Supporting Information

A highly stable potentiometric Li^+-sensing chip based on hydrophobic laser-induced graphene

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Reagents and materials. 6, 6-Dibenzyl-14-crown-4 (lithium ionophore VI), potassium tetrakis (4-chlorophenyl) borate (KTpClPB), 2-nitrophenyl octyl ether (*o*-NPOE), poly(vinyl chloride) (PVC), and polyvinyl butyral (PVB) were purchased from Sigma-Aldrich. PI film with a thickness of 200 μm, PI insulating tape and self-adhesive PVC insulating sheet were obtained from a computer network store (Taobao, China). Tetrahydrofuran (THF) was obtained from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). The commercial Ag/AgCl paste was purchased from Shenzhen Sryeo Electronic Paste Co., Ltd. Other chemical reagents were of analytical grade, and all of the aqueous solutions were prepared using deionized water (18.2 MΩ cm specific resistance) produced by an ultrapure water system.

Fabrication of the hydrophobic LIG electrode and the integrated potentiometric sensing chip. A commercial PI film was sequentially washed with acetone, anhydrous ethanol and deionized water before the further use. Then, a portable laser engraving machine (DJ6, DAJA Intelligent Technology Co., Ltd., China) with a laser wavelength of 450 nm and a laser head power of 3.0 W was used to fabricate LIG on the PI film surface with a specific size (Fig. S1). For preparing the single LIG electrode, the PI film with LIG was cut into 20 mm (length) × 10 mm (width), and a self-adhesive PVC insulating sheet with the size of 12 mm (length) ×

10 mm (width) × 1 mm (thickness) and a hole diameter of 3 mm was placed on the PI film surface to remain the LIG circle section. For preparing the integrated potentiometric sensing system, the PI film with LIG was cut into 20 mm (length) × 20 mm (width), and a self-adhesive PVC insulating sheet with the size of 12 mm (length) × 10 mm (width) × 1 mm (thickness) and two-hole diameter of 3 mm was placed on the PI film surface to remain the two LIG circle sections. Afterwards, the above LIG electrode was treated with an electrochemical reduction step through consecutively cycling from 0.0 to -1.7 V for 5 cycles in 0.2 M KCl under a nitrogen atmosphere. After being washed by deionized water and dried in the air, the obtained electrode is the hydrophobic LIG electrode, which is denoted as the er-LIG electrode.

The Li^+-selective membrane cocktail was prepared by dissolving 180 mg of the membrane components, containing 1.0 wt% lithium ionophore VI, 0.7 wt% KTpClPB, 70.3 wt% *o*-NPOE and 28.0 wt% PVC, in 2 mL THF with vigorous stirring for 2 h. Then, 20 μL of the obtained membrane cocktail was drop-cast on the surface of the er-LIG electrode for preparing the solid-contact Li^+-ISE (er-LIG/Li^+-ISE). For fabricating the er-LIG-based reference electrode (er-LIG/RE), the commercial Ag/AgCl paste was coated on the er-LIG surface, and then 20 μL of the reference membrane cocktail, prepared by dispersing 79.1 mg PVB and 50 mg LiCl in 1 mL methanol with vigorous stirring, was drop-cast on the Ag/AgCl modified er-LIG electrode. Similarly, the LIG/Li^+-ISE was also fabricated through drop-casting the Li^+-selective membrane cocktail on the LIG electrode for comparison. For the potentiometric measurements, the prepared er-LIG/Li^+-ISE, LIG/Li^+-ISE and integrated Li^+-ISE device were conditioned in 1.0 × 10^{-3} M LiCl, respectively. For the selectivity measurements, the obtained er-LIG/Li^+-ISE was conditioned in 1.0 × 10^{-3} M $MgCl_2$.

Apparatus and measurements. Potentiometric measurements were carried out by using a CHI760C electrochemical workstation (Chenhua Instrument Co., Ltd., Shanghai, China) and a 16-channel high input impedance potentiometer (10^{15} Ω, Lawson Labs., Inc., USA) at room temperature in the galvanic cell: Ag/AgCl (3 M KCl)/sample solution/Li^+-selective membrane/er-LIG or er-LIG/Ag/AgCl/sample solution/Li^+-selective membrane/er-LIG. The ion activities were calculated using the Debye-Hückel equation, and the liquid-junction potentials were corrected through the Henderson equation.

