

Contents lists available at ScienceDirect

Journal of Power Sources



journal homepage: www.elsevier.com/locate/jpowsour

All-in-one flexible asymmetric supercapacitor with high mechanical durability achieved by controllable interfacial molecular level entanglement

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- A controllable interfacial molecular level entanglement strategy is proposed to develop all-in-one FASCs.
- The interfacial molecular level entanglement is controlled by solvent induced re-entanglement and alcoholysis of matrix.
- The all-in-one FASCs achieve unprecedented mechanical durability exceeding 10 000 bending and twisting cycles.

ARTICLE INFO

Keywords: All-in-one Interfacial molecular entanglement Interfacial structure Flexible supercapacitor Mechanical durability



ABSTRACT

Currently, all-in-one flexible supercapacitors have achieved great attainment, but their intrinsic weak physical interfacial interfacial interfacial fatigue debonding during violent and long-term deformations. Herein, a controllable interfacial molecular level entanglement strategy (CIMES) is proposed to design and build such highly flexible and mechanical robust asymmetric supercapacitors (FASCs) with all-in-one configurations. The controllable interfacial molecular level entanglement is achieved by controlled solvent induced re-entanglement and alcoholysis of the electrolyte homogeneous matrix - ethylene vinyl alcohol (EVOH) copolymer. With the generated electrolyte-philic and electrolyte-proof matrix and all-in-one configuration of

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https://doi.org/10.1016/j.jpowsour.2024.235491

Received 22 July 2024; Received in revised form 10 September 2024; Accepted 17 September 2024 Available online 24 September 2024 0378-7753/© 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

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anode/electrolyte/cathode used in the FASCs, low interfacial charge transfer resistances, good mechanical properties, and high interfacial peeling strength are achieved simultaneously. Thus, the all-in-one FASCs exhibit a much higher areal capacitance, superior cyclic stability, and unprecedented mechanical durability with capacitance retention of 100.6 % and 100.7 % exceeding 10 000 bending and twisting cycles respectively. Furthermore, the all-in-one FASCs are demonstrated to work under bending, twisting, and even folding conditions. Those findings can provide a new platform on the design of all-in-one configurations for the FASCs with superior mechanical durability, highly desired for many flexible devices such as geotextiles.

1. Introduction

To meet the power supply demands of rapidly growing flexible and wearable electronic equipment, next-generation energy storage devices need to be designed with lightweight, miniaturization and flexibility [1-4]. Currently, flexible energy storage devices mainly include flexible rechargeable batteries and flexible supercapacitors (FSCs) [5-7]. Among them, flexible supercapacitors have generated considerable interests because of their competitive advantages of high security, high power density and long cyclic life [8,9]. In addition to the practical requirements of steady-state output under various deformation condition such as bending, twisting and folding, even repetitive deformation hundreds of times, FSCs are also expected to exhibit with high durability to violent and long-term deformation [10,11]. Indeed, while much work has been done in this regard [12], the assembled FSCs exhibit poor mechanical durability below expectation [13,14], though high mechanical durability has been achieved for individual flexible anode and cathode. The performances gap come from that in the laminated configuration comprising stacked layers of flexible anode materials/hydrogel polymer electrolyte/flexible cathode materials (anode/electrolyte/cathode), the interfacial interactions still belongs to weak physical interactions among the anode/electrolyte/cathode depend on [15,16]. Thus, during repetitive or violent deformation, it is inevitable that relative displacement and delamination would happen among the conventional anode/electrolyte/cathode assembly approach, resulting in the rapid performance degradation and ultimate failure of flexible supercapacitors [17-19].

Addressing the challenge of FSCs using the conventional assemble (laminated) strategy, several strategies have been proposed to enhance interfacial interactions for the entire device integration [20]. This comes to the all-in-one strategy, where all the anode/electrolyte/cathode are integrated into all-in-one configuration, avoiding the conventional sandwich approach [21]. The main point of this direct strategy is to construct the cathode/electrolyte/anode into one single body [22]. One of such approaches is to use the separators or polymer electrolytes as the flexible supports and integrate the cathode and anode materials on both sides directly using strong bonding force or even chemical bonding [23]. For instance, using chemical and electrochemical deposition of Au and polypyrrole-graphene oxide, Wang et al. fabricated the separator-polypropylene film based all-in-one flexible symmetrical supercapacitors (FSSCs) with capacitance retention of 80 % after bending deformations for 5000 times [24]. Wang et al. proposed a surface polymerization on polymer electrolyte technique to fabricate all-in-one FSSCs based on crosslinked polyvinyl alcohol electrolyte, which delivered slight capacitance decay after bending deformations for 1000 times [25]. An alternative strategy is to integrate cathode/electrolyte/anode layer by layer though compression bonding. Du et al. reported a step-by-step vacuum filtration method to fabricate all-in-one FSSCs with small changes to the capacitance at bending deformation angles of 90° and 180° [26]. With these great developments, there are still some issues, such as limited mechanical durability caused due to weak physical interfacial interactions in nature [27,28]. This inevitably leads to the interfacial fatigue debonding of these reported all-in-one configurations during violent and long-term deformations. Thus, there are significant challenges to construct intrinsic strong interfacial interactions in all-in-one configurations for flexible supercapacitors.

In this work, we propose a strategy using solvent induced controllable interfacial molecular level entanglement (CIMES) to achieve intrinsic and strong interfacial interactions in the all-in-one configuration for flexible asymmetric supercapacitors (FASCs). The key lies in the introduction of both electrolyte-philic and electrolyte-proof ethylene vinyl alcohol (EVOH) copolymers as the homogeneous matrixes for anode/electrolyte/cathode, which are derived from the alcoholysis of ethylene vinyl acetate (EVA) copolymers. Under the inducement of selective solvent, EVA molecular chains on the surface get reentanglement at the interface of anode/electrolyte/cathode, followed by control of alcoholysis degree to construct all-in-one EVOH-MWNT/ EVOH/EVOH-MWNT, in which multiwalled carbon nanotubes (MWNT) serve as conductive network skeletons. After electrodeposition of electroactive FeOOH and MnO₂ on the opposite sides respectively, EVOH-MWNT-FeOOH/EVOH/EVOH-MWNT-MnO2 all-in-one FASCs are achieved with seamlessly integrated interfacial (chemical bonding) structures, leading to excellent mechanical properties and high interfacial peeling strength. With the unique and strong interface bonded structures, the all-in-one FASCs exhibit low interfacial resistance, high areal capacitance of 19.3 mF cm⁻² at 5 mV s⁻¹ and also superb cyclic stability with capacitance retention of 103.5 % after 30 000 charge-discharge cycles. Significantly, the interfacial resistances remain the same under an original flat state, bending and even twisting deformations to various angles. Hence the capacitance retention reaches to 100.6 % and 100.7 % after bending and twisting deformations for 10 000 cycles respectively, surpassing most of the previous reports. With this excellent performance, it is expected that this all-in-one FASCs should have high potential for various flexible devices such as wearable sensors, flexible displays, and artificial skins, which require stable and robust power supply under the seneoris bending, twisting and even folding deformations.

