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COMMUNICATION

Non-corrosive, Low-Toxicity Gel-based Microbattery from Organic and Organometallic Molecules†

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Microbatteries with safe, non-corrosive electrolyte chemistries can have an immediate positive impact on modern life applications, such as ingestible electronic pills and system-on-chip bioelectronics. Here a safe, non-corrosive and non-flammable microbattery is reported. A natural agarose hydrogel is the electrolyte-supporting matrix, and organic and organometallic molecules are the redox-active species. This device can safely meet the needs of ingestible medical microdevices as a primary battery. Additionally, this redox gel system can be used as a secondary battery for on-chip electronics applications, potentially enabling safe and cost-effective small-scale energy storage.

The current and future generations of micro- and nano-electronics include applications requiring a safe microbattery technology not available today. There is an increasing demand for microbatteries for applications such as environmental sensors, ingestible sensors (e-medical),[1–3] wireless communication devices,[4] autonomous microelectromechanical systems,[5] the internet of things,[6,7] sensor fusion,[8,9] wearable devices[7,9,10] and quantum computers.[11] Nanomaterials-based systems-on-a-chip have been specifically designed to be directly attached to a battery featuring ultra-low-power output, e.g. operation at near-threshold voltages of 0.6 V with a few microamperes of current.[6] Due to the challenges of miniaturizing energy storage technologies, microchips typically use power supplied off-chip, limiting their autonomy, or use microbatteries with corrosive electrolytes, restricting their range of application.[1–4,12] Despite the fast-paced advances in microelectronics miniaturization[3,6] and integration,[6] there has been relatively slow progress in the miniaturization of power sources.

Here we report the development of a microbattery based on redox-gel active components that are non-corrosive, low-toxicity and non-flammable in contact with air or water. The gel is composed entirely of Earth-abundant elements and is safe to use in medical devices. We report the ability of organic redox active molecules to be incorporated into the hydrogel to form a redox-active gel (Figure 1a) that acts as a stable, non-corrosive electrolyte at pH 7.0 in the body environment. This system can help to resolve corrosion and safety concerns of microbattery chemistries currently available in the market, such as lithium ion[1,3] and silver-oxide.[3]

As illustrated in Figure 1b the gel-based microbattery is composed of four parts: hydrogel-based negative side (gel-N), hydrogel-based positive side (gel-P), two flexible carbon fiber (FCF) microelectrodes, and a separator. Both gel-N and gel-P are composed of agarose, KCl, water, and a redox molecule. Bis(3-trimethylammonio) propyl viologen tetrachloride (BTMAP-Vi) and bis((3-trimethylammonio)propyl)ferrocene (BTMAP-Fc) were used in the gel-N and gel-P, respectively.[13] The redox active molecules were synthetized and purified as reported by Beh et al.[13] These molecules are well suited for gel batteries because both BTMAP-Fc and BTMAP-Vi show reversible and stable cyclic voltammetry behavior on FCF electrodes in 1.0 M KCl at pH 7.0 (Figure 1c). Based on voltammetry, the theoretical cell voltage using these two molecules is expected to be approximately 0.75 V (Figure 1c). The hydrogels are attractive due their structure and morphology, allowing diffusion of the redox active species, while maintaining predetermined shapes, as shown in Figure 1b.

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†Electronic Supplementary Information (ESI) available: Synthesis of BTMAP-Vi and BTMAP-Fc, cyclic voltammetry, hydrogel preparation and cost, microbattery assembly and measurements, and Capability of the microbattery to hold its charge. See DOI: 10.1039/x0xx00000x

