0^{t_{\text{cut}}} (I_0/m)V(t)dt$  where  $t_{\text{cut}}$  (h) is the discharge time,  $I_0$  (A) is the constant current,  $m$  (kg) is a mass of the active material at a single electrode, and  $V(t)$  is a time-dependent voltage in the dimension of  $V$ . Specific power  $P$  ( $\text{W kg}^{-1}$ ) can be calculated by  $P = E/t_{\text{cut}}$ . We show a Ragone plot with the total mass of BPPFs in a cell. To measure the electrochemical properties, the cells were charged up to 1.75 V and discharged until  $-1.75 \text{ V}$ . Thus, the cells show a cell voltage ranging between 0 and 3.5 V.

## 3. Results and discussion

The BPPFs have been synthesized following already reported procedures [9–11] and characterized by nitrogen physisorption and Raman spectroscopy, and X-ray diffraction (XRD). The Raman spectroscopy measurement reveals the formation of a short-range ordered two-dimensional (2D) graphitic network in the BPPF by showing relatively strong *D* and *G* peaks at around  $1300 \text{ cm}^{-1}$  and

$1600 \text{ cm}^{-1}$ , respectively (Fig. 1a) [11]. The nitrogen physisorption measurements show a high specific surface area of over  $1000 \text{ m}^2 \text{ g}^{-1}$  and a typical isotherm shape suggesting a microporous structure. The physisorption measurements confirm the successful formation of a porous network (Fig. 1b). The broad XRD pattern suggests that the BPPF is comprised of non-coplanar two-dimensional (2D) organic frameworks made up of aromatic rings like hard carbon (Fig. 1c) [17]. These results agree well with previous studies on the characterization of porous polymeric frameworks [9–11].

The fundamental electrochemical characteristics of the all-organic Li-batteries using BPPF are studied by investigating the charge–discharge properties. Charge–discharge profiles at various current densities from  $0.05 \text{ A g}^{-1}$  to  $2 \text{ A g}^{-1}$  in the working voltage range of 0.0–3.5 V are shown in Fig. 2a. At a constant current density of  $0.05 \text{ A g}^{-1}$ , the all-polymer system shows a specific capacity of  $\sim 65 \text{ mA h g}^{-1}$  based on the mass of the BPPF at a single electrode with a sloping voltage profile. If we calculate the amount of the coordinated  $\text{Li}^+$  into the BPPF ( $=x$  in Eqs. (1)–(3)), we obtain  $x \sim 1.86 \text{ mol}$ . The unit is defined by trimerized *p*-dicyanobenzene, which has a molecular weight of  $384.09 \text{ g mol}^{-1}$ . This result also suggests that our battery system uses 1.86 mol of the electrolyte for 1 mol of the BPPF at the current density of  $0.05 \text{ A g}^{-1}$  (Eq. (3)).

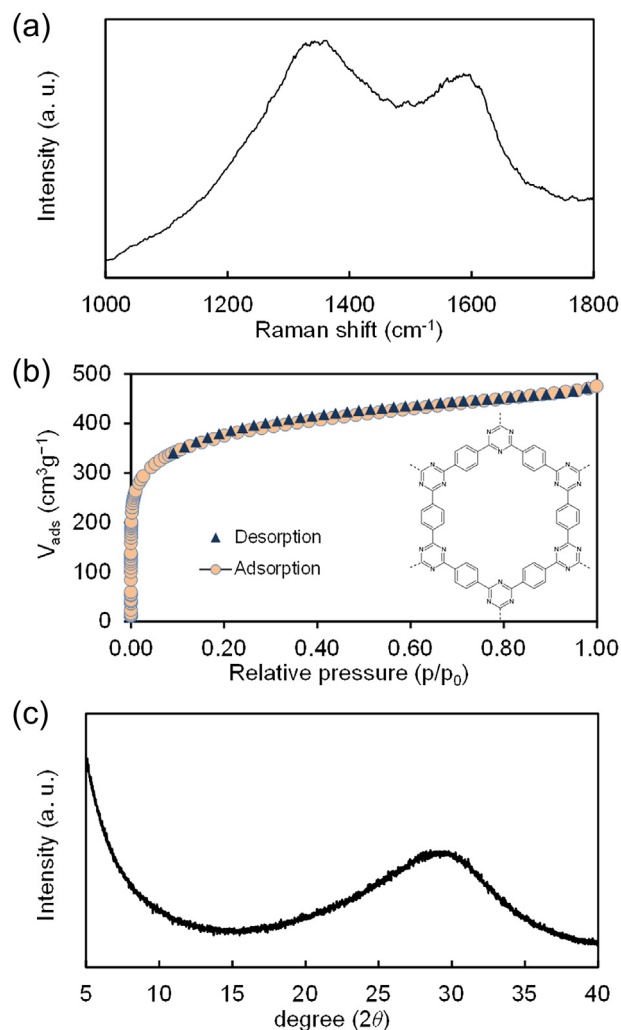


Fig. 1. Characterization of the BPPF. (a) Raman spectrum, (b)  $\text{N}_2$  physisorption isotherm with a schematic illustration of the BPPF, and (c) XRD pattern.

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