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A physical organogel electrolyte: characterized by *in situ* thermo-irreversible gelation and single-ion-predominant conduction

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Electrolytes are characterized by their ionic conductivity (σ_i). It is desirable that overall σ_i results from the dominant contribution of the ions of interest (e.g. Li^+ in lithium ion batteries or LIB). However, high values of cationic transference number (t_+) achieved by solid or gel electrolytes have resulted in low σ_i leading to inferior cell performances. Here we present an organogel polymer electrolyte characterized by a high liquid-electrolyte-level σ_i ($\sim 10^1 \text{ mS cm}^{-1}$) with high t_+ of Li^+ (> 0.8) for LIB. A conventional liquid electrolyte in presence of a cyano resin was physically and irreversibly gelled at 60°C without any initiators and crosslinkers, showing the behavior of lower critical solution temperature. During gelation, σ_i of the electrolyte followed a typical Arrhenius-type temperature dependency, even if its viscosity increased dramatically with temperature. Based on the Li^+ -driven ion conduction, LIB using the organogel electrolyte delivered significantly enhanced cyclability and thermal stability.

Fluids conveying ions, called electrolytes, are omnipresent in nature. Ions in cytoplasmic and extracellular fluids develop potential difference through cell membranes for transferring cell signals or activating intracellular processes. As an ionic conductor, the electrolytes complete a circuit in electrochemical cells together with electrodes as electric conductors. Therefore, they are the essential part of supercapacitors, batteries and fuel cells. Fluidity of matrix materials is not necessarily required (e.g. solid-state electrolytes) only if the movement of ions through the matrix is guaranteed.

The most important parameter of electrolytes used in electrochemical cells is ionic conductivity (σ_i). A wide spectrum of electrolyte systems covers a wide range of σ_i from $10^{-5} \sim 10^0 \text{ mS cm}^{-1}$ for solid electrolytes to $10^0 \sim 10^2 \text{ mS cm}^{-1}$ for liquid electrolytes¹⁻³. The use of solid-state electrolytes has been limited due to low σ_i caused by their immobile matrix, even if they have their own merits such as no leak, non-volatility, mechanical strength and processing flexibility. Gel electrolytes were invented to combine high σ_i of liquid electrolytes with the advantages of solid electrolytes.

The second parameter we should consider is transference number of ions of interest. Cationic transference number (t_+) of Li^+ ions in liquid electrolytes for lithium ion batteries ranges from 0.20 to 0.50, indicating that anions are more responsible for overall conduction⁴⁻⁶. Li^+ ions strongly solvated by solvent molecules move slowly compared with naked anions⁴. High t_+ is a desired property in cases that the cationic species in electrolyte are involved in electrochemical reactions on or in electrodes such as H^+ in fuel cells and Li^+ in lithium ion batteries. In lithium ion batteries as a representative case, the anion-dominant conduction ($t_+ < 0.5$) leads to a serious concentration polarization due to highly concentrated population of anions instead of Li^+ in vicinity of electrode surface during operation^{3,4,7}. The mass-transfer problems are even more serious in highly viscous or solid electrolytes.

To avoid the reverse polarization caused by low t_+ , cationic conduction needs to prevail over its counterpart. One of the extreme cases is the single ion conductor ($t_+ = 1$) as a form of solid polymer electrolytes in which polymer backbone have anionic moieties and Li^+ ions move from one anionic sites to another along polymeric backbone⁸⁻¹¹. However, the satisfactory values of σ_i as high as that of liquid electrolyte have not been reached even if such a high t_+ was obtained. From a commendable review on electrolytes for lithium ion batteries⁴, the following comment is worthy to be cited: “the increase in the overall conductivity should originate, at least partially, from the improvement in the cation conductivity.”