2. Experimental

2.1. Sample preparation

Preparation of EVA membrane: EVA with VA content of 70 wt% (The Polyolefin Company (Singapore) Pte Ltd) was dissolved in moderate xylol solvent (General-Reagent) and poured into a Teflon open container. After solvent evaporation, EVA membrane was obtained through mechanical disengagement.

Preparation of EVA-MWNT membrane: MWNT (Nanocyl NC7000 series) was dispersed in moderate xylol solvent with continuous ultrasonic and stirring treatment for half an hour, followed by introduction of EVA at a mass ratio of 2:8 to MWNT through continuous stirring. Subsequently, the derived EVA-MWNT solution was poured into a Teflon open container. After solvent evaporation, EVA-MWNT membrane was obtained through mechanical disengagement.

2.2. Device assembly

Assembly of EMFe/E/EMMn all-in-one FASCs: First, the as-prepared EVA membranes precut in the size of 20×10 mm and EVA-MWNT membranes precut in the size of 20×10 mm for working area with the addition of 5×8 mm for connection of external circuits were soaked in solvent free, poor solvent alcohol (General-Reagent) and good solvent



Fig. 1. (a) Schematic illustration for fabrication of EMFe/E/EMMn all-in-one FASCs. Digital photos of EMFe/E/EMMn all-in-one FASCs in the (b) flat, (c) bending, (d) twisting states. Cross-sectional optical images of EMFe/E/EMMn all-in-one FASCs in the (e) flat, (f) bending, (g) twisting states. (h) Cross-sectional SEM images, (i) EDX images and (j) high-resolution SEM images of EMFe/E/EMMn all-in-one FASCs.

xylol to form various states of disentanglement for external EVA molecular chains. Subsequently, two EVA-MWNT membranes and one EVA membrane were taken out and assembled in sequence of EVA-MWNT/ EVA/EVA-MWNT, followed by thermocompression to facilitate molecular chains reentanglement at the two boundaries of EVA-MWNT/EVA and solvent evaporation for fixation of entangled states. After solvent evaporation, an all-in-one configuration EVA-MWNT/EVA/EVA-MWNT was obtained. Third, the all-in-one configuration EVA-MWNT/EVA/ EVA-MWNT was treated with a series of NaOH concentration (1.5, 3.0 and 4.5 M) of water/alcohol mixture in given volume ratios (10/0, 9/1 and 8/2) at the reaction temperature of 80 °C for several hours (0, 1, 3, 6 and 9 h) alcoholysis of EVA to achieve the all-in-one configuration EVOH-MWNT/EVOH/EVOH-MWNT with various levels interfacial molecular chain entanglement. Fourthly, using one side EVOH-MWNT of the EVOH-MWNT/EVOH/EVOH-MWNT as working electrode, a Pt electrode as counter electrode, and a saturated calomel electrode (SCE) as reference electrode, FeOOH was electrodeposited in the working area of EVOH-MWNT with a mixture of aqueous electrolyte containing 0.1 M $Fe(NH_4)_2(SO_4)_2.6H_2O$ (General-Reagent), 0.2 M CH₃COONa (General-Reagent) and 0.1 M Na_2SO_4 (General-Reagent). The constant current electrodeposition was conducted on an electrochemical workstation (Wuhan Corrtest Instruments Corp. Ltd., CS2150H) with various current of 0.05, 0.1, 0.25 and 0.5 mA, and various times of 15, 30, 45 and 60 s. Similarly, using another side EVOH-MWNT of the EVOH-MWNT/ EVOH/EVOH-MWNT as working electrode, a Pt electrode as counter electrode, and a SCE as reference electrode, MnO₂ was electrodeposited in the working area of EVOH-MWNT with a mixture of aqueous electrolyte containing 0.1 M Mn(CH₃COO)₂.4H₂O (General-Reagent) and

0.1 M Na₂SO₄. The constant current electrodeposition was conducted with various current of 0.25, 0.5, 0.75, 1 and 1.5 mA, and various times of 15, 30 and 45s. The derived EMFe/E/EMMn was washed with distilled water, and dried in a vacuum oven at 60 °C. Finally, after saturated adsorption of 1M LiCl (General-Reagent) aqueous solution, the EMFe/E/EMMn was packaged in a plastic sealing bag with carbon cloth as external conductors to obtain the EMFe/E/EMMn all-in-one FASCs.

Assembly of EMFe/PVA/EMMn laminated FASCs: First, the precut EVA-MWNT membranes were alcoholyzed with 3.0M NaOH concentration of water/alcohol mixture in given volume ratios of 9/1 at the reaction temperature of 80 °C for 3 h to obtain EVOH-MWNT membranes. Subsequently, FeOOH was electrodeposited in the working area of EVOH-MWNT using the same method mentioned above with the optimized electrodeposition current of 0.25 mA and time of 45s to obtain EMFe anode. MnO₂ was electrodeposited in the working area of another EVOH-MWNT using the same method mentioned above with the optimized electrodeposition current of 1.0 mA and time of 30s to obtain EMMn cathode. Finally, using PVA/LiCl hydrogel electrolyte prepared by dissolving 2.1 g LiCl and 1.0 g PVA (General-Reagent) in 10 mL deionized water in between, the EMMn cathode and EMFe anode were assembled and packaged into the EMFe/PVA/EMMn laminated FASCs like those above.

2.3. Material characterizations

The interfacial structures were characterized by ultra-depth-of-field three-dimensional microscope (Keyence, VHX-7000) and SEM (Zeiss Sigma 500). The microstructures were observed by SEM. XRD spectra were obtained on an X-ray diffractometer (Rigaku Ultima IV) with Cu radiation. XPS spectra were recorded on an X-ray Photoelectron Spectroscopy (Thermo Scientific Nexsa) equipped with a mono Al Ka X-ray radiation. The water contact angles were measured by a DSA25 instrument (KRUSS). The FTIR spectra were obtained on an infrared spectrometer (Thermo Scientific iN10). The mechanical properties were tested on a testing machine (Instron, Legend 2366) according to GBT 528. The bending and twisting tests were conducted on a flexible electronic tester (Shanghai Mifang Electronic Technology Co. Ltd., FT2000).