Cyclic voltammetry (CV) and chronopotentiometry were performed by using CHI760C electrochemical workstation with a three-electrode system containing the LIG or er-LIG electrode as the working electrode, an Ag/AgCl (3 M KCl) electrode as the reference electrode, and a Pt wire as the auxiliary electrode. Field-emission scanning electron microscope (SEM) (S-4800, Hitachi, Japan) and water contact angle measurement system (V5, Yunfan Tech., China) were used to characterize the morphologies and wetting properties of LIG and er-LIG. Raman spectra were performed by using a laser Raman spectrometer (DXR, Thermo Fisher Scientific, USA) equipped with a 780 nm excitation laser (100 mW power) and a 10× objective, covering the spectral range of 500-3000 cm^{-1}. Each pixel spectrum was recorded as the average of five measurements with 5 s of the acquisition times. X-ray photoelectron spectroscopy (XPS) measurements were performed by using Al K_α radiation (E = 1486.6 eV) at a spot size of 400 μm with survey scans acquired at 150 eV pass energy (Thermo Scientific K-Alpha, Thermo Fisher Scientific, USA).

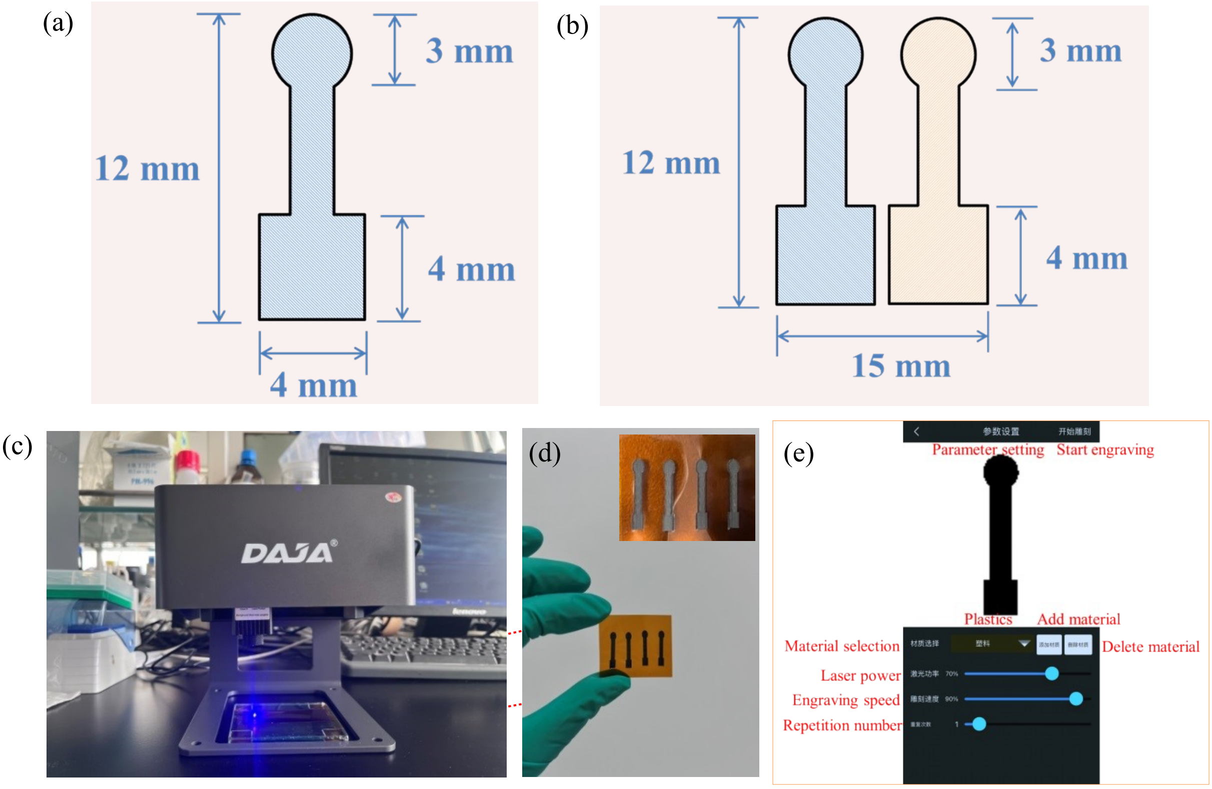

Fig. S1 The detailed sizes of the single (a) and double

(b) laser-induced graphene prepared on the polyimide films, and photographs of the portable laser engraving machine at working (c), the prepared laser-induced graphene on the polyimide film (d) and user interface of the parameter setting of the portable laser engraving machine (e).

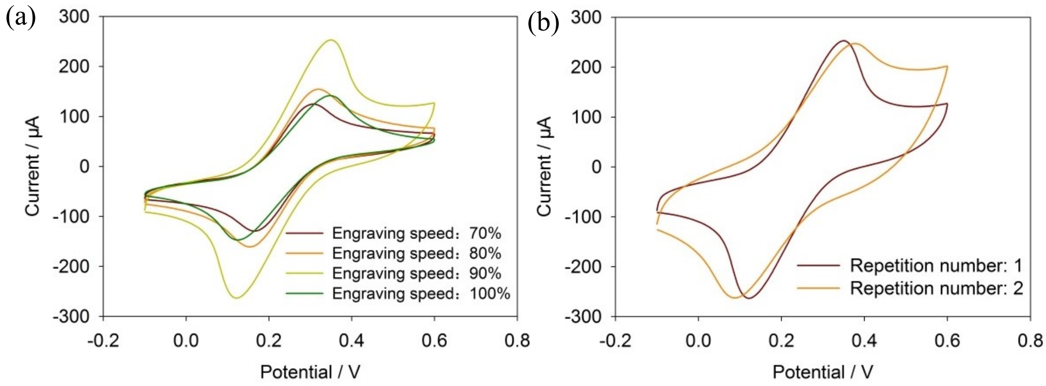

Fig. S2 Cylic voltammograms of the LIG electrodes prepared by the different engraving speed (a) and the different repetition numbers (b) under the laser power of 2.1 W in 0.1 M KCl containing 5 mM $K_3Fe(CN)_6$/ $K_4Fe(CN)_6$.