In this work, therefore, we materialized the two required properties simultaneously in a polymer gel electrolyte: a liquid-electrolyte-level σ_i ($\sim 10^1$ mS cm $^{-1}$) with high t_{Li^+} (>0.8). Cyanoethyl polyvinyl alcohol (PVA-CN) played a key role in the highly conductive *gel* electrolyte while another cyano resin, cyanoethyl pullulan (Pullulan-CN), were used as a control representing a *liquid* electrolyte containing cyano chains (Fig. 1a). The PVA-CN-containing *liquid* electrolyte was thermally gelled even without any chemical crosslinkers or polymerization initiators (Fig. S1 and S2). Following the increasing temperature history, the polymer-containing electrolyte showed the behaviour of lower critical solution temperature (LCST) with an endothermic first-order transition¹² (onset = 46.5°C, peak = 57°C, completion = 70°C in Fig. 1b). There were no chemical changes between before and after gelation in infrared spectra. Phase separation or gelation indicated by a growing viscosity

was observed after the onset point (Fig. 1c). The LCST phase separation leading to gelation is driven by unfavored entropic change of mixing ($\Delta S_{mix} < 0$)¹³.

Results

Gelation. PVA is difficult to be solvated by polar or high dielectric solvent molecules such as ethylene carbonate (EC)-based electrolytes due to its strong intrachain or interchain hydrogen bonding or dipole-dipole interaction (Fig. S3). On the contrary, the dosing of cyanoethyl groups to PVA depresses or hinders the intra/interchain hydrogen bonding, enabling PVA-CN soluble in polar solvents or EC-based electrolytes (cf. polyacrylonitrile (PAN) is solubilized in the same electrolyte, Fig. S3). By first-principles density functional calculations, PVA-CN was estimated to be bound with EC at a closer distance with a higher binding energy when compared with PVA (as