2.4. Electrochemical measurements

The CV tests of EMFe anode with potential range of -0.8-0 V and EMMn cathode with potential range of 0-0.8 V were carried out in a three-electrode system equipped with a Pt electrode as counter electrode, and a saturated calomel electrode (SCE) as reference electrode, 1M LiCl aqueous solution as electrolyte using a CS2150H electrochemical workstation (Wuhan Corrtest Instruments Corp. Ltd.). For the EMFe/E/EMMn all-in-one FASCs, the CV curves from 5 to 100 mV s^{-1} and GCD curves from 0.5 to 4 mA $\rm cm^{-2}$ with potential range of 0–1.6 V were collected by a CS2150H electrochemical workstation. The EIS analyses in the frequency range of 1-100 kHz at a sinusoidal amplitude of 5 mV and zero V DC bias were conducted on a CHI660E electrochemical workstation (Chenhua, Shanghai) with data points of 12 per decade of frequency. All the electrochemical tests were performed at room temperature. The capacitance retention in the bending and twisting tests was calculated from the CV curves at 50 mV s^{-1} on a CS2150H electrochemical workstation.

3. Results and discussion

The main priority of CIMES is to select a polymer suitable for the homogeneous matrix. Taking account of the ion transport requirement of the electrolyte matrix, the polymer should have an electrolyte-philic characteristic in favor of adsorption aqueous electrolyte and thus fast ion transport, but also has an electrolyte-proof characteristic to prevent the interfacial molecular chains from disentanglement and dissolution with long-term infiltration in the aqueous electrolyte. EVOH is a kind of random copolymer alcoholyzed from EVA, containing ethylene structural units, vinyl alcohol structural units and residual vinyl acetate structural units (Fig. S1) [29]. The hydrophobic ethylene and vinyl acetate structural units shoulder the responsibility of electrolyte-proof characteristic, while the vinyl alcohol structural units bearing strongly hydrophilic hydroxyl groups show electrolyte-philic ability. Furthermore, the equilibrium between electrolyte-philic and electrolyte-proof characteristics of EVOH can be achieved by controlled alcoholysis of EVA. Thus, EVOH are alcoholyzed from EVA to serve as the homogeneous matrixes. The disentanglement of surface molecular chains (surface disentanglement) followed by re-entanglement at the interface (interfacial re-entanglement) of the anode/electrolyte/cathode is of secondary concern for CIMES, which can be driven by swelling behavior using good solvent. Accordingly, the fabrication of all-in-one FASCs is schematically illustrated in Fig. 1a. First, the precut EVA-MWNT and EVA membranes (Fig. S2) prepared by a scalable solution-casting method soaked in the xylene to swell surface molecular chains for disentanglement. After removal from the xylene, two EVA-MWNT membranes and one EVA membrane were assembled into a sandwich-like EVA-MWNT/EVA/EVA-MWNT, which was thermal-pressed to facilitate molecular chains re-entanglement at the two interfaces of EVA-MWNT/EVA and solvent evaporation for fixation of entangled states, thereby achieving an all-in-one EVA-MWNT/E-VA/EVA-MWNT. Subsequently, the EVA-MWNT/EVA/EVA-MWNT was treated with a series of NaOH concentration of water/alcohol mixture in given volume ratios at the reaction temperature of 80 °C for several alcoholysis of EVA hours to achieve the EVOH-MWNT/EVOH/EVOH-MWNT (EM/E/EM). Finally, taking advantage of the conductive characteristic of EM on the opposite sides, FeOOH and MnO2 were electrodeposited successively to fabricate EVOH-MWNT-FeOOH/EVOH/EVOH-MWNT-MnO2 (EMFe/E/EMMn) all-in-one FASCs.

As shown in Fig. 1b, the EMFe/E/EMMn all-in-one FASCs in the flat state are made up of three parts of anode/electrolyte/cathode, whose overlapping region is the working area with the size of 20 \times 10 cm in rectangle. There is no obvious crack or delamination when the EMFe/E/ EMMn all-in-one FASCs are arbitrarily bent (Fig. 1c) or twisted (Fig. 1d). To get insight into the changes to anode/electrolyte/cathode configuration at the microscopic level, ultra-depth-of field three-dimensional microscopes were adopted to survey the cross-section of EMFe/E/ EMMn all-in-one FASCs in the flat, bending and twisting states. Fig. 1e shows the cross-sectional optical image of EMFe/E/EMMn all-in-one FASCs in the flat state. It can be observed an integrated configuration without any gap and interface. According to the morphological difference, the two similar EMFe anode and EMMn cathode in the upper and under parts can be distinguished and marked from the E electrolyte in the middle. When the EMFe/E/EMMn all-in-one FASCs are bent and twisted from the flat state, the seamlessly integrated interfacial structures can be preserved perfectly (Fig. 1f-g), which can be attributed to intertwined EVOH networks across the interfacial structures, leading to the synergistic deformation and strong chemical bonding interfacial interactions among the EMFe/E/EMMn. For comparison, a conventional EMFe/PVA/EMMn laminated FASCs was assembled with a typical PVA electrolyte and showed two sharp interfaces in the flat state, which face even tougher debonding and cracking induced by bending or twisting deformation (Fig. S3), indicating the inconsistent deformation and weak van der Waals (VDW) force interfacial interaction among the EMFe/ PVA/EMMn. The dramatic comparisons on the interfacial structures and interfacial interactions confirm the formation of the seamlessly integrated interfacial structures with strong chemical bonding interfacial interaction in the EMFe/E/EMMn all-in-one FASCs. Moreover, the crosssectional scanning electron microscope (SEM) images also depict a similar integrated configuration without any gap and interface and tightly bonding between EMMn cathode and E electrolyte (Fig. 1h). The cross-sectional SEM-EDX images show Fe and Mn elements evenly distributed in the EMFe anode and EMMn cathode respectively (Fig. 1i),



Fig. 2. Cross-sectional optical image and interfacial enlarged view of EMFe/E/EMMn FASCs fabricated (a) without solvent, (b) with poor solvent alcohol and (c) with good solvent xylene. (d) Raman spectrum of the EMFe/E/EMMn all-in-one FASCs. (e) Schematic illustration for formation mechanism of the EMFe/E/EMMn all-in-one configurations.

indicating homogeneous synthesis of FeOOH and MnO₂. The highresolution SEM images in Fig. 1j display an intertwined nanofibers microstructure formed by the entanglement between long tubular MWNT and EVOH molecular chains. The derived conductive MWNT skeletons can provide numerous conductive passages for assurance of the electron transports with high fault-tolerant ability under deformation conditions. Furthermore, it can be observed the nanorod-shaped FeOOH particles with 100–200 nm in length in the EMFe anode (upper inset of Fig. 1j) while the irregular-shaped MnO₂ particles with hundreds of nanometers size in the EMMn cathode (lower inset of Fig. 1j), whose traces are verified by the X-ray Diffraction (Fig. S5) [30, 31] and X-ray photoelectron spectroscopy (Fig. S6) [32,33] results.