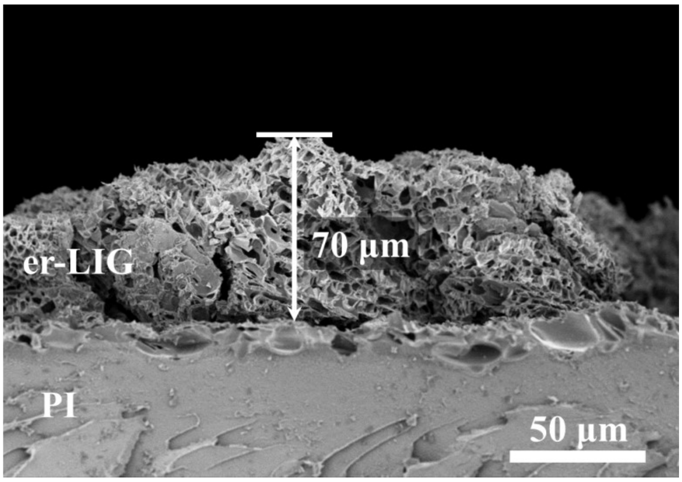

Fig. S3 SEM image of the view side of the er-LIG5 electrode

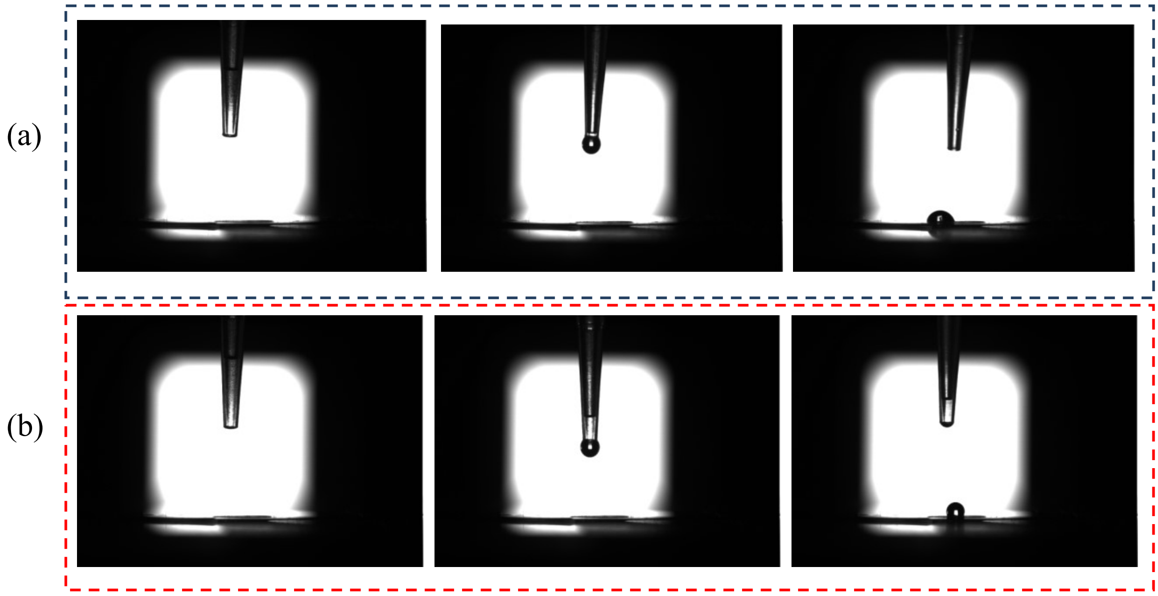

Fig. S4 Images of the dynamic processes of the water droplet contact on the LIG (a) and er-LIG5 electrode (b).

Table S1 Summarizations of the fabrication conditions and the contact angles of hydrophobic laser-induced graphene used for construction of the solid-contact ion-selective electrodes

Laser type	Ambient condition	Contact angle	Ref.
CO_2 laser with a wavelength of 930 nm	Argon	128.4° for 0.30 W 133.7° for 0.45 W 116.3° for 0.60 W	[1]
	Air	65.7° for 0.3 W 15.7° for 0.45 W 2.3° for 0.60 W	
CO_2 laser with a wavelength of 10.6 μm	Air	30.2° for one lasing process 135.5° for double lasing process	[2]
A laser with a wavelength of 450 nm	Air	114.0°, 123.7° and 127.0° for electrochemical reduction by applying the multicycle scanning potential of 2, 5 and 10 cycles	This work

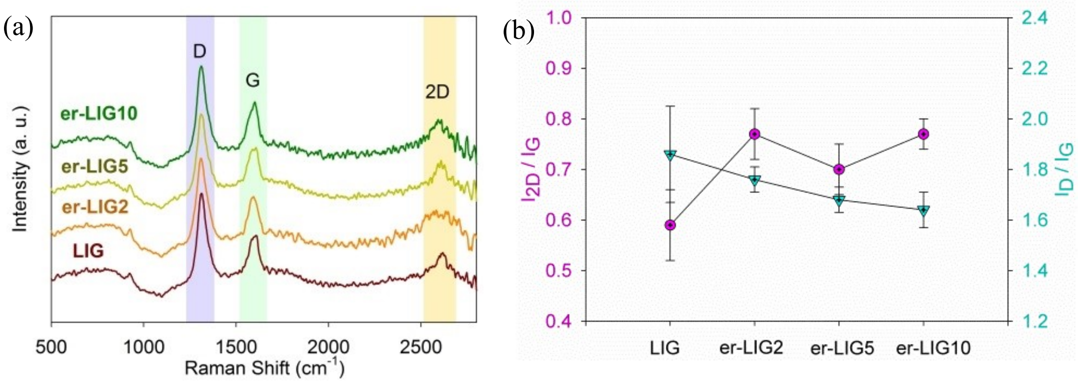

Fig. S5 Raman spectra (a) and the I_{2D}/I_G and I_D/I_G ratios (b) of PI, LIG, er-LIG2, er-LIG5 and er-LIG10.