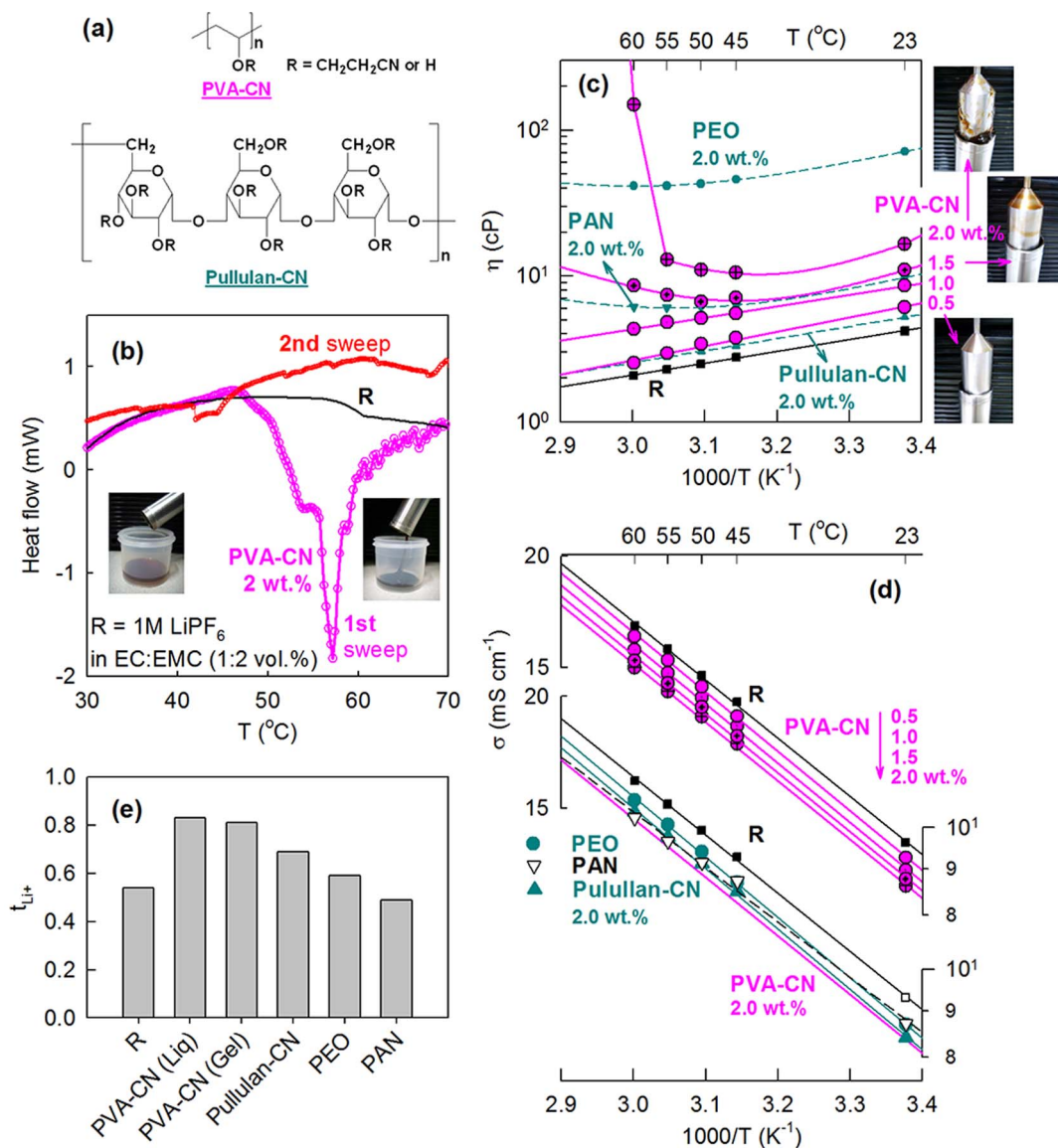


Figure 1 | Properties of the organogel electrolyte based on PVA-CN. (a) Molecular structures of nitrile-containing polymers. (b) Differential-scanning-calorimetric (DSC) thermograms of a liquid electrolyte (R = 1 M LiPF₆ in 1:2 (vol.) EC:EMC where EMC = ethyl methyl carbonate) in absence and presence of PVA-CN in 2 wt.%. The PVA-CN-containing electrolyte was scanned at 5°C min⁻¹ two times consecutively under nitrogen atmosphere. The inset photos show that the PVA-CN-containing electrolyte becomes highly viscous or thicker after thermal treatment around 60°C in the first scan (from left photo to right one). (c to e) Viscosity (η), electric conductivity (σ) and cationic transference number of Li⁺ (t_{Li^+}) of various polymer-containing electrolytes as a function of temperature. Viscosity and conductivity were measured from room temperature to 60°C after thermal equilibrium was reached at each temperature. The photos on the right of (c) are the pictures of disassembled spindle/chamber units of viscometer after viscosity measurement at 60°C. The larger amount of sticky dark brown gel is observed with 2.0 wt.% PVA-CN between spindle and chamber.



an OH-only control) and PAN (as a CN-only control): equilibrium distance = 2.48 Å for PVA-CN versus 2.9 Å for PVA and 2.92 Å for PAN; binding energy = -0.37 eV for PVA-CN versus -0.02 eV for PVA and -0.19 eV for PAN (Fig. S4).

