

Supporting Information

**Effect of polymer polarity on the interface
interaction of polymer/liquid metal composites**

*Yuhang Li , Hangyu Guo , Zilong Xie *, Qiang Fu **

^a College of Polymer Science & Engineering, State Key Laboratory of Polymer
Materials Engineering, Sichuan University, Cheng Du, 610065, PR China.

* Corresponding author. Zilong Xie, Qiang Fu

E-mail addresses: xiezilong0731@qq.com (Z. Xie); qiangfu@scu.edu.cn (Q. Fu).

Table of contents

1. Experimental section	3
2. The optical photographs of LM and polymer/LM composites	5
3. The statistical size of LM in polymer/LM composites	6
4. The XPS spectra of polymer/LM composites	8
5. The sum table of molecular weights of the polymers	17
6. The sum table of the dielectric properteis of polymer/LM composites	18

Experiments

Materials

Galinstan alloy (62.5 wt% gallium, 21.5 wt% indium, 16 wt% tin) was provided by Hunan Santech Materials Co., Ltd. Polypropylene (PP) (HC318BF) particles with a wide molecular weight distribution, was purchased from Borealis (Austria). Polyethylene terephthalate (PET) (602) was purchased from Far Eastern Industries LTD(Shanghai). Polyvinylidene fluoride (PVDF) (HSV900) was from Arkema (France). Another PVDF polymers with different molecular weight (named as PVDF-1) (427144) was purchased from Sigma-Aldrich (Germany). Polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene (P(VDF-TrFE-CFE)) (RT-FS) was purchased from Piezotech (France). All the raw materials were used as received without further purification.

Characterization and Measurement

The polymer/LM composites were fractured in liquid nitrogen for the observation of cross-section morphologies by scanning electron microscopy (SEM, Nova NanoSEM 450, USA). The gel permeation chromatography (GPC, Agilent PL-GPC220, USA) was used to measure the number-average (M_n) and weight-average (M_w) molecular weights of the polymers. The change in crystal structures and chemical states of polymer/LM composites were analyzed by X-ray diffraction (XRD, Ultima IV, Rigaku, Japan) and X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, UK). Fourier transform infrared spectroscopy (FTIR, Nicolet is50, USA) further analyzed the vibration and stretching of the chemical bond of polymer/LM composites. The surface of the sample films was sputtered with a thin layer of gold by a thermal evaporator (Q150R Plus, Quorum) as the electrodes for the test of dielectric energy storage performance. Dielectric properties (dielectric constant and dissipation factor) were measured at room

temperature from 10^1 Hz to 10^5 Hz using a broad-band dielectric spectrometer (Concept 50, Novo control, Germany). At least three samples are prepared for the dielectric tests. The electric displacement and capacitive energy storage performances were measured by a ferroelectric polarization tester (Radiant Premier II, USA) at room temperature.

Synthesis

For the preparation of composites, predetermined amounts of polymer raw materials and preliminary liquid metal droplets were physically pre-mixed together (90 vol% polymer, 10 vol% liquid metal). Afterward, a micro-compounder (Haake Minilab), with a screw speed of 120 rpm, temperature of 210 °C, and mixing time of 8-10 mins was further used to prepare relatively uniform composites. Then, composites were put in between two polyimide films with a pressure of 10 MPa and temperature of 210 °C for hot-pressing to obtain the composites films for testing, and the film thickness were around 100 to 150 μm . For the composites of PET, the processing temperatures was changed from 210 °C to 265 °C, owing to its high melting temperatures. The pristine pure polymer films were prepared at the same procedure as corresponding composites.

For the preparation of PVDF (PVDF/LM) capacitor biaxial-stretching films, the PVDF (PVDF/LM) were hot-pressed between two polyimide films at 210 °C and 10 MPa to form the thin sheets (9*9*0.02 cm). Then, the sheets were stretched using a biaxial extensometer (Bruckner Karo IV) according to the following programs: (1) preheating at 170 °C for 30 s; (2) stretching synchronously at a stretching temperature of 170 °C, stretching ratio of 2.0*2.0, and stretching speed of 25%/s; (3) cooling at room temperatures. Finally, the middle region of the stretched films was cut as the final substrate film for its uniformity in orientation, thickness, and performance.