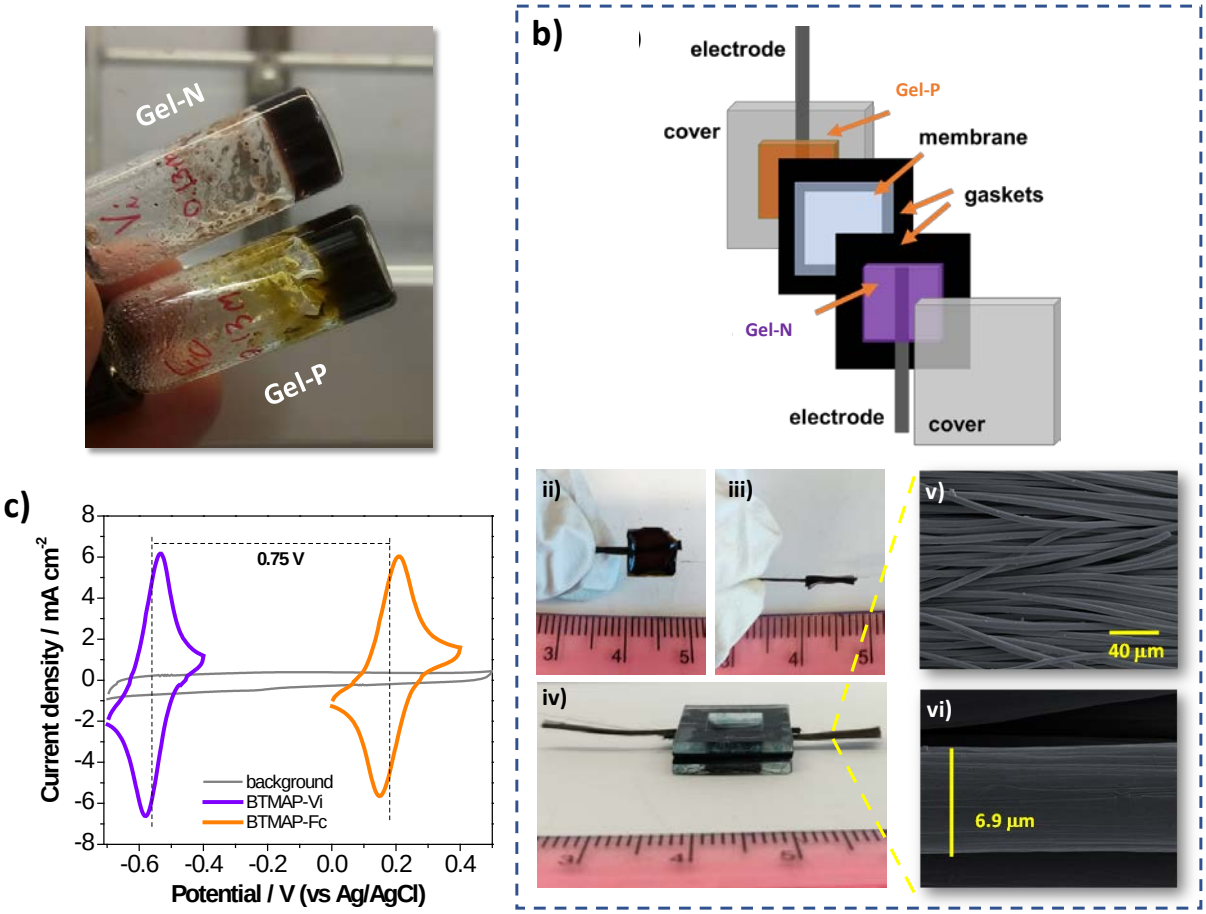

Figure 1. (a) Gels containing agarose, KCl, and BTMAP-Vi (gel-N) and BTMAP-Fc (gel-P). (b) Scheme of the microbattery (i), photos of the gel on FCF electrode (ii and iii) and of the device (iv), and scanning electron microscopic images of FCF at different magnifications (v and vi). (c) Cyclic voltammograms of BTMAP-Vi and BTMAP-Fc and background recorded on FCF microelectrodes. Conditions: 2.0 mM of BTMAP-Vi and BTMAP-Fc in 1.0 M KCl, 50 mV s^{-1}, Ar atmosphere. The expected cell potential is indicated.

Agarose was chosen as the inert electrolyte support because it is widely available, low cost, mechanically versatile, safe for human consumption, stable at body temperature and prepared from naturally sourced polymers. One dollar's worth of agarose can be used to produce 770 batteries with 100 µL of gel filling each electrode compartment (see the calculation in the ESI†). The redox-gel was prepared using redox-active compounds (BTMAP-Fc or BTMAP-Vi) dissolved in an agarose gel. BTMAP-Fc and BTMPA-Vi exhibit relatively high diffusion coefficients in the hydrogel electrolyte, 2.4×10^{-6} cm^2 s^{-1} for BTMAP-Fc and 2.8×10^{-6} cm^2 s^{-1}, for BTMAP-Vi, as measured by PFGE-^{1}H-NMR (see ESI†). These values are 20%-27% lower than those for the same molecules measured at the same concentration in a KCl solution, (3.29×10^{-6} cm^2 s^{-1} for BTMAP-Fc and 3.45×10^{-6} cm^2 s^{-1} for BMAP-Vi).[13] Our measurements are consistent with a previous report.[14] Using the gel composition described in the ESI†, the redox-active molecules can readily diffuse through the hydrogel pores. In order to prevent redox-active molecule crossover, we inserted an anion-conducting membrane as a separator between the electrolyte gels, producing the cell shown in Figure 1b. The concentration of redox molecules in each gel was 0.50 M and a Selemion DSV anion exchange membrane was used as the separator.