To clarify the formation mechanism of the seamlessly integrated interfacial structures with strong chemical bonding interfacial interaction, contrast samples EMFe/E/EMMn FASCs were fabricated without solvent and with poor solvent alcohol. It can be obviously observed the sharp interfaces in the EMFe/E/EMMn fabricated without solvent (Fig. 2a) while the inconspicuous interfaces containing transition regions in the EMFe/E/EMMn fabricated with poor solvent (Fig. 2b), in stark contrast to the seamlessly integrated interfaces in the EMFe/E/ EMMn fabricated with good solvent (Fig. 2c). The interfacial enlarged views also witness these interfacial structures clearly (Fig. S7). To give a direct proof of the strong chemical bonding interfacial interaction,

Raman spectroscopy was used. As shown in Fig. 2d, all the Raman spectrum collected in the EMFe anode, interfaces, electrolyte and EMMn cathode show a representative peak at approximately 2933 cm^{-1} , which is assigned to the asymmetric stretch of -CH₂- in the backbone of EVOH. The differences in peak intensities can be attributed to the relatively low EVOH content in the interfaces, EMFe anode and EMMn cathode compared with the electrolyte. It means the EVOH chains across the integrated interfaces of all-in-one EMFe/E/EMMn. From these data it can be deduced the formation mechanism of the EMFe/E/EMMn all-inone configurations (Fig. 2e). The surface molecular chains of the EMFe anode, E electrolyte and EMMn cathode are highly entangled in the original states. Without solvent treatment, the molecular chains fail to get surface disentanglement, only forming VDW forces adhered distinct interfaces among the EMFe/E/EMMn. With poor solvent treatment, the molecular chains partially achieve surface disentanglement, forming molecular low-level entanglement across the inconspicuous interfaces of the EMFe/E/EMMn. With good solvent treatment, the molecular chains are swollen and allowed surface disentanglement, followed by reentanglement in the following assembly and thermocompression process, thereby achieving molecular high-level entanglement across the seamlessly integrated interfaces of all-in-one EMFe/E/EMMn. Thus, the all-in-one configurations can be controlled by solvent induced interfacial molecular level entanglement to achieve the EMFe/E/EMMn all-in-



Fig. 3. (a) Alcoholysis solvent, (b) NaOH concentration and (c) alcoholysis times as a function of the electrolyte absorption ratio and areal capacitance of the EMFe/ E/EMMn all-in-one FASCs. (d) Contact angle, (e) FTIR spectra, (f) Nyquist plots, (g) tensile strength, elongation at break and elastic modulus of the EMFe/E/EMMn all-in-one FASCs as a function of alcoholysis times. The inset shows the stress-strain curves as a function of alcoholysis times.

one FASCs.

Moreover, the interfacial molecular level entanglement in the EMFe/ E/EMMn all-in-one FASCs can be also controlled by the alcoholysis degree of EVOH. It must be noted that the pre-swelling time, thermalpressing stress and time in the fabrication have little effect on the EMFe/E/EMMn all-in-one FASCs (Fig. S8). To investigate the influence of primary contributing factor - alcoholysis solvent, various volume ratio of water/alcohol including 10/0, 9/1 and 8/2 were used as the solvents, in which the introduction of alcohol has a significant influence on the alcoholysis efficiency because of the hydrophobic nature of precursor EVA. For convenience, the alcoholysis degree is represented by the electrolyte absorption ratio. As shown in Fig. 3a, the electrolyte absorption ratio rises with the proportion of alcohol, and reaches a high level at the water/alcohol ratio of 9/1, but rises inconspicuously with the higher proportion of alcohol. The rise of electrolyte absorption ratio means the formation of more electrolyte-philic hydroxyls in the side chains of EVOH, resulting in fast ion transports along the EVOH molecular chains. This point can be reflected by the similar changing rules of areal capacitance of the EMFe/E/EMMn all-in-one FASCs with the increase in the proportion of alcohol. To get insight into the influence of alcoholysis solvent to the EMFe/E/EMMn all-in-one configurations, the interfacial structures were further observed. It can be observed from Fig. S9 that the seamlessly integrated interfaces become partial debond at the water/alcohol ratio of 8/2. This phenomenon can be explained by that the interfacial EVOH molecular chains containing high hydroxyl content get disentanglement with the swelling of the aqueous

electrolyte. In short, the excessive alcoholysis degree of EVOH leads to the interfacial molecular low-level entanglement in the EMFe/E/EMMn all-in-one FASCs. Consequently, the mixed solvents of water/alcohol at the volume ratio of 9/1 are chosen as appropriate the alcoholysis solvent. To explore the influence of the secondary contributing factor -NaOH concentration, various concentration of water/alcohol mixed solvents including 1.5, 3.0 and 4.5 M were adopted. The electrolyte absorption ratio and areal capacitance show the similar changing rules with rapid increase and then slow decrease as the NaOH concentration increases (Fig. 3b). The cross-sectional optical images in Fig. S10 witness the partial debond of the seamlessly integrated interfaces at the NaOH concentration of 4.5 M, which can be also explained by the excessive alcoholysis degree of EVOH induced interfacial molecular low-level entanglement. Accordingly, the NaOH concentration of 3.0 M in the water/alcohol mixed solvents is suitable for alcoholysis. To clarify the influence of the ternary contributing factor - alcoholysis time, the alcoholysis times were set to 0, 1, 3, 6 and 9h. The electrolyte absorption ratio and areal capacitance share the same fast followed by slow growing trends with the alcoholysis times increasing (Fig. 3c). The contact angle tests can reflect the electrolyte-philic characteristic from different side. The contact angles show an initial value of 134.9° in 0h, and increase to 90.7° in 1h, 77.3° in 3h, 63.7° in 6h and 51.5° in 9h, respectively (Fig. 3d). The growth laws of contact angles are consistent with those of the electrolyte absorption ratio and areal capacitance, indicating the enhanced electrolyte-philic characteristic of the EMFe/E/EMMn with the alcoholysis times increasing. To get insight into the internal cause of



Fig. 4. (a) CV curves of the EMFe anode and EMMn cathode at a scan rate of 5 mV s⁻¹ in a three-electrode test setup. (b) CV curves of the EMFe/E/EMMn all-in-one FASCs collected from 5 to 100 mV s⁻¹. (c) Areal capacitance as a function of scan rate from 5 to 100 mV s⁻¹, (d) Nyquist plots, (e) capacitance retention as a function of cyclic number of the EMFe/E/EMMn all-in-one FASCs and EMFe/PVA/EMMn laminated FASCs. The inset shows the CV curves of the EMFe/E/EMMn all-in-one FASCs collected at the 1st, 5000th, 10000th, 15000th, 20000th, 25000th and 30000th cycles. (f) Comparison of the EMFe/E/EMMn all-in-one FASCs with recently reported FeOOH/MnO₂ ASCs in cyclic stability.

enhanced electrolyte-philic characteristic, Fourier transform infrared spectroscopy (FTIR) were further used to detect the changes in functional groups of the EMFe/E/EMMn. For comparison, all the FTIR spectra of the EMFe/E/EMMn alcoholyzed from 0 to 9h were normalized in Fig. 3e. On the one hand, the intensities of characteristic peaks including the stretching vibration at 1735 cm⁻¹ and symmetric stretching vibration at 1020 cm^{-1} of C=O bonds in the side chains of EVA gradually decrease with the alcoholysis times increasing. On the other hand, the characteristic peak at 3350 cm^{-1} is assigned to the stretching vibration of -OH groups in the side chains of EVOH, whose intensities gradually increase with the alcoholysis times increasing [34]. These indicate that acetoxy groups in the side chains are gradually alcoholyzed into hydroxyl groups in the EVOH molecular chains, which accounts for the enhanced electrolyte-philic characteristic of the EMFe/E/EMMn. The increasing alcoholysis times contribute to the enhanced electrolyte-philic characteristic but have an adverse effect on the electrolyte-proof characteristic due to the excessive alcoholyzed hydroxyl groups in the side chains of EVOH. This can be confirmed by Fig. S11 that the seamlessly integrated interfaces of the EMFe/E/EMMn become partial debond when the alcoholysis time reaches to 6h. The response of interfacial structures to alcoholysis times can be reflected by the electrochemical impedance spectroscopy (EIS) analysis. The Nyquist plots comprise a rough semicircle in high frequencies representing interfacial charge transfer resistance (R_{ct}) and a straight line in low frequencies concerning Warburg impedance (Z_w) . The R_{ct} of the EMFe/E/EMMn reach 150.7, 72.2, 9.9, 50.2 and 99.38 Ω at the alcoholysis times of 0, 1, 3, 6 and 9h (Fig. 3f), respectively. It indicates that the interfacial charge transfer resistances of the EMFe/E/EMMn decrease rapidly with the alcoholysis times increasing from 0 to 3h because of the enhanced electrolyte-philic characteristic of EVOH molecular chains across the interfaces, but increase rapidly with the

alcoholysis times over 3h due to the gradual interfacial debond over 3h. Consequently, it is appropriate to alcoholyze for 3h. Based on the above results, it can be inferred that the electrolyte-philic characteristic derived from the alcoholyzed vinyl alcohol structural units in the EVOH molecular chains has access to low interfacial charge transfer resistances and thus good electrochemical performance, but the electrolyte-proof characteristic derived from the ethylene and residual vinyl acetate structural units prevents the interfacial molecular chains from disentanglement and thus guarantees interfacial molecular high-level entanglement for the EMFe/E/EMMn all-in-one FASCs. Consequently, controllable interfacial molecular level entanglement plays a pivotal role in the formation of the EMFe/E/EMMn all-in-one configurations, which can be achieved the equilibrium between electrolyte-philic and electrolyte-proof characteristics.

The tensile tests are an effective way to evaluate the mechanical properties of flexible energy storage devices, but difficult to conduct for the conventional laminated flexible energy storage devices in the previous reports because of the VDW forces adhered interfaces. Remarkably, the mechanical properties can be tested on the EMFe/E/EMMn FASCs fabricated by various conditions to illustrate the relevant relationships between the mechanical properties and interfacial molecular level entanglement (The tensile test details are shown in Fig. S12a). Fig. S13a depict the stress-strain curves of the EMFe/E/EMMn fabricated without solvent, with poor solvent, and with good solvent, and the relevant parameters are compared in Fig. S13b. It can be seen that the elastic modulus, tensile strength and elongation at break increase with the adoption of solvent and especially good solvent, all of which are higher than those of the EMFe/PVA/EMMn laminated FASCs (Fig. S14). This can be attributed to the distinct interfacial molecular level entanglement, which is supported by the aforementioned cross-sectional optical images of their interfacial structures. Fig. 3g is the stress-strain



Fig. 5. (a) Capacitance retention of the EMFe/E/EMMn all-in-one FASCs as a function of bending angles of 0° , 90° and 180° . The insets show the corresponding digital photos. (b) Nyquist plots of the EMFe/E/EMMn all-in-one FASCs at the bending angles of 0° , 90° and 180° . (c) Capacitance retention of the EMFe/E/EMMn all-in-one FASCs at the bending angles of 0° , 90° and 180° . (c) Capacitance retention of the EMFe/E/EMMn all-in-one FASCs at the bending angles of 0° , 90° and 180° . (c) Capacitance retention of the EMFe/E/EMMn all-in-one FASCs as a function of twisting angles of 0° , 20° , 40° and 60° . The insets show the corresponding digital photos. (e) Nyquist plots of the EMFe/E/EMMn all-in-one FASCs at the twisting angles of 0° , 20° , 40° and 60° . (f) Capacitance retention of the EMFe/E/EMMn all-in-one FASCs at the twisting angles of 0° , 20° , 40° and 60° . (f) Capacitance retention of the EMFe/E/EMMn all-in-one FASCs at the twisting angles of 0° , 20° , 40° and 60° . (f) Capacitance retention of the EMFe/E/EMMn all-in-one FASCs as a function of twisting cycles. The inset shows the CV curves collected at the 1st, 2000th, 4000th, 6000th, 8000th and 10000th twisting cycles. (g) Comparison of the EMFe/E/EMMn all-in-one FASCs reported previously in the bending and twisting durability. (h) Schematic illustration of mechanically durable mechanism behind the EMFe/E/EMMn all-in-one FASCs during the long-term mechanical deformation.