Supporting figures

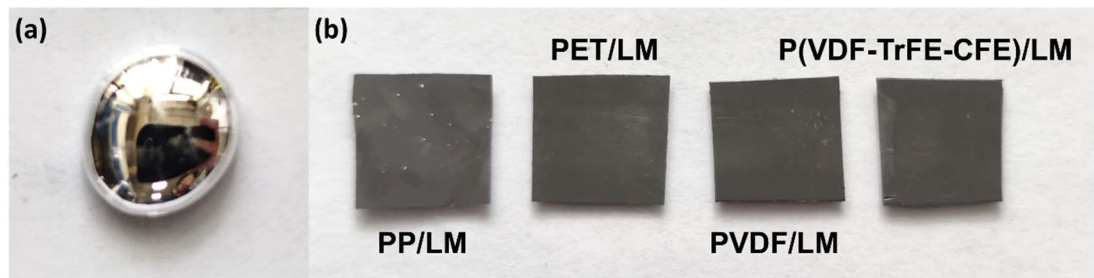


Figure S1. (a) Optical photographs of the Galinstan alloy. (b) Optical photo of PP/LM, PET/LM, PVDF/LM, P(VDF-TrFE-CFE)/LM films.

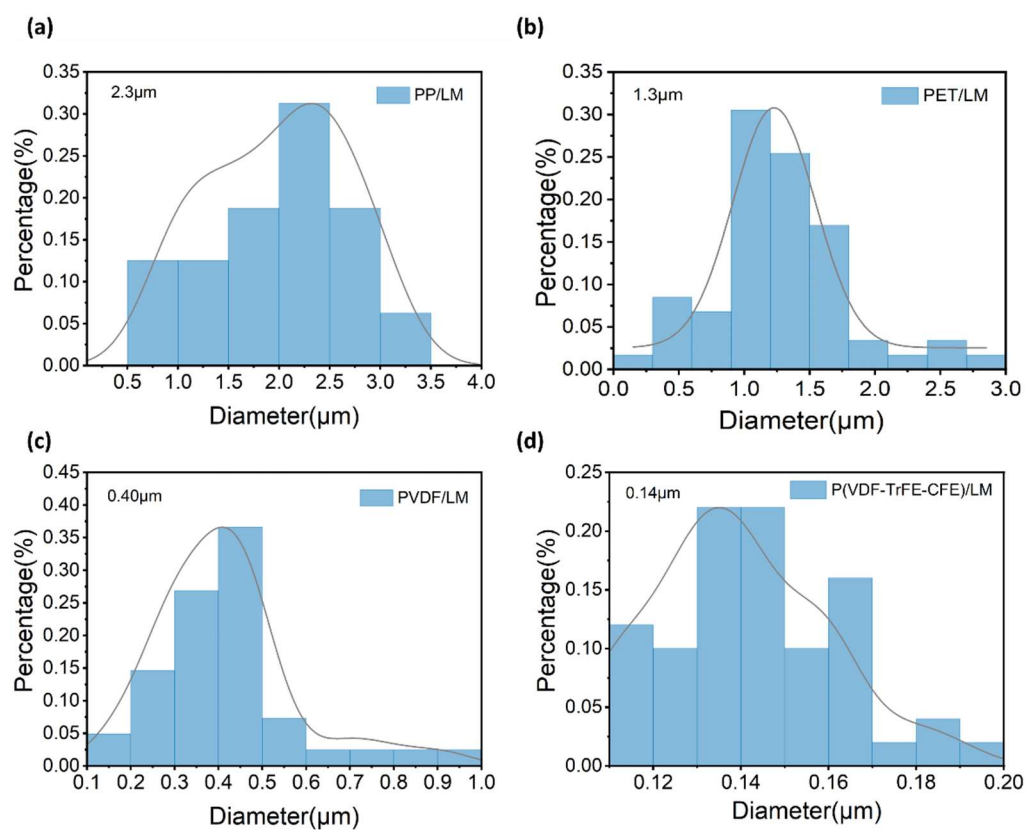


Figure S2. Statistical size distributions from the SEM images using nano-measure software: (a) PP/LM composite, (b) PET/LM composite, (c) PVDF/LM composite, (d) P(VDF-TrFE-CFE)/LM composite.

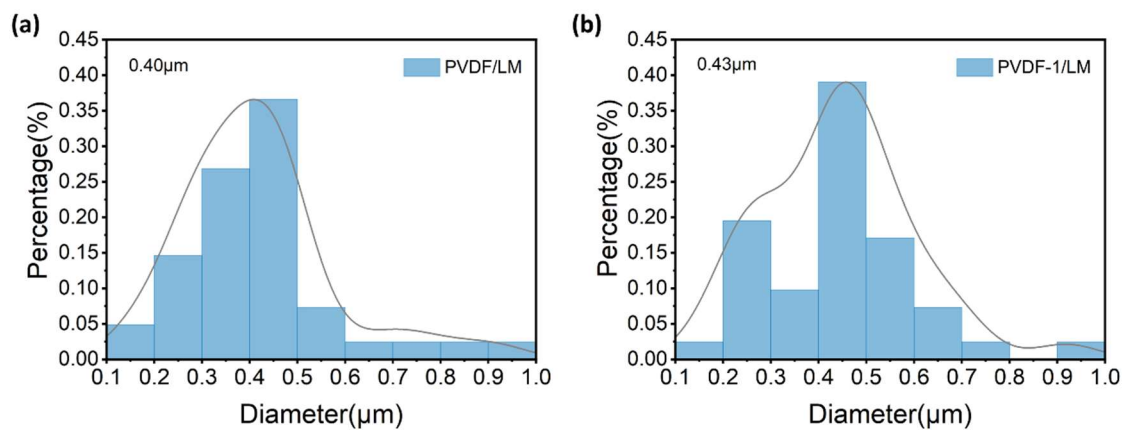


Figure S3. Statistical size distributions from the SEM images using nano-measure software: (a) PVDF/LM composite ($M_w, PVDF = 158725$), (b) PVDF-1/LM composite ($M_w, PVDF-1 = 175771$).

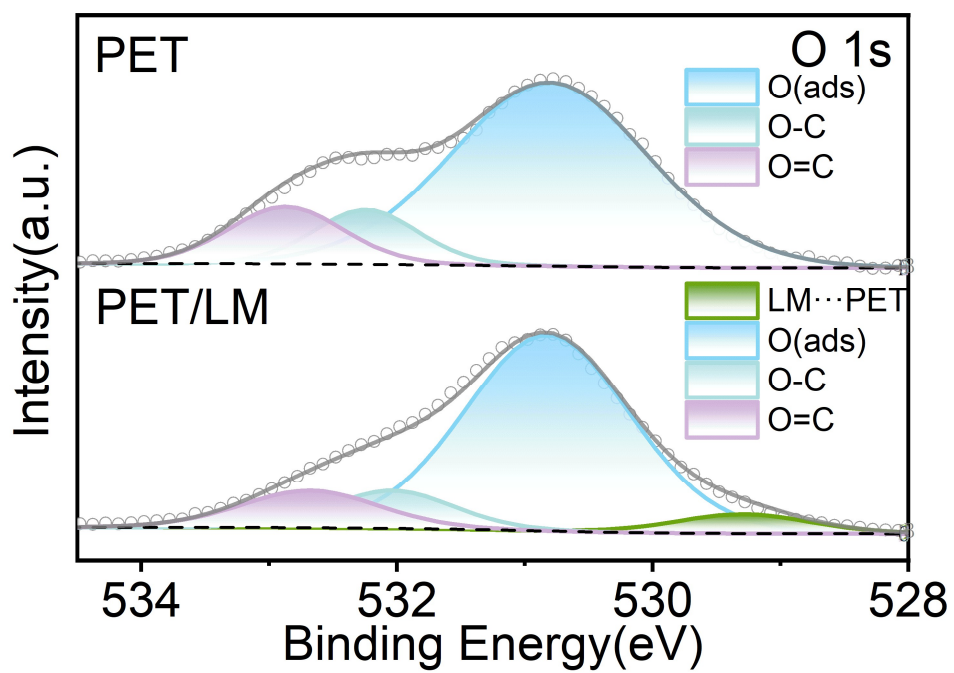


Figure S4. O 1s spectra of XPS for the PET film and PET/LM film.

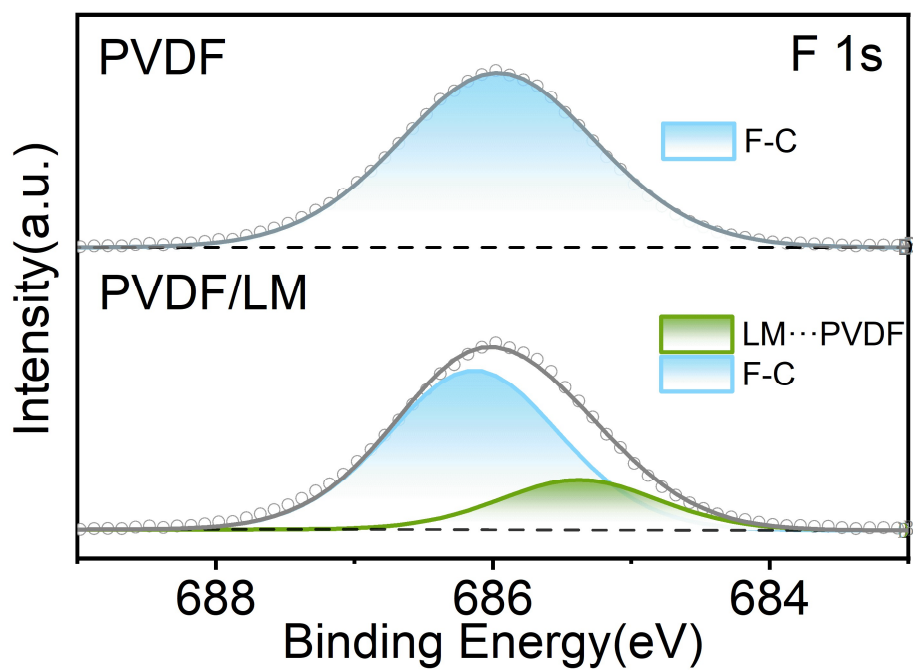


Figure S5. F 1s spectra of XPS for the PVDF film and PVDF/LM film.

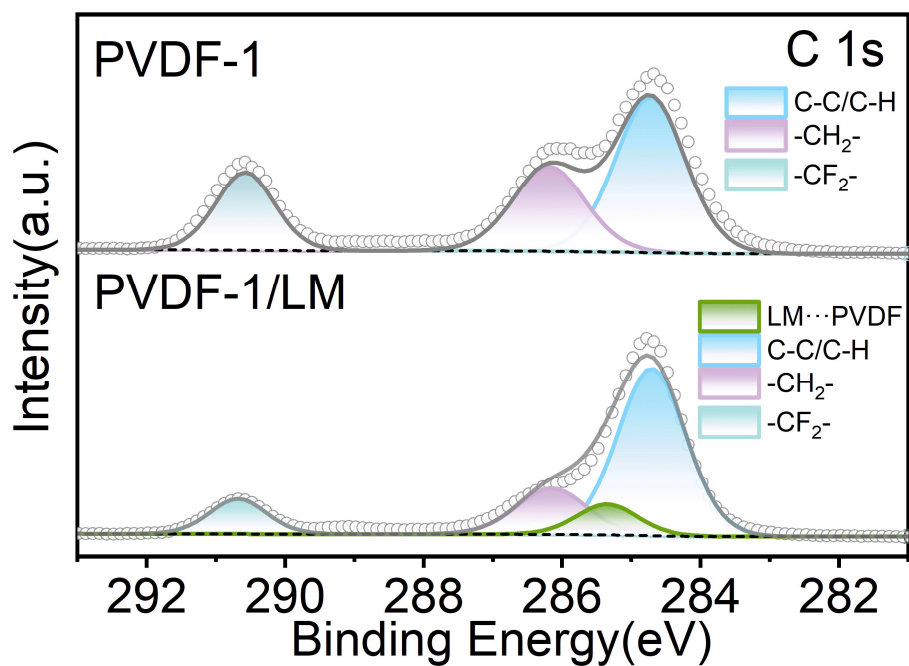


Figure S6. C 1s spectra of XPS for the PVDF-1 film and PVDF-1/LM film. (PVDF-1 is the polymer of different molecular weight).