Figure 2 shows the performance of these microbatteries. First, the cell was charged at 1.10 V for 30 min (to reach approximately 20% state of charge, SOC), and then a discharge curve was recorded at a constant current density of 20 µA cm^{-2} (Figure 2a). This curve indicates that the microbattery can be discharged steadily over 100 h and provides a volumetric capacity of 0.021 µAh cm^{-2} $µm^{-1}$. The microbattery can hold its charge for at least 48 h when no current is drained (Figure S3 of the ESI†). The power curve in terms of current and power densities are shown in Figure 2b. From this curve, we obtained an OCV of approximately 0.70 V and a maximum volumetric power density of 3.4 µW cm^{-2} $µm^{-1}$ at 8.7 µA cm^{-2} $µm^{-1}$ (20% SOC).

In order to evaluate the volumetric capacity, the microbattery was charged and discharged at a constant voltage of 1.10 V (to 92% SOC) and 0.30 V, respectively, as illustrated in Figure 2c. The experimental volumetric capacity was calculated to be 1.42 mC cm^{-2} $µm^{-1}$, which corresponds to 0.39 µAh cm^{-2} $µm^{-1}$ (or 3.94 µAh $µL^{-1}$), giving a total capacity of 0.79 mAh. This total capacity is lower than those measured for commercial lithium and silver-oxide microbatteries, 5 mAh and 80 mAh, respectively.[3] Nevertheless, these redox-gel microbatteries can power an ingestible sensor, requiring 4.69 µA,[1] for 168 h, and also other medical microdevices, as shown in Table 1.

Cycling tests were performed to evaluate the potential use of these redox-gel microbattery as a secondary battery, (Figures 2d-e). The coulombic efficiency for the galvanostatic cycling at 40 mA cm^{-2} ranges between 94% and 97% during 13 h, corresponding to 100 cycles. The cycles are highly reproducible and indicate good electrochemical stability and a highly efficient storage system.

within ingestible wireless endoscopy capsules,[15] or probiotic biosensors to monitor gastrointestinal health.[1] In contrast with the low toxicity and non-corrosive nature of the microbatteries described here, accidental leakage of the electrolyte solution within alkaline silver-oxide disk batteries, can result in damage and in perforation of the esophagus if not removed surgically.[16] Similarly, a lithium microbattery[1] has a risk of