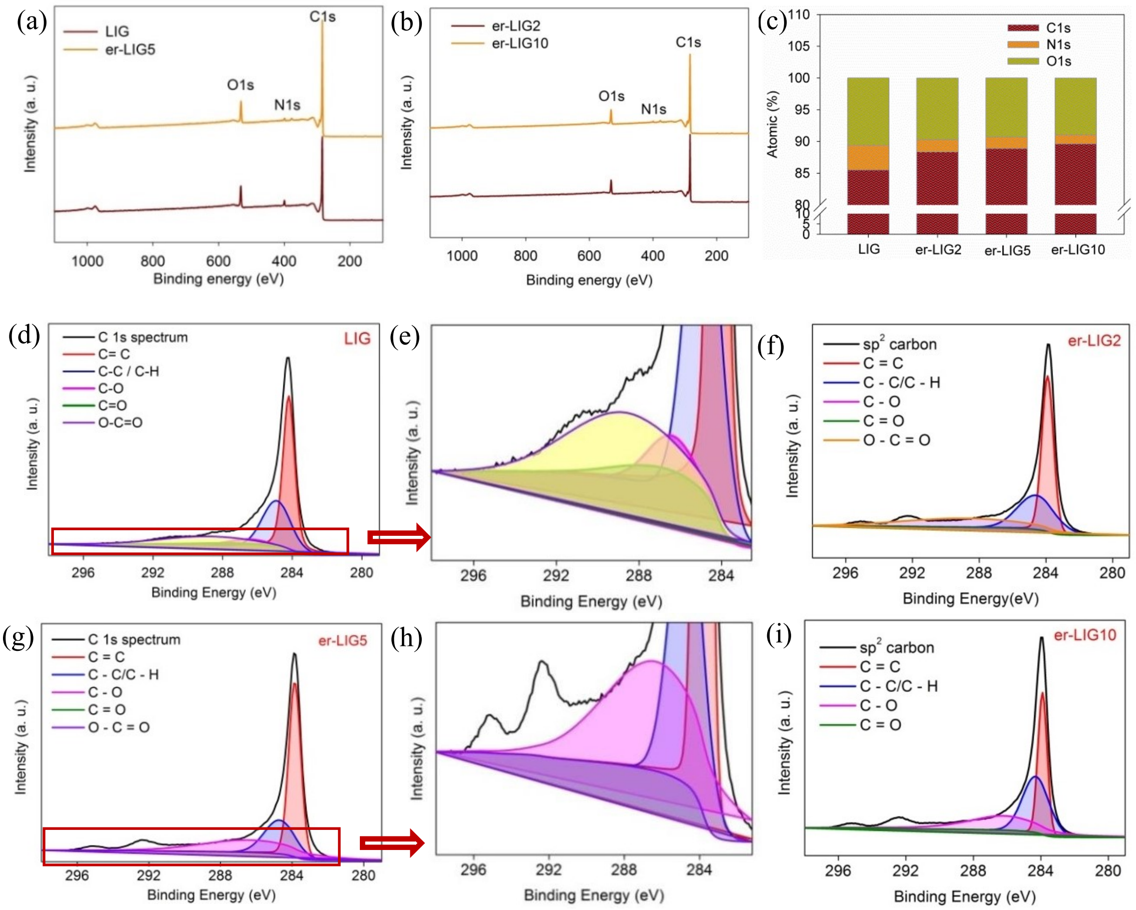

Fig. S6 XPS survy spectra of LIG and er-LIG5 (a) and er-LIG2 and er-LIG10 (b), the atomic ratios of C1s, N1s and O1 s of the LIG, er-LIG2, er-LIG5 and er-LIG10 (c), C1s spectra of LIG (d) and the corresponding enlarged image (e), er-LIG5 (g) and the corresponding enlarged image (h), and er-LIG2 (f) and er-LIG10 (i).

Table S2 Deconvolution of C1s XPS peaks for LIG, er-LIG2, er-LIG5 and er-LIG10

	LIG			er-LIG2			er-LIG5			er-LIG10		
	BE (eV)	FWHM (eV)	Area (%)	BE (eV)	FWHM (eV)	Area (%)	BE (eV)	FWHM (eV)	Area (%)	BE (eV)	FWHM (eV)	Area (%)
C = C	284.2	0.80	44.9	284.0	0.83	41.0	284.0	0.80	48.8	284.0	0.65	32.2
C- C/ C- H	284.9	1.94	28.3	284.5	2.51	31.7	284.7	2.02	22.8	284.3	1.85	36.2
C - O	286.4	2.79	5.8	286.4	2.50	0	286.3	6.55	28.4	286.2	4.92	31.6
C = O	287.0	5.38	3.7	287.0	1.54	1.5	287.0	0.5	0	286.8	0.50	0
O - C = O	288.7	6.50	17.3	288.7	9.22	25.8	288.0	0.5	0	-	-	-

BE: binding energy.

FWHM: full width at half maximum.

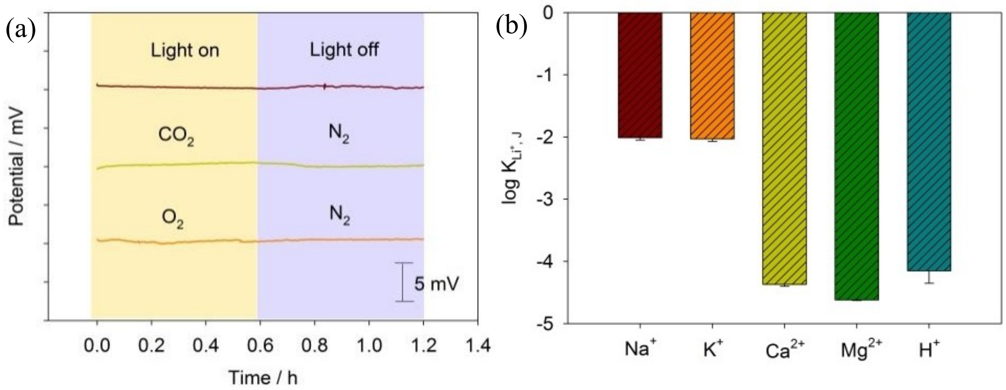

Fig. S7 Effects of O_2, CO_2 and light on the potential stability of the er-LIG/Li^+-ISE (a), and selectivity of the er-LIG/Li^+-ISE (b)

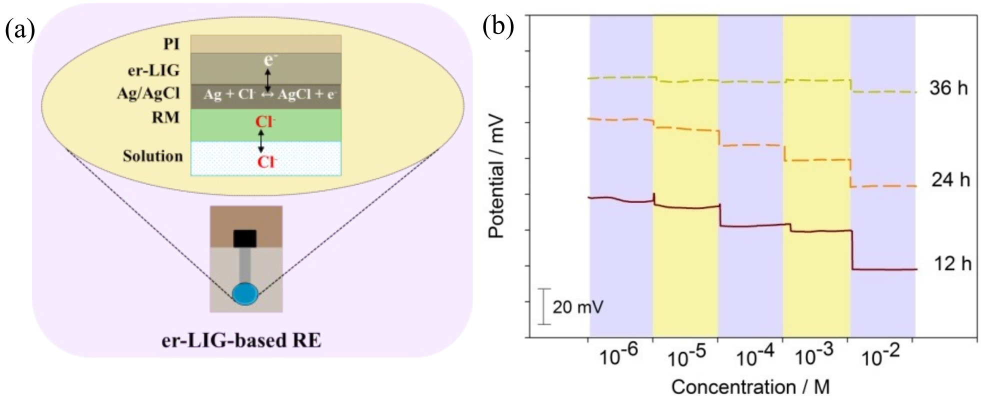

Fig. S8 Schematic representation of the er-LIG-based reference electrode (a), and potential stabilities of the er-LIG-based reference electrode (b), conditioned for 12, 24 and 36 h, in LiCl solutions at different concentrations, respectively.