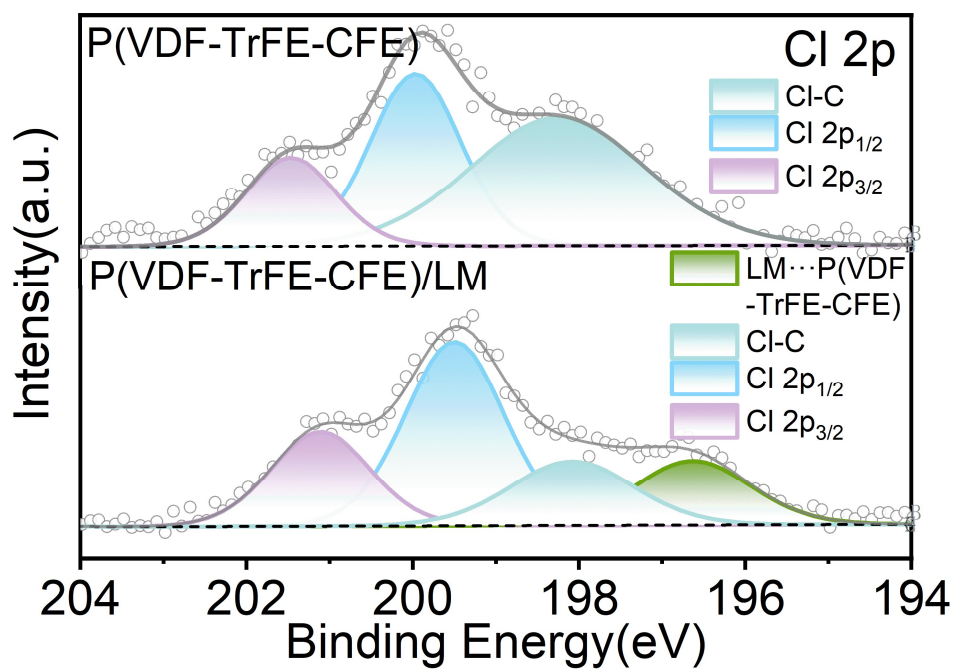


Figure S7. Cl 2p spectra of XPS for the P(VDF-TrFE-CFE) film and P(VDF-TrFE-CFE)/LM film.

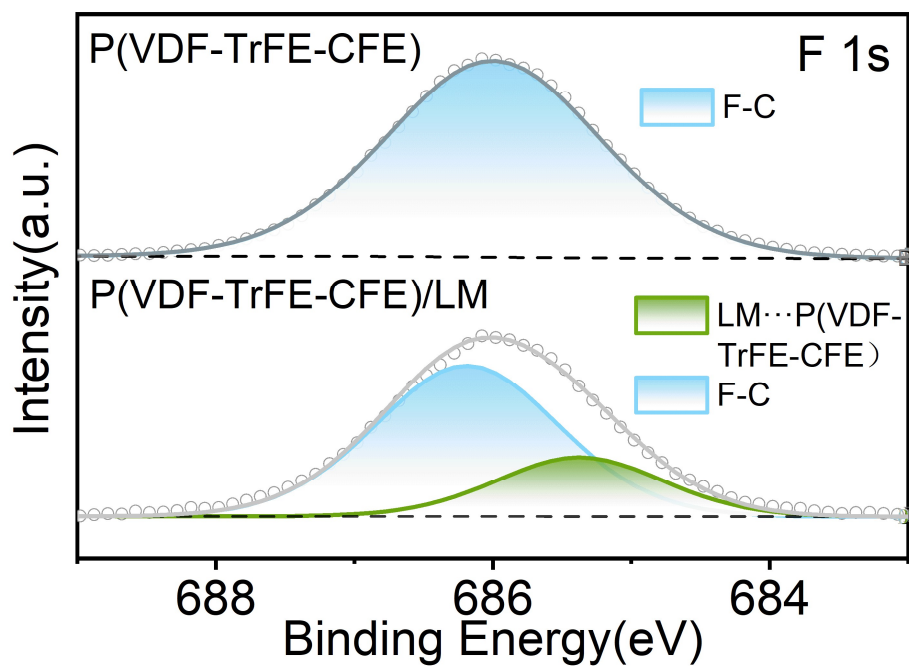


Figure S8. F 1s spectra of XPS for the P(VDF-TrFE-CFE) film and P(VDF-TrFE-CFE)/LM film.

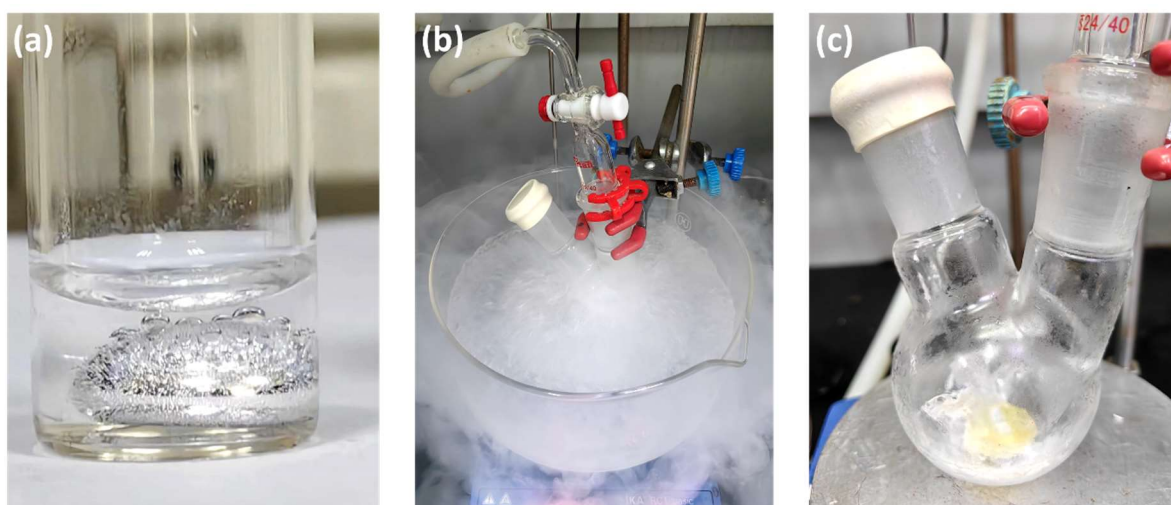


Figure S9: (a) Optical photo of LM immersed in HCl solution for removing the oxide layer. (b) A nitrogen-filled flask was used for the solution mixing of PVDF/LM composites under no-oxygen environment, and a freeze-drying step assisted by the vacuum pump and liquid nitrogen was used for the drying of PVDF/LM composites under no-oxygen environment, (c) Optical photos for the final product of PVDF/LM composites without oxide layer.

***Note:**

The preparation of PVDF/LM composites without oxide layer includes the following steps:

Firstly, the LM was immersed in several droplets of 2 m HCl for 0.5 h to etch the oxide layer (Figure. S9a). Secondly, a solution mixing procedure (500 rpm, room temperature, 1 h) was carried out to prepare the PVDF/LM composites solution, where the flask for mixing was preliminarily vacuumed and filled with nitrogen gas to remove the oxygen. Preliminary determined content of PVDF/acetone solution was put into the no-oxygen flask, followed by adding the LM droplets along with the HCl to segregate the air. Thirdly, after the sufficient mixing of PVDF/LM solution, the solution was dried under no-oxygen environment by a freeze-drying procedure (vacuum and liquid nitrogen bath). The final product without oxide layer is shown in Figure. S9c.

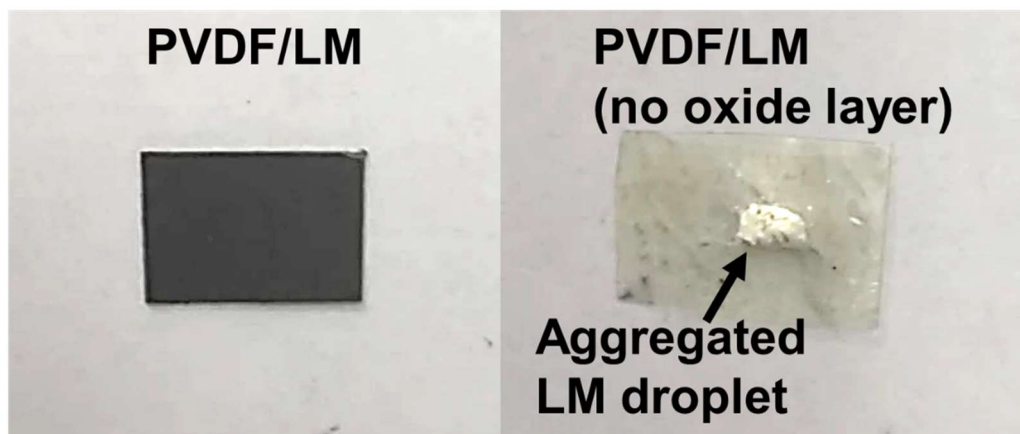


Figure S10: Optical photo of the PVDF film and PVDF/LM(no oxide layer) film.