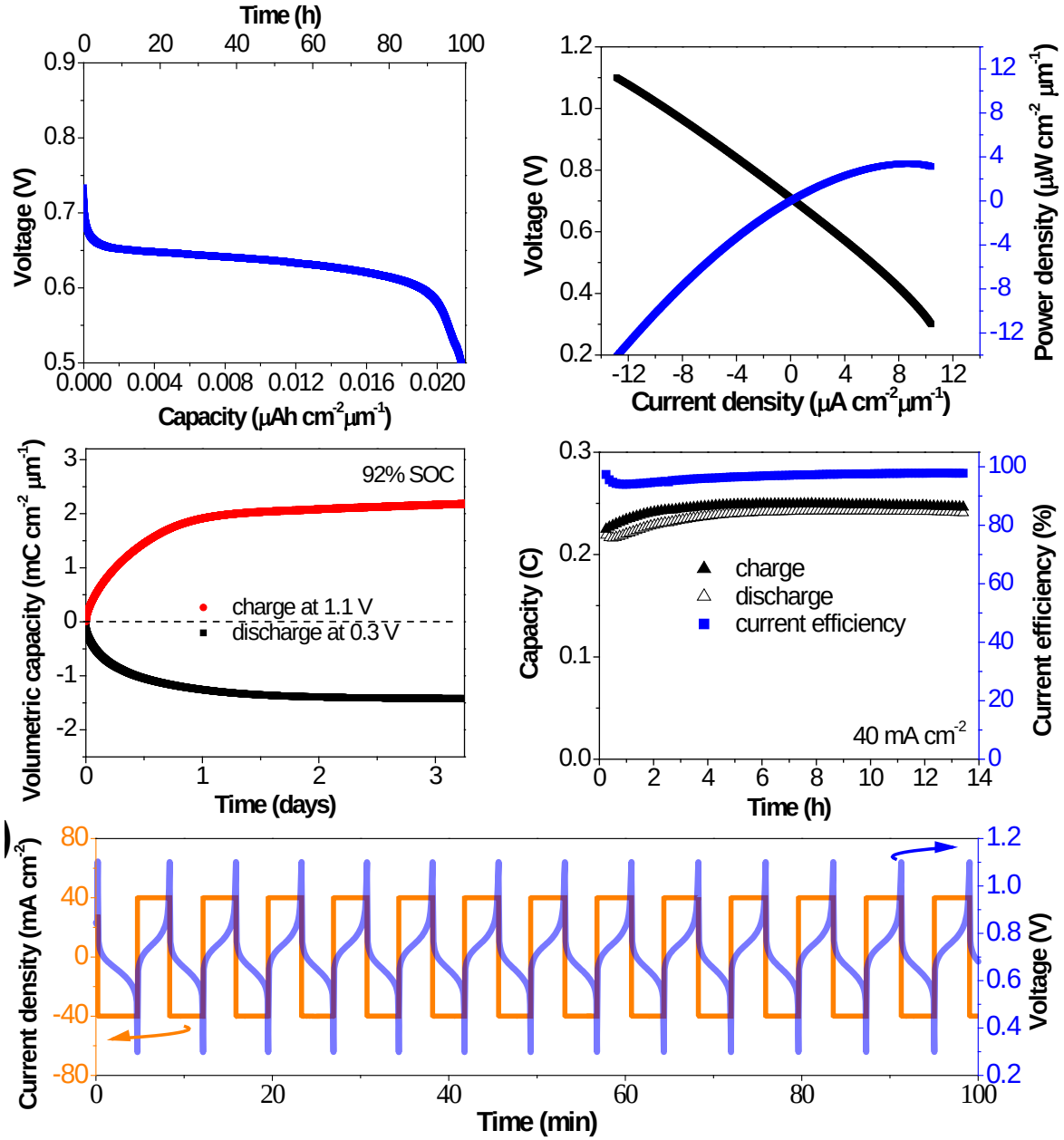

Figure 2. (a) Voltage vs time for galvanostatic discharge at 40 μA cm^{-2}. (b) Cell voltage and power density versus current density at 20% SOC. (c) Charge and discharge curves at 1.10 V and 0.30 V, respectively. (d) Capacity and current efficiency values of 100 cycles. (e) Representative voltage and current density vs. time curves during 100 charging-discharging cycles at 40 mA cm^{-2}. All data here were collected at room temperature, under N_2 atmosphere, and using gel containing 1.0 M KCl and 0.50 M BTMAP-Fc on the positive side and gel containing 1.0 M KCl and 0.50 M BTMAP-Vi on the negative side, and Selemion DSV as anion exchange membrane.

The size and non-corrosive composition of these redox-gel microbatteries constitute attractive advantages compared to typical lithium manganese button-cell and alkaline silver-oxide disk batteries.[1] The cells described in this work can be encased in volumes suitable to replace the traditional power sources

burning in air or releasing a strongly corrosive solution and flammable hydrogen when in contact with water causing severe injuries.[17] The amounts of redox active molecules used in our redox-gel microbatteries are too small to produce harmful effects on humans. In terms of toxicity, viologens similar to those used in our battery have an oral LD 50 (lethal

dose) of 126 mg kg^{-1} for rats, 22 mg kg^{-1} for pigs, and 50 mg kg^{-1} for monkeys. The lethal dose in humans is estimated to be about 7,000 mg.[18] Our redox-gel microbatteries use a total of 29 mg of viologen derivative, which is 240 times smaller. Ferrocene derivatives show LD 50 of 25 mg kg^{-1} for rats and 50 mg kg^{-1} for mice.[19] Considering our microbattery contains 23 mg of ferrocene derivative, no harmful effect is expected for humans. In the event of accidental rupture while in the digestive system, this viologen/ferrocene-based microbattery poses a lower risk than the commercially available alternatives.

Table 1. Examples of low-power medical microdevices.

System	Operation Current (µA* or µA MHz^{-1}**)	Operation Voltage (V)	Power consumption (nW)	Ref.
Ingestible biosensor to monitor gastrointestinal health	4.69*	n/a	n/a	1
Integrated system-on-chip for Internet of Things, sensor fusion, wearables, and e-medical applications	9**	0.5 - 0.6	n/a	6
Integrated circuit for miniature sensor nodes	n/a	0.6	3	20
Temperature sensor for low power wireless sensor nodes	n/a	0.075	71	21
Sensing, controlling and signal processing circuit for implantable CMOS	n/a	n/a	921	22

In summary, we describe a gel-based microbattery for use as a safe primary power source for several ingestible and implantable medical microdevices (Table 1). This gel-based approach can be expanded to include other redox molecules (e.g. natural product-based redox molecules) and can be further miniaturized. The combination of hydrogel and redox-active organic and organic-metallic molecules could represent an attractive strategy for developing non-toxic rechargeable microbatteries.

Conflicts of interest

There are no conflicts to declare.

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