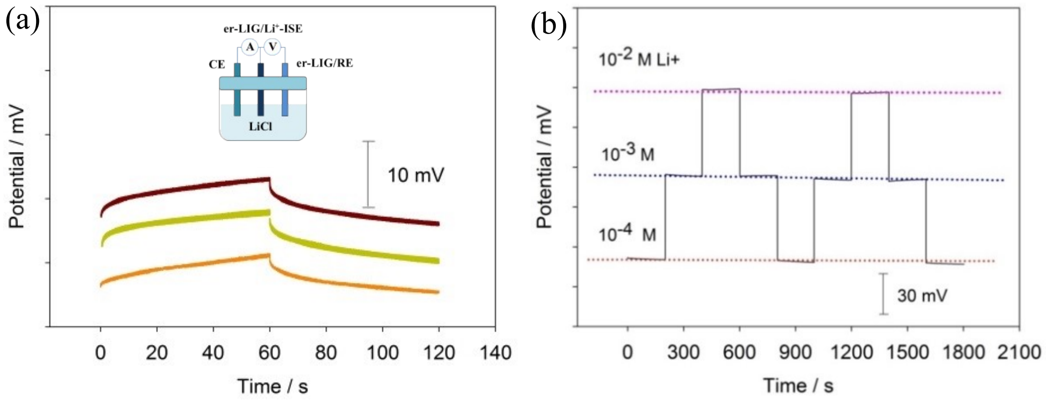

Fig. S9 Chronopotentiograms obtained by applying ± 1 nA on three er-LIG based integrated potentiometric sensing chips (a), and potential reversibility (b) of the er-LIG based integrated potentiometric sensing chip, conditioned in 10^{-3} M LiCl for 36 h.

Table S3 Summarizations of the potentiometric performances of the reported solid-contact Li^+-selective electrode

Substrate	Solid-contact material	Linear range / M	Slope / mV/dec	Short-term Stability [b]	Long-term Stability [c]	Cost of the whole electrode	Ref.
Pt disk	$LiFePO_4$	1.0×10^{-5}-0.1	59.4	0.5 µV/s	< 10 mV/15 days	> \$0.5	[3]
Pt	Platinum nanoflower	1.0×10^{-5}-0.1	58.7	0.03 mV/s	< 5 mV/h	> \$0.5	[4]
GC	Ni-HAB MOF [a]	1.0×10^{-5}-1.0	57.6	-	1.15×10^{-6} mV/h	> \$0.5	[5]
GC	$LiFePO_4$	1.0×10^{-5}-0.1	60.4	-	-1.1 µV/h	> \$0.5	[6]
PI	er-LIG	1.0×10^{-5}-1.0×10^{-2}	57.5	0.02 mV/s	65.8 µV/h	< \$0.5	This work

[a] HAB: 1, 2, 3, 4, 5, 6-benzenehexamine, MOF: metal-organic framework.

[b] The values were obtained by using the constant-current chronopotentiometry.