*For the observation of the appearance of the composites film, the product was hot-pressed between two polyimide films with a pressure of 10 MPa and temperature of 210 °C to obtain the film.

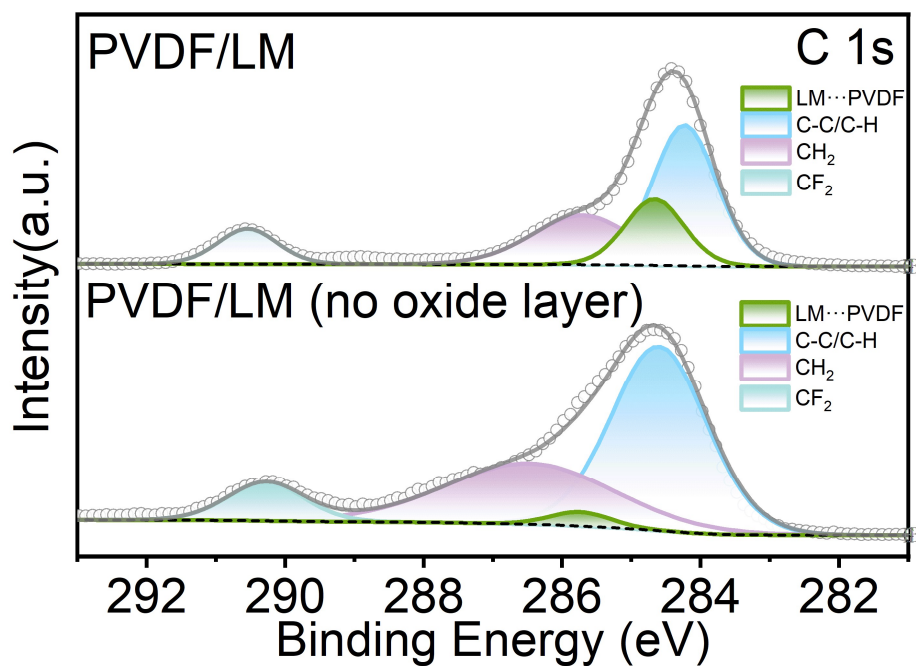


Figure S11. C 1s spectra of XPS for the PVDF/LM film and PVDF/LM (no oxide layer) film.

*For the XPS characterization of the product, the product was vacuum-sealed before sending to the test. And before the final test of XPS characterization, the top surface (10 nm) of the product was etched by the ion cluster to remove the surface oxidation layer of products.

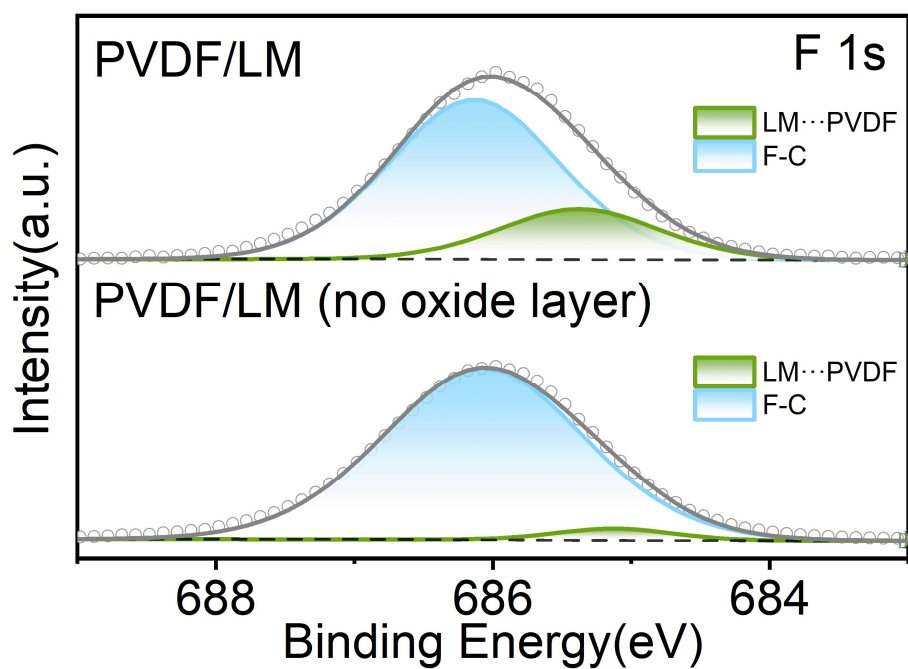


Figure S12. F 1s spectra of XPS for the PVDF/LM film and PVDF/LM(no oxide layer) film.

*For the XPS characterization of the product, the product was vacuum-sealed before sending to the test. And before the final test of XPS characterization, the top surface (10 nm) of the product was etched by the ion cluster to remove the surface oxidation layer of products.

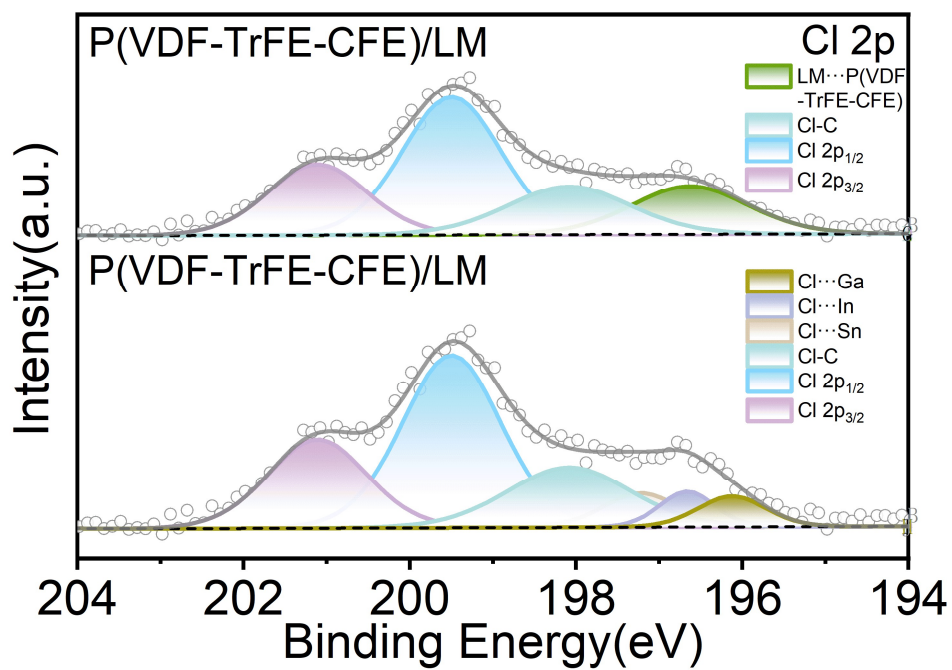


Figure S13. Cl 2p spectra of XPS for the P(VDF-TrFE-CFE)/LM film.

Table S1. GPC results for PP、PET、PVDF、P(VDF-TrFE-CFE) and PVDF-1.

Materials	Mn [g mol ⁻¹]	Mw [g mol ⁻¹]	Mw/Mn (PDI)
PP	77006	223952	2.90824
PET	154525	236968	1.53353
PVDF	68525	158725	2.31631
P(VDF-TrFE-CFE)	123436	232329	1.88218
PVDF-1	79136	175771	2.22113

Note: PVDF-1 is an additional PVDF raw materials with different Mw for singly investigating the influence of molecular weight on interaction (seen Figure. S3).

Table S2. Comparison of the permittivity and dissipation factor of pure polymer and four different polymer/LM composites.

Materials	Permittivity (at 1k Hz)	Permittivity change (percentage)	Dissipation factor (at 1k Hz)	Dissipation factor change
PP	2.5173		0.00175	
PP	6.2684	+249%	0.01645	+0.0147
PET	4.7023		0.02831	
PET/LM	7.8267	+166%	0.73462	+0.7063
PVDF	8.8148		0.02650	
PVDF/LM	13.0534	+148%	0.01876	-0.0077
P(VDF-TrFE- CFE)	42.4698		0.08021	
P(VDF-TrFE- CFE)/LM	48.2134	+114%	0.09217	+0.0120

Note: LM – galinstan liquid metal.