Tuning Infrared Emissivity of Multilayer Graphene using Ionic Liquid Gel Electrolytes

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S1 Comparison of gel polymers

Some key parameters (i.e., ionic conductivity, electrochemical stability windows (ESW), and decomposition temperature) of ILGPEs prepared using PVA, PMMA, PVDF, and PVDF-HFP are shown in Table S1. The comparison suggests that PVDF-HFP is a promising candidate for preparing ILGPEs for use in an IR modulator, due to its high ionic conductivity, wide ESW, and good thermal stability.

Name	Conductivity	ESW	Decomposition
	(mS/cm)	(V)	temperature (°C)
PVDF ¹⁻⁴	1.7-11.4	3.0-5.5	>300
PVDF-HFP ⁵⁻¹¹	1.9-8.4	4.0-5.5	>350
PVA ¹²⁻¹⁷	1.2-5.7	2.0-4.7	150-250
PMMA ¹⁸⁻²¹	8.8×10 ⁻² -2.9	3.0-4.0	220-300

Table S1 Key parameters for ILGPE prepared using different gel polymers

S2 Optical images of ILGPE



Figure S1 Optical images of as-prepared ILGPE

S3 Thermal image of modulator without a Celgard separator

The thermal images of the modulator without a Celgard separator, before and after applying a 3 V bias voltage, are shown in Figure S2. Clearly, removing the Celgard separator from the modulator does not affect its ability to tune IR emissivity. Unlike pure IL, the ILGPE can serve as a separator to prevent short-circuiting in the modulator. However, it remains challenging to directly transfer an intact MLG onto the ILGPE.



Figure S2 Thermal images of the modulator without a Celgard separator before and after ion intercalation

S4 Thermal stability of ILGPE

The decomposition temperatures of ILGPE are slightly lower than that of the pure polymer (i.e., PVDF-HFP), but remain significantly higher than the operation temperature of 70 °C, as shown in Figure S3.



Figure S3 Percentage of mass loss for pure polymer and ILGPEs with varying concentrations

S5 Electrochemical stability of ILGPE

The electrochemical stability windows (ESW) of the ILGPE with an IL content of 6 is evaluated by linear sweep voltammetry (LSV), as shown in Figure S4. Both the oxidation and reduction limits exceed 3.0 V.



Figure S4 LSV for ILGPE with an IL content of 6

S6 Dynamic modulation of MLG IR emissivity with different ILGPE concentrations

Representative thermal images of the modulator with varying ILGPE concentrations (4, 5, 7, and 8) before and after ion intercalation are shown in Figure S5. The thermal response of the modulator with an ILGPE concentration of 6 is provided in the main text.



Figure S5 Thermal images of the modulator with different concentrations of ILGPE before and after applying a bias voltage

S7 Ionic conductivity of ILGPE

The electrochemical impedance spectra (EIS) of ILGPE with different concentrations were measured using an electrochemical workstation. The measurements were conducted with an AC potential amplitude of 10 mV over a frequency range of 1 Hz to 100 kHz. Figure S6a presents typical Nyquist plots for the impedance analysis of ILGPEs. In the high-frequency region of the Nyquist plot, the intercept of the curve with the real axis (Z') corresponds to the intrinsic resistance of the

ILGPE $(R)^{11, 22}$. The ionic conductivity (σ) of the ILGPE was derived using the equation $\sigma = \frac{L}{c_{r,P}}$.

where L is the thickness of the ILGPE, and S is the geometric area of the electrode/electrolyte interface. The error in conductivity estimation is approximately ± 0.07 S/m. The conductivity of the ILGPE increases with increasing IL concentration (as shown in Figure S6b). This is in good agreement with other literature²³.



Figure S6 Ionic conductivity of ILGPE. (a) Nyquist plot of ILGPE with different concentrations; (b) Ionic conductivity of ILGPE as a function of IL concentration

S8 Change in crystal structure of ILGPEs

The XRD analyses of ILGPEs with different IL content, as well as the pure polymer (i.e., PVDF-HFP), are shown in Figure S7. The peaks at 18.3° , 20.2° , and 26.7° in the XRD pattern of pure PVDF-HFP represent the (100), (020), and (110) planes of the α -phase PVDF-HFP¹¹. After the addition of ionic liquids (ILs), the intensity of the α -phase characteristic features decreases dramatically, while that of the β -phase peaks, (110/200), appears at $21.1^{\circ 8, 11}$. Moreover, the full width at half maximum (FWHM) of the peak increases with increasing IL content, which suggests that the amorphousness of the polymer matrix increases. This creates more conduction sites for efficient ion transport¹¹, which helps to improve ionic conductivity, as evidenced in Supplementary Materials S7.



Figure S7 XRD patterns of ILGPE with various IL concentrations

S9 Completed cyclic test of MLG with an ILGPE concentration of 6



Figure S8 Cyclic test of MLG-based IR modulator using ILGPE with a concentration of 6



S10 Cyclic test of MLG with different ILGPE concentrations

Figure S9 Modulation depth as a function of number of cycles for MLG-based IR modulators using ILGPE concentrations of 4, 5, 7 and 8

S11 Performance of IR modulator with pure [AMIM]NTf₂ and ILGPE prepared using [AMIM]NTf₂

ILGPEs have also been prepared using PVDF-HFP and [AMIM]NTf₂, which shares the same anion as [HMIM]NTf₂ but has a different cation. The thermal images in Figure S10a indicate that the modulation depth of [AMIM]NTf₂-ILGPE is similar to that of [HMIM]NTf₂-ILGPE (around 0.42) when a 3 V bias voltage is applied. Meanwhile, the lifetime of the modulator using [AMIM]NTf₂-ILGPE is approximately 270 cycles (Figure S10b), which is seven times longer than that of the modulator using pure [AMIM]NTf₂ (Figure S10c) in a cyclic test (with 3 V applied for 10 s and -1 V for 5 s in each cycle). These results suggest that using a gel polymer electrolyte to improve the long-term stability of the MLG-based IR modulator is applicable to other ILs.



Figure S10 (a)Thermal images before and after ion intercalation and (b) cyclic test of the MLGbased IR modulator using [AMIM]NTf₂-ILGPE with an IL concentration of 6, with the inset demonstrating the emissivity of MLG during the initial 400 s of the cyclic test;(c) cyclic test of the MLG-based IR modulator using pure [AMIM]NTf₂

S12 Electrochemical impedance of ILGPE with a concentration of 6 at different temperatures



Figure S11 Nyquist plot of ILGPE at different temperatures

S13 SEM images of MLG before and after ion intercalation



Figure S12 SEM images of (a) pristine MLG, and MLG after ion intercalation using (b) ILGPE and (c) pure IL as the doping sources

S14 XRD of MLG before and after ion intercalation

The MLG supported by a Celgard separator was evaluated under three distinct conditions: (1) Pristine state, representing MLG before any ion intercalation; (2) Undamaged state, representing MLG after undergoing a moderate number of ion intercalation cycles; (3) Failed state, representing MLG subjected to extensive ion intercalation cycles. In the failed state, the emissivity of MLG no longer shows a significant decrease upon applying a bias voltage, indicating an inoperable modulator. The XRD patterns shown in Figure S13 indicate that the intensity of the feature associated with the periodic stacking of graphene layers (MLG (002)) decreases dramatically after ion intercalation and eventually disappears in the failed MLG. This observation underscores that the stability of the modulator is closely linked to the structural integrity of MLG.



Figure S13 XRD patterns of MLG from an operational modulator and an inoperable modulator, with pristine MLG as reference

References

- 1. H. Niu, M. Ding, N. Zhang, X. Guo, P. Guan and X. Hu, *ChemElectroChem*, 2023, **10**, e202201015.
- 2. N. Demarthe, L. A. O'Dell, B. Humbert, R. D. Arrua, D. Evans, T. Brousse and J. Le Bideau, *Advanced Energy Materials*, 2024, **14**, 2304342.
- 3. M. Wei, P. Zhai, Y. Li, X. Zhao, J. Li, T. Zhang, G. Liu, Z. Yu and S. Xu, *International Journal of Hydrogen Energy*, 2024, **79**, 1278-1288.
- 4. F. C. A. Silva, P. F. R. Ortega, R. A. dos Reis, R. L. Lavall and L. T. Costa, *Electrochimica Acta*, 2022, **427**, 140831.
- 5. D. Kumar, *Solid State Ionics*, 2018, **318**, 65-70.
- 6. D. Kumar and D. K. Kanchan, *Journal of Energy Storage*, 2019, **22**, 44-49.
- 7. S. A. Hashmi, M. Y. Bhat, M. K. Singh, N. T. K. Sundaram, B. P. C. Raghupathy and H. Tanaka, *Journal of Solid State Electrochemistry*, 2016, **20**, 2817-2826.
- 8. V. K. Singh and A. Chandra, *Solid State Ionics*, 2024, **405**, 116448.
- 9. D. Kumar and S. A. Hashmi, *Solid State lonics*, 2010, **181**, 416-423.
- Y. Q. Yang, Z. Chang, M. X. Li, X. W. Wang and Y. P. Wu, *Solid State lonics*, 2015, **269**, 1-7.
- 11. R. Mishra, S. K. Singh, H. Gupta, R. K. Tiwari, D. Meghnani, A. Patel, A. Tiwari, V. K. Tiwari and R. K. Singh, *Energy & Fuels*, 2021, **35**, 15153-15165.
- 12. J. Wang, G. Chen and S. Song, *Electrochimica Acta*, 2020, **330**, 135322.
- 13. J. Wang, Z. Zhao, R. Muchakayala and S. Song, *Journal of Membrane Science*, 2018, **555**, 280-289.
- 14. J. Wang, Z. Zhao, S. Song, Q. Ma and R. Liu, *Polymers*, 2018, **10**, 1179.
- 15. C. C. Q. Wong, A. Y. Yap and C.-W. Liew, *Journal of Electroanalytical Chemistry*, 2021, **886**, 115146.
- 16. M. Jiang, J. Zhu, C. Chen, Y. Lu, Y. Ge and X. Zhang, *ACS Applied Materials & Interfaces*, 2016, **8**, 3473-3481.
- 17. C.-W. Liew, S. Ramesh and A. K. Arof, *International Journal of Hydrogen Energy*, 2014, **39**, 2917-2928.
- 18. S. P, M. S. Thayyil, M. P. Pillai and T. K.K, *Journal of Molecular Liquids*, 2019, **294**, 111671.
- T. Sharma, B. Gultekin, P. S. Dhapola, N. G. Sahoo, S. Kumar, D. Agarwal, H. K. Jun, D. Singh,
 G. Nath, P. K. Singh and A. Singh, *Journal of Molecular Liquids*, 2022, **352**, 118494.
- Q. Tang, H. Li, Y. Yue, Q. Zhang, H. Wang, Y. Li and P. Chen, *Materials & Design*, 2017, 118, 279-285.
- 21. Y. Lian, M. Li, Y. Gao, M. Zhao, J. Liu and L. Xiao, *Acs Applied Energy Materials*, 2023, **6**, 11364-11375.
- 22. S. Wang, Y. Jiang and X. Hu, *Advanced Materials*, 2022, **34**, 2200945.
- 23. X. Yang, F. Zhang, L. Zhang, T. Zhang, Y. Huang and Y. Chen, *Advanced Functional Materials*, 2013, **23**, 3353-3360.