[c] The values were obtained under the zero-current conditions

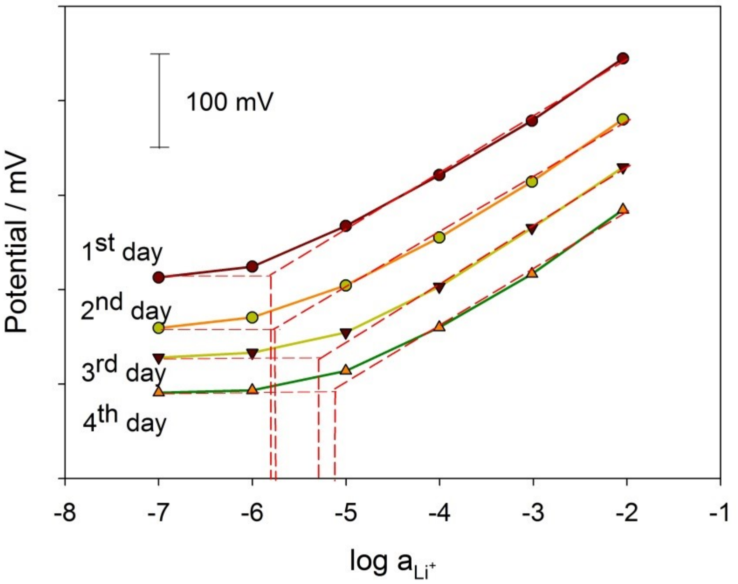

Fig. S10 Lifetime of the er-LIG based integrated potentiometric sensing chip

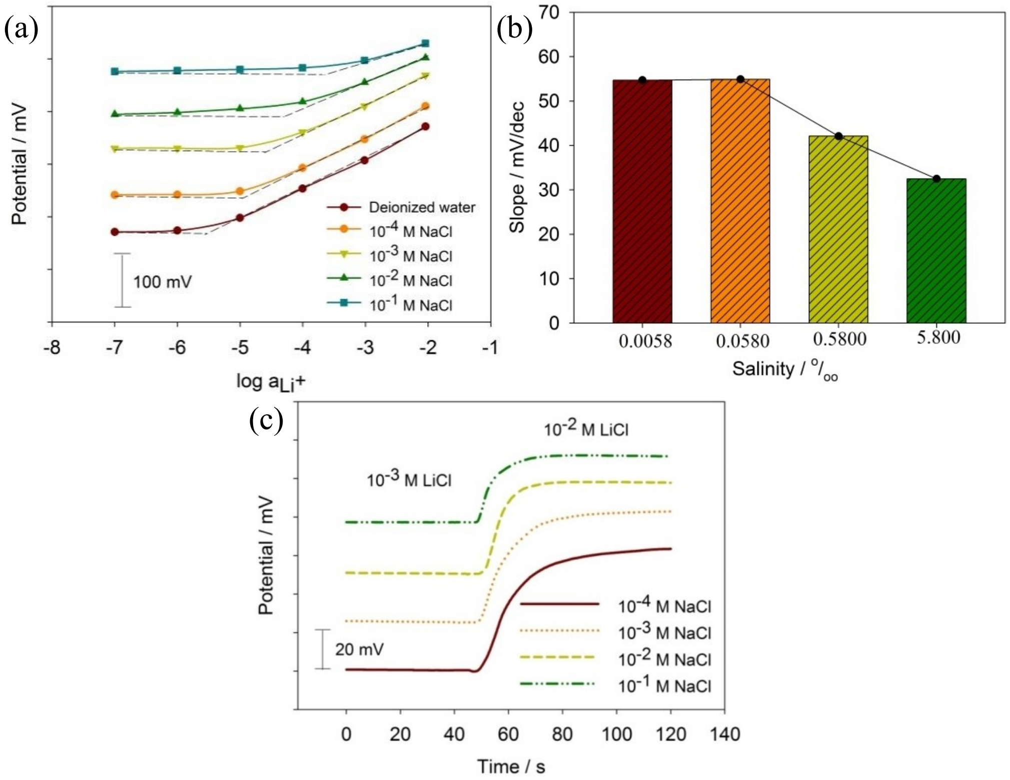

Fig. S11 Effect of NaCl at different concentrations on the potentiometric responses of the er-LIG based integrated potentiometric sensing chip (a), the relationship curve of the slope vs. salinity (b), and effects of NaCl at the different concentrations on the response time (c).

Table S4 Results of Li^+ concentration in spiked tap water, mineral water and river water obtained by using the er-LIG based integrated potentiometric sensing chip

Sample	pH	Salinity (‰)	Added (10^{-4} M)	Found (10^{-4} M) [a]	Recovery (%)
Tap water 1	7.6	0.3	0	n.d.	
			1.00	1.04 ± 0.05	104
Tap water 2	7.7	0.3	0	n.d.	
			1.50	1.49 ± 0.02	99
Mineral water	7.0	0	0	n.d.	
			0.15	0.15 ± 0.02	100
River water 1 [b]	8.0	0.5	0	n.d.	
			1.00	1.05 ± 0.04	105
River water 2 [b]	8.0	0.5	0	n.d.	
			1.50	1.53 ± 0.07	102

[a] n.d: not detectable. The other values are the average values of three determination ± standard deviation

[b] The samples were diluted to 10 times.

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