curves and comparison on the relevant parameters of the EMFe/E/ EMMn fabricated with the alcoholysis times from 0, 1, 3, 6-9h. With increase of alcoholysis times, the elastic modulus decreases slowly from initial 127.7 to 108.9 MPa at the alcoholysis times of 3h and then decrease rapidly to 73.9 MPa at the alcoholysis times of 9h, the tensile strength from 1.87 to 1.69 MPa and then to 0.79 MPa, and the elongation at break from 4.94 to 4.81 % and then to 2.53 %. The rapid decreases in mechanical properties can be explained by the excessive alcoholysis degree of EVOH induced interfacial molecular low-level entanglement with increase of alcoholysis times. Hence the elastic modulus, tensile strength and elongation at break reach the moderate values of 104 MPa, 2.2 MPa and 6.7 % respectively at the alcoholysis time of 3h. The interfacial molecular level entanglement of the EMFe/E/ EMMn fabricated by various conditions are further characterized through a peeling test (The peeling test details are shown in Fig. S12b). As shown in Fig. S15, there are similar curves among the EMFe/E/ EMMn all-in-one FASCs fabricated with the alcoholysis times from 0, 1, 3, 6-9h, except for the EMFe/E/EMMn FASCs fabricated without solvent and with poor solvent. This can be attributed to the fact that the EMFe anode or EMMn cathode had fractured in advance of interfacial debonding and cracking (Fig. S16). Only the interfacial molecular lowlevel entanglement of EMFe/E/EMMn FASCs fabricated without solvent and with poor solvent can be detected in the peeling test. Actually,

the collected curves of the EMFe/E/EMMn all-in-one FASCs fabricated with various alcoholysis times in the peeling test are the stress-stain curves of the EMFe anode or EMMn cathode, due to the high interfacial bonding strength of the EMFe/E/EMMn even higher than the mechanical strength of the EMFe anode or EMMn cathode. All these findings indicate that the optimized EMFe/E/EMMn all-in-one FASCs alcoholyzed by 3.0 M NaOH in the water/alcohol mixed solvents of 9/1 by volume at 3h achieve the equilibrium between electrolyte-philic and electrolyte-proof characteristics, thereby exhibiting interfacial molecular high-level entanglement with low interfacial charge transfer resistance, good mechanical properties, and high interfacial peeling strength.

By virtue of the all-in-one configuration, the optimized EMFe/E/ EMMn all-in-one FASCs exhibit good electrochemical performance. Fig. 4a plots the cyclic voltammetry (CV) curves the EMFe anode and EMMn cathode at a scan rate of 5 mV s⁻¹ in a three-electrode test setup. The stable potential ranges of the EMFe anode and EMMn cathode are -0.8-0 and 0-0.8 V, which derive an operation voltage window of 0-1.6V for the EMFe/E/EMMn all-in-one FASCs. The areal capacitance of the EMFe anode and EMMn cathode is optimized by the electrochemical deposition current and time as shown in Figs. S17–18. After capacity optimization, the areal capacitance of the EMFe anode and EMMn cathode is matched with the proportion of approximately 1:1. Fig. 4b shows the CV curves collected from 5 to 100 mV s⁻¹of the EMFe/E/ EMMn all-in-one FASCs. The curves in an approximately rectangular shape indicate the reversible charge-discharge behavior of the EMFe/E/ EMMn all-in-one FASCs at various scan rate. The galvanostatic chargedischarge (GCD) curves collected from 0.5 to 4 mA cm⁻¹ have the symmetrical charge and discharge curves (Fig. S19), which also manifest the good reversibility. Fig. 4c compares the areal capacitance calculated from the CV curves collected from 5 to 100 mV s⁻¹ between the EMFe/ PVA/EMMn laminated FASCs and EMFe/E/EMMn all-in-one FASCs. The EMFe/PVA/EMMn laminated FASCs show an areal capacitance of 10.2 mF cm⁻², while the EMFe/E/EMMn all-in-one FASCs achieve a much higher areal capacitance of 19.3 mF cm⁻² at a scan rate of 5 mV s⁻¹, which is considered to reach a moderate level of the previously reported values of FASCs. To get insight into the good electrochemical performance, the EIS analyses were conducted. It is obvious that the EMFe/E/ EMMn all-in-one FASCs exhibit the R_{ct} of 9.9 Ω , much smaller than 75.7 Ω of the EMFe/PVA/EMMn laminated FASCs (Fig. 4d). It indicates that the construction of all-in-one configuration significantly reduces the interfacial charge transfer resistance, which has access to good electrochemical performance for the EMFe/E/EMMn all-in-one FASCs. Furthermore, the cyclic stability of the EMFe/E/EMMn all-in-one FASCs and EMFe/PVA/EMMn laminated FASCs are compared in Fig. 4e. The EMFe/PVA/EMMn laminated FASCs exhibit a familiar cyclic stability with capacitance retention of 52 % after 5000 charge-discharge cycles. In sharp contrast, the EMFe/E/EMMn all-in-one FASCs achieve an unprecedented cyclic stability with capacitance retention of 103 % after 30 000 charge-discharge cycles. The slight improvement in capacitance during the long-term cycles can be attributed to the electrolyte infiltration into the internal FeOOH and MnO₂ [35]. As shown in Fig. 4f, the unprecedented cyclic stability of the EMFe/E/EMMn all-in-one FASCs is superior to those of recently reported FeOOH/MnO2 ASCs, such as rGO-CNC-FeOOH/rGO-CNC-MnO_2 ASCs (capacitance retention of 88 %after 3000 charge-discharge cycles) [36], CF-FeOOH-PPy/CF-MnO2 ASCs (capacitance retention of 82 % after 5000 charge-discharge cycles) [32], Ni-FeOOH/Ni-MnO2 ASCs (capacitance retention of 90 % after 1000 charge-discharge cycles) [37], FeOOH NS/MnO2 NW ASCs (capacitance retention of 96.5 % after 10000 charge-discharge cycles) [33], and FeOOH-C/MnO₂ ASCs (capacitance retention of 65 % after 5000 charge-discharge cycles) [38]. To get insight into the unprecedented cyclic stability, the post-mortems were conducted on the EMFe/E/EMMn all-in-one FASCs after 30 000 charge-discharge cycles. From the cross-sectional optical image in Fig. S21a, it can be seen that the seamlessly integrated interfacial structures are incredibly well preserved, meanwhile, the EMFe anode (Fig. S21b) and EMMn cathode (Fig. S21c) also show a similar microstructure to the initial state after 30 000 charge-discharge cycles. The similar FTIR spectra of the electrolyte before and after 30 000 charge-discharge cycles confirm that no soluble by-products of FeOOH and MnO₂ form in the electrolyte (Fig. S22). Based on the above analysis, the unprecedented cyclic stability of the EMFe/E/EMMn all-in-one FASCs can be attributed to the facts (1) the all-in-one configurations with interfacial molecular high-level entanglement play a key role to stability in the interfacial structures and microstructure of anode and cathode, (2) unique homogeneous matrixes EVOH with both equalized electrolyte-philic and electrolyte-proof characteristics have a good inhibition for Mn^{2+} and Fe dissolution [39,40]. The all-in-one configuration is supposed to give a fresh perspective on improvement of the cyclic stability for FASCs, which will be the next priority in our works.

Apart from good electrochemical performance under static state, the stable electrochemical performance under dynamic state is another performance indicator of great concern for flexible energy storage devices. Bending deformation test is common in the previous reports concerning flexible energy storage devices. The EMFe/E/EMMn all-inone FASCs were bent to various bending angles for CV tests from initial 0°–90° and final 180°, as shown in upper inset of Fig. 5a. The collected CV curves at a scan rate of 50 mV s⁻¹ under bending angles of 90° and 180° coincide with that of initial 0° flat state (Fig. S23). The calculated capacitance retention reaches a high value of 99.5 % and 99.3 % for bending angle of 90° and 180° respectively (Fig. 5a), which indicates the stable electrochemical performance under various bending angles. By contrast, the EMFe/PVA/EMMn laminated FASCs just maintain the capacitance retention of 87.7 % for bending angle of 90°, and 58.2 % for bending angle of 180°. Additionally, the EMFe/E/EMMn allin-one FASCs at the excessive alcoholysis time of 6h exhibit the capacitance retention of 92.0 % and 80.0 % for bending angle of 90° and 180° respectively (Fig. S24). To get insight into the stable electrochemical performance, the EIS analyses were conducted. As displayed in Fig. 5b, the microscopic changes in R_{ct} with the bending angles increasing reveal the stable interfacial structures among EMFe/E/EMMn, in accordance with the aforementioned cross-sectional observation on the EMFe/E/ EMMn all-in-one FASCs under bending condition. However, there are noticeable increases in R_{ct} with the bending angles increasing for the EMFe/E/EMMn all-in-one FASCs at the excessive alcoholysis time of 6h (Fig. S25), much more serious for the EMFe/PVA/EMMn laminated FASCs (Fig. S26). The sharp contrasts demonstrate the seamlessly integrated interfacial structures with interfacial molecular high-level entanglement in the EMFe/E/EMMn all-in-one FASCs account for the stable electrochemical performance under various bending angles. Further bending fatigue tests were conducted by investigating the response of capacitance retention to bending cycles. In one bending cycle, the EMFe/E/EMMn all-in-one FASCs were bent from bending angles of 0° –180° and released to initial 0° , followed by CV tests to record the capacitance retention. It is highlight that the EMFe/E/EMMn all-in-one FASCs achieve an unprecedented capacitance retention of 100.6 % over 10 000 bending cycles (Fig. 5c), indicating the outstanding fatigue resistance to long-term bending deformation. The slight improvement in capacitance is probably assignable to the electrolyte infiltration into the internal FeOOH and MnO2 induced by the repetitive bending deformation and compression. To put into perspective the unprecedented bending deformation durability, the post-mortems were conducted on the EMFe/E/EMMn all-in-one FASCs after 10 000 bending cycles. From the cross-sectional optical image in Fig. S27, it can be observed the seamlessly integrated interfacial structures the same as the initial one. This confirms the outstanding fatigue resistance of the all-inone configuration to long-term bending deformation. Compared to bending deformation, twisting deformation tends to cause the inconsistent deformation and thus the interfacial debonding among the anode/electrolyte/cathode, leading to disappearance from the previous reports. The twisting deformation tests are of great challenge, especially twisting fatigue tests. Significantly, the EMFe/E/EMMn all-in-one FASCs are twisted from an initial angle 0° -20°, 40°, and 60° without any macroscopic crack and delamination (upper inset of Fig. 5d). The collected CV curves overlap each other (Fig. S28). The capacitance retention is calculated to be 98.8 % for twisting angles of 20°, 99.5 % for 40° , and 100.0 % for 60° (Fig. 5d), indicating the excellent stability in electrochemical performance under various twisting angles. To highlight the excellent stability in electrochemical performance of the EMFe/ E/EMMn all-in-one FASCs, the twisting deformation tests were also conducted on the EMFe/PVA/EMMn laminated FASCs and the EMFe/E/ EMMn all-in-one FASCs at the excessive alcoholysis time of 6h. However, the EMFe/PVA/EMMn laminated FASCs exhibit poor capacitance retention of 84.2 %, 80.7 % and 54.4 %, and the EMFe/E/EMMn all-inone FASCs at the excessive alcoholysis time of 6h show moderate capacitance retention of 94.5 %, 91.4 % and 90.5 % for the twisting angles of 20°, 40°, and 60° respectively (Fig. S29). The great contrast in capacitance retention can find hard evidence from the EIS analyses. Fig. 5e witnesses the microscopic changes in R_{ct} with the twisting angles increasing, which indicate the stable interfacial structures, in accordance with the aforementioned cross-sectional observation on the EMFe/E/EMMn all-in-one FASCs under twisting condition. However, both the EMFe/E/EMMn all-in-one FASCs at the excessive alcoholysis time of 6h (Fig. S30) and the EMFe/PVA/EMMn laminated FASCs (Fig. S31) experience such a rapid increase in R_{ct} with the twisting

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Fig. 6. (a) CV curves of the EMFe/E/EMMn all-in-one FASCs in single, parallel and series. Digital photos of a red LED board lightened by the EMFe/E/EMMn all-in-one FASCs under (b) flat, (c) bending, (d) twisting, and (e) folding conditions. (f) Digital photo of an electronic watch powered by the EMFe/E/EMMn all-in-one FASCs. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

angles increasing, which depend on the deformation degrees of interfacial structures associated with the interfacial molecular level entanglement. Hence the seamlessly integrated interfacial structures with interfacial molecular high-level entanglement guarantee stable electrochemical performance under various twisting angles for the EMFe/E/ EMMn all-in-one FASCs. Furthermore, twisting fatigue tests were conducted on the EMFe/E/EMMn all-in-one FASCs by alternating twisting from the twisting angles of 0° -60° and back to 0° , in cooperation with the CV tests for calculation of capacitance retention. It is highlight that the EMFe/E/EMMn all-in-one FASCs reach an unprecedented level of twisting deformation durability with capacitance retention of 100.7 %exceeding 10 000 twisting cycles (Fig. 5f), indicating the outstanding fatigue resistance to long-term twisting deformation. The post-mortems on the EMFe/E/EMMn all-in-one FASCs after 10 000 twisting cycles confirm that the seamlessly integrated interfacial structures are incredibly well preserved (Fig. S32), which can explain the outstanding twisting deformation durability. Fig. 5g compares the bending and twisting deformation durability between the EMFe/E/EMMn all-in-one FASCs and previously reported all-in-one FSCs. It is noteworthy that the unprecedented bending and twisting durability of the EMFe/E/ EMMn all-in-one FASCs is superior to those of the reported all-in-one FSCs, such as PANI/β-cyclodextrin-cellulose/PANI FSCs (capacitance retention of 95 % after 100 bending cycles) [41], MoN-CNT/PVA-AA/MoN-CNT FSCs (capacitance retention of 95 % after 200 bending cycles) [42], PPy/PAM-MMT/PPy FSCs (capacitance retention of 93 % after 500 twisting cycles) [43], PPy-rGO/GO/PPy-rGO FSCs (capacitance retention of 93 % and 92 % after 1000 bending and twisting cycles) [44], MB-rGO/GO/MB-rGO FSCs (capacitance retention of 91 % after 1200 bending cycles) [45], and PEDOT-AgNFs/PVA/PEDOT-AgNFs FSCs (capacitance retention of 98 % after 5000 twisting cycles) [46].

Based on the above results, the mechanism diagram of the unprecedented bending and twisting durability is depicted in Fig. 5h. The conventional laminated FASCs tend to exhibit poor deformation durability, which originates from the different deformation of the anode/ electrolyte/cathode with distinct mechanical properties and VDW force adhered interfaces. During deformation, external forces first cause inconsistent deformation among the three of anode/electrolyte/ cathode, resulting in local stress concentration in the interfaces which are the weakest part of laminated configuration. During repetitive deformation, it will inevitably lead to partial interfacial debonding, and even relative displacement and delamination among the anode/electrolyte/cathode. In our design of all-in-one configuration, EVOH is introduced as the homogeneous matrixes, whose molecular chains are induced to form interfacial molecular high-level entanglement across the interfacial structures. During bending or twisting deformation, despite different deformation among the EMFe/E/EMMn, the molecular high-level entanglement distributed in the EMFe/E/EMMn and across the interfacial structures plays a key role in optimal stress dispersion and synergistic deformation in the all-in-one configuration. Moreover, the intrinsic flexibility of EVOH molecular chains effectively endures the large deformation and prevent damage to the all-in-one configuration. Meanwhile, the EVOH entanglement points and MWNT skeletons work as numerous anchor points to avoid EVOH molecular chains from slippage under large deformation. Additionally, the dense MWNT skeletons provide numerous conductive passages for reliable electron transports, while the electrolyte-philic EVOH molecular chain networks adsorb aqueous electrolyte for construction of ion transport channels. In brief, the robust all-in-one configurations with interfacial molecular high-level entanglements facilitate optimal stress dispersion and synergistic deformation among the EMFe/E/EMMn to suppress relative displacement and interfacial debonding, thereby achieving the unprecedented bending and twisting durability for the EMFe/E/EMMn all-in-one FASCs.

The EMFe/E/EMMn all-in-one FASCs with good electrochemical performance and unprecedented mechanical durability hold great potential application in the flexible and wearable electronic equipment. To show the application in the field of large current or high potential, two EMFe/E/EMMn all-in-one FASCs were connected in parallel or in series. As shown in Fig. 6a, the two EMFe/E/EMMn all-in-one FASCs in parallel have the enclosed areas of CV curves approximately twice as large as the single one. The electrochemical window of two EMFe/E/EMMn all-in-one FASCs in series is expanded from 1.6 V to 3.2 V. It indicates that the EMFe/E/EMMn all-in-one FASCs have a promising prospect in large current and high potential application scenarios. Once fully charged, the two EMFe/E/EMMn all-in-one FASCs in series can light up a red LED

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2024.235491.

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under flat condition (Fig. 6b), and keep brightness under bending (Fig. 6c), twisting (Fig. 6d), and even folding (Fig. 6e) conditions. And the two EMFe/E/EMMn all-in-one FASCs in series can work as a watch strap to power an electronic watch, demonstrating the great potential application in the flexible and wearable electronic equipment.

4. Conclusion

In summary, the EMFe/E/EMMn all-in-one FASCs are constructed by the CIMES, which is achieved by controlled solvent induced reentanglement and alcoholysis of homogeneous matrixes EVOH. The optimized EMFe/E/EMMn all-in-one FASCs with seamlessly integrated interfacial structures exhibit low interfacial charge transfer resistances, good mechanical properties, and high interfacial peeling strength. In comparison with the conventional EMFe/PVA/EMMn laminated FASCs. the EMFe/E/EMMn all-in-one FASCs show a much higher areal capacitance of 19.3 mF $\rm cm^{-2}$ and superior cyclic stability with capacitance retention 103 % after 30 000 charge-discharge cycles. It is highlight that the EMFe/E/EMMn all-in-one FASCs achieve unprecedented mechanical durability with capacitance retention of 100.6 % and 100.7 % exceeding 10 000 bending and twisting cycles respectively, superior to those of allin-one FASCs reported previously. Furthermore, the EMFe/E/EMMn allin-one FASCs are demonstrated to light up a red LED under flat condition, and keep brightness under bending, twisting, and even folding conditions. From the molecular chain perspective, this work is supposed to provide an advanced design concept of controllable interfacial molecular level entanglement to construct robust all-in-one configurations with chemical bonding interfacial structures for mechanically durable FASCs toward flexible and wearable electronic equipment applications.

CRediT authorship contribution statement

Zeyu Jiang: Methodology, Investigation, Data curation. Ping Zhang: Methodology, Investigation. Qiying Zhang: Methodology, Investigation. Zhiyin Lin: Investigation. Zhaoye Wu: Investigation. Xi Hu: Investigation. Weiqian Feng: Investigation. Liyong Tian: Methodology, Investigation. Yancheng Wu: Methodology, Investigation. Yangfan Zhang: Writing – review & editing, Writing – original draft, Visualization, Supervision, Funding acquisition, Conceptualization. Ningbo Yi: Writing – review & editing, Funding acquisition, Formal analysis, Data curation. Yongsheng Chen: Writing – review & editing, Project administration, Funding acquisition, Data curation. Nan Zhang: Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work is financially supported by the Guangdong Basic and Applied Basic Research Foundation (No. 2023A1515010999), National Natural Science Foundations of China (No. 52003200), Jiangmen Key Project of Research for Basic and Basic Application (No. 2021030102800007443), Science Foundation of High-Level Talents of Wuyi University (No. 2019AL019, 2020AL021, BSQD2014), Wuyi University–Hong Kong/Macau Joint Research Funds (No. 2021WGALH05). Z. Jiang et al.

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