Increase in temperature reduced viscosity of the PVA-CN-containing electrolyte (before gelation) due to thermal motion as expected from typical polymer solutions such as PAN in electrolyte (Fig. 1c). However, the typical temperature dependency of viscosity was bound up to the onset temperature of the endothermic peak of thermogram (Fig. 1b). Viscosity dramatically increased during the endothermic process and could not be measured after the peak temperature because torque of rotating bar of viscometer reached its maximum value (>150 cP). The thermally initiated physical gelation would be induced by entropic gain of Gibbs free energy¹³. The ordered polar solvent molecules surrounding hydroxyl and nitrile groups of PVA-CN are escaped from the local interaction and came back to its original liquid phase with a disordered configuration. Endothermic energy is utilized to overcome the interaction between solvent molecules and functional groups bound to polymeric chains. Simultaneously, a strong intra/interchain bonding in PVA-CN is expected to be developed. Ions of lithium salt in electrolyte (both Li⁺ and PF₆⁻) is thought to play an important role in the interaction for gelation. Gelation was not reached with the solvent (EC:EMC) in absence of LiPF₆ and with LiClO₄, LiN(CF₃SO₂)₂ and TBAPF₆ (TBA = tetrabutylammonium) in the same solvent. Once the intra/interchain bonding is formed thermally, the phase separation or gelation was not reversibly liquidated. There were no apparent peaks indicating the first order transition in the second scan of temperature (Fig. 1b).

Transport properties. The most impressive observation comes with the ionic conductivity (σ_i) of PVA-CN-containing electrolyte (Fig. 1d). Practically, high viscosity (η) accompanies with low σ_i . Contrary to the practical η -dependency of σ_i , the values of σ_i of PVA-CN-containing electrolyte monotonically increased with temperature independent of η . Even after serious gelation with high viscosity at 60°C, the gel electrolyte did not show any serious decrease in conductivity: 15.0 mS cm⁻¹ for PVA-CN-based gel electrolyte versus 16.7 mS cm⁻¹ for the base electrolyte at 60°C. Also, the conductivity of PVA-CN gel electrolyte at 23°C was estimated at 8.63 mS cm⁻¹ (c.f., 9.63 mS cm⁻¹ for the base electrolyte), the value of which is exactly the same as that of PVA-CN-containing liquid electrolyte before gelation. The room-temperature σ_i values obtained with our PVA-CN gel electrolyte is the highest or the most competitive values among gel electrolytes developed until now as far as we know. Top values of σ_i of gel electrolyte include 7 mS cm⁻¹ for 5 wt.% PMMA¹⁴ and 4 mS cm⁻¹ for 19 mol% PAN¹⁵.

With such a high value of σ_i , the conduction mechanism was investigated in terms of cationic transference number (t_+). Typical electrolytes containing Li⁺ have t_+ from 0.3 to 0.5 for liquid type⁶ and from 0.4 to 0.6 for gel type⁶. The t_+ of Li⁺ ions was estimated by electrochemical methods with Li⁺ metal symmetric cells in presence of a polymer separator (Fig. 1e). The PVA-CN-containing liquid electrolyte and its gelated version showed not complete single ion conduction but Li⁺ ion-dominant conduction with $t_+ = 0.84$. The value was clearly distinguished from that of the base electrolyte estimated at $t_+ = 0.52$ on which cationic and anionic currents are well balanced. By first-principles density functional calculations, introduction of the cyanoethyl groups into PVA backbones resulted in the contrary effects on PF₆⁻ and Li⁺ (Fig. 2). PVA-CN was more strongly bound with PF₆⁻ and more loosely bound with solvated Li⁺ (Li⁺(EC)) when compared with PVA and PAN: PVA_{H-H}-CN (-1.3 eV) < PVA_{H-H}-CN_H (-0.71 eV) < PVA_H (-0.42 eV) in equilibrium binding energies (BE_{eq}) of PF₆⁻ (Fig. 2a, refer to the figure caption for the notation of binding sites); PVA-CN_{N-N} (-2.64 eV) < PVA_{O-O} (-2.5 eV) < PVA_O-CN_O (-2.0 eV) in

BE_{eq} of Li⁺ (Fig. 2e). Also, the migration barriers (E_a) to hinder the ionic transport from an equilibrium position (IS, initial state) to the next one (FS, final state) through polymeric backbone of PVA-CN were estimated higher with PF₆⁻ and lower with Li⁺(EC) than those of PVA and PAN (b to d for PF₆⁻ and f to h for Li⁺(EC) in Fig. 2); preferred E_a of PF₆⁻ transport = 0.09 eV (0.22 eV not preferred) for PVA-CN > 0.06 eV for PVA > 0.05 eV for PAN; preferred E_a of Li⁺ transport = 0.19 eV (0.61 eV not preferred) for PVA-CN < 0.46 eV for PAN < 0.56 eV for PVA. Accordingly, Li⁺ transport is more preferred to PF₆⁻ transport in PVA-CN in comparison with PVA and PAN. This forced conduction mechanism supports the fast ion conduction in the highly viscous or gelled media.

Electrolyte for lithium ion batteries. The PVA-CN gel electrolyte, characterized by high ionic conductivity that single ion is dominantly responsible for, was tested in lithium ion rechargeable batteries. Its thermo-irreversible gelation property is helpful to develop well-contacted electrolyte-active material composite. The liquid electrolyte prepared by dissolving 2 wt.% PVA-CN in 1:2 (vol.) EC:EMC of 1 M LiPF₆ in presence of fluoroethylene carbonate (FEC) as an additive was injected through one-side opening into pouch cells of LiCoO₂ as a cathode and graphite as an anode with a polymer separator. After enclosing them, the pouch full cells experienced thermal curing at 60°C for one day, which is a typical (not additional) procedure adopted in battery cell makers to stabilize electrochemistry inside cells. During the aging process, thermo-irreversible gelation of PVA-CN proceeds wherever the polymer mass penetrates during wetting (inside pores of porous composite electrodes and separators).

At the first charge of polarizing the cathode material positively and the anode material negatively, FEC was anodically decomposed to form a passive layer called solid-electrolyte interface (SEI) layers at 2.9 V cell potential (Fig. 3a). When compared with the base liquid electrolyte (liq.ELF), the charge consumed for the SEI layer formation (Q_{SEI}), equivalent to the amount of the SEI layer, significantly decreased with PVA-CN gel electrolyte (gel.ELF + PVA-CN) and pullulan-CN liquid electrolyte (liq.ELF + Pullulan-CN): from $Q_{SEI} = 34.8$ C for liq.ELF to 12.3 C for gel.ELF + PVA-CN or 14.2 C for liq.ELF + Pullulan-CN. The resultant higher initial coulombic efficiency obtained by depressing the electrolyte decomposition would be a positive point only if cell performances were not negatively affected. The cyanoethyl polymers probably hinder the decomposition process by their adsorption on surface (liq.ELF + Pullulan-CN)¹⁷ or direct contact of the gel mass on graphite (gel.ELF + PVA-CN).

Over its liquid controls (liq.ELF and liq.ELF + Pullulan-CN), gel.ELF + PVA-CN showed equivalent or slightly better rate capability delivering slightly higher capacity at room temperature especially at discharge rates higher than 3 C rate: capacity at 3 C (Q_{3C}) = 64.6% for gel.ELF + PVA-CN versus 62.7% for liq.ELF + Pullulan-CN and 57.9% for liq.ELF (Fig. 3b and Fig. S5). The potential profiles during discharge were exactly the same between the gel electrolyte and its liquid controls at 0.1 C ($t_{dCh} = 1$ h) as a slow rate. The main enhancement at 3 C with gel.ELF.PVA-CN is observed at high over-potential range of 3.2 V to 3.0 V in which concentration polarization is dominant over activation polarization. The high value of t_+ of our organogel electrolyte is expected to be helpful to solve the mass transfer limitation problems.

The extent of capacity decrease with cycles was clearly less serious for our organogel electrolyte when compared with that of liq.ELF as well as liq.ELF + Pullulan-CN (Fig. 3c and d). At higher temperature (60°C), the difference of capacity between the gel-type and the liquid-type electrolytes became more emphasized. The enhanced thermal stability is evidently shown in the change of pouch cell thickness caused by gas evolution due to side reactions (Fig. 3e). The side reactions can be depressed by blocking direct contacts of electrolyte

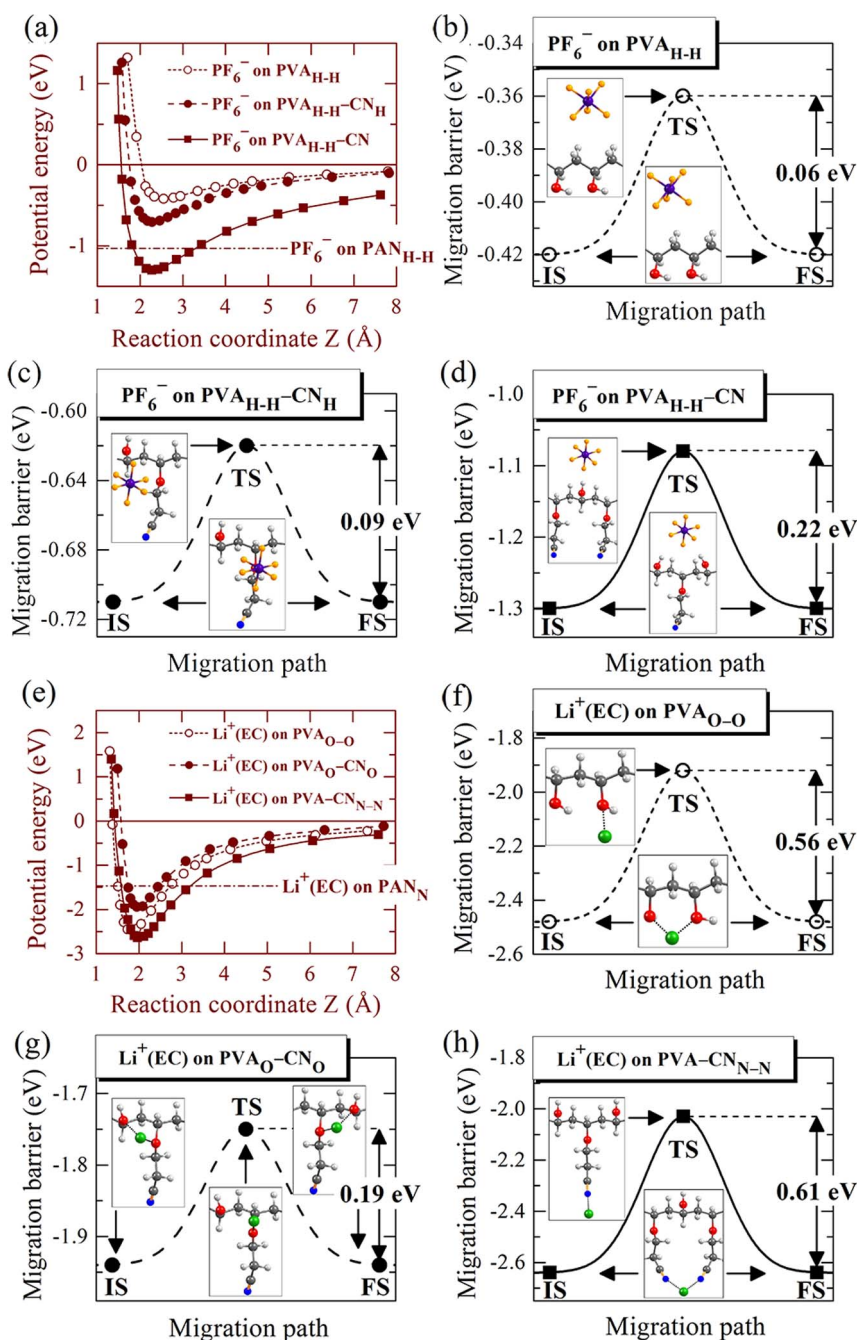


Figure 2 | Binding affinity and migration barriers of PF_6^- and solvated Li^+ ($\text{Li}^+(\text{EC})$) on PVA-CN, PVA (as the OH-only control) and PAN (as the CN-only control). (a and e) Binding energy profile with respect to the distance between the polymers and PF_6^- (a) or $\text{Li}^+(\text{EC})$ (e). Each curve in (a) corresponds to the binding sites favored by PF_6^- located at the intermediate position between hydrogen atoms of alcoholic groups of PVA or PVA-CN (PVA_H or $\text{PVA}_\text{H-CN}$); and between hydrogen atoms of alcoholic and cyanoethyl groups in PVA-CN ($\text{PVA}_\text{H-CN}_\text{H}$). Each curve in (e) corresponds to the binding sites favored by $\text{Li}^+(\text{EC})$ between O atoms of alcoholic groups of PVA ($\text{PVA}_\text{O-O}$); between O atoms of alcoholic and cyanoethyl groups in PVA-CN ($\text{PVA}_\text{O-CN}_\text{O}$); and between N atoms from cyanoethyl groups of PVA-CN ($\text{PVA-CN}_\text{N-N}$). Horizontal dash-dotted lines indicate the calculated binding energy of PAN at its equilibrium distance. (b to d and f to h) Migration coordinates of PF_6^- (b to d) or $\text{Li}^+(\text{EC})$ (f to h) from an equilibrium position (IS, initial state) to the next one (FS, final state). Insets depict atomic visualization of binding configurations at transient states (TS) as well as IS and FS. Atoms are depicted as balls with H = white small, C = gray, O = red, N = blue, P = purple, F = yellow and $\text{Li}^+(\text{EC})$ = green. Li^+ solvated by a single EC molecule ($\text{Li} + (\text{EC})$) is assumed, which is symbolized by a single ball for simplicity.

with electrode like a coating effect. In addition, the mechanical strength of the organogel as well as the adhesion force between the gel and current collectors is partly responsible for the smaller swelling of cells. At higher temperatures, the exothermic heat flows triggering thermal runaway were also mitigated by use of the cyano

resins as clearly shown in the first peak around 215°C of differential scanning calorimetry (DSC) thermogram (Fig. 3f). The second peak was observed in the organogel electrolyte at the same temperature of the base electrolyte (~270°C) while the exothermic process started at lower temperature (~255°C) with liq.ELF + Pullulan-CN.

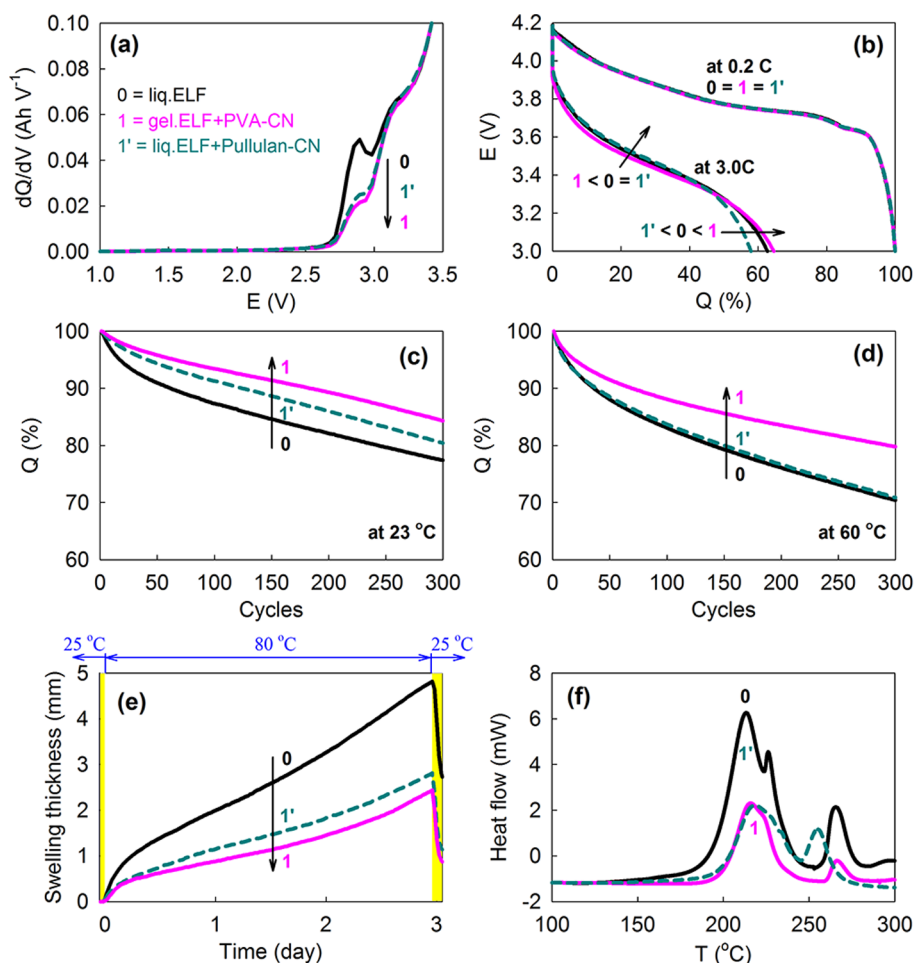


Figure 3 | Electrochemical and electrochemistry-associated behaviours of pouch-type lithium-ion-battery full cells using the organogel electrolytes based on PVA-CN (gel.ELF + PVA-CN). Liquid electrolytes (liq.ELF and liq.ELF + Pullulan-CN) are included for comparison. LiCoO_2 and graphite were used as cathode and anode, respectively. (a) dQ/dV as a function of potential (E) during the 1st charge related to forming solid-electrolyte interface (SEI) layers. (b) Potential profiles during galvanostatic discharges at 0.2 C and 3.0 C. The cells were charged at 0.2 C galvanostatically and then at 4.2 V potentiostatically until their current reached 5% of 0.2 C. (c and d) Capacity retention through cycles at 23 °C and 60 °C, respectively (Q = capacity, % relative to a designed value, 750 mAh). A single cycle consisted of galvanostatic charging at 1 C with following potentiostatic mode at 4.2 V up to 5% of 1 C and galvanostatic discharging at the same rate. (e) Dimensional change of pouch-type cells stored at 80 °C for three days. (f) DSC thermograms of 4.2 V-charged Li_xCoO_2 cathodes. Temperature was scanned at 10 °C min^{-1} .

Discussion

In this work, we reported on a new type of physical organogel electrolyte that is represented by two unique characteristics: (1) an irreversible thermal gelation and (2) a high value of Li^+ transference number ($t_+ = 0.84$). Its ionic conductivities were estimated at the values close to that of liquid electrolytes at a temperature range from room temperature ($\sigma_{RT} = 8.63 \text{ mS cm}^{-1}$) to 60 °C ($\sigma_{60} = 15 \text{ mS cm}^{-1}$). When the organogel was used as an electrolyte for a lithium ion battery cell, performances especially at high rate discharges and thermal stability were enhanced. The organogel could be applied to other electrochemical cells including other type of rechargeable batteries, supercapacitors, dye-sensitized solar cells and electrochromic devices, accommodating various pairs of ionic species and solvents. We believe that this new type of electrolyte gel provides design flexibility of devices as well as enhanced safety and stability to electrochemical devices.

Methods

Electrolytes. 1 M LiPF_6 in 1 : 2 (vol.) EC:EMC was used as a base liquid electrolyte for investigating basic physicochemical properties. All solvents were dried with activated molecular sieves and then distilled before use. 2 wt.% of polymers (Pullulan-CN, PEO or PAN) was dissolved in the base electrolyte while the content of PVA-CN was tuned

from 0.5 wt.% to 2.0 wt.%. For lithium ion battery tests, 2 wt.% FEC was added as an SEI-forming additive into the electrolytes. All electrolytes were prepared in a glove box ($<0.1 \text{ ppm H}_2\text{O}$ and O_2 ; MBraun).

Ionic conductivity (σ). The σ of electrolytes was measured in a dry room by a conductivity meter (Mettler-Toledo, SevenGo Duo pro with a InLab 731 carbon 4-pole conductivity probe).

Viscosity (η). The η of electrolytes was measured at a controlled temperature by using a viscometer (Brookfield, DV-II+ Pro with SC4-18 spindle).

Cationic transference number (t_+). The values of t_+ for Li^+ in electrolytes were determined using a potentiostatic polarization method¹⁸. Symmetric cells were configured with liquid or gel electrolytes in a porous separator that is sandwiched by lithium metals. The initial and steady-state values of current of the cells were measured in a Faraday cage after and before polarization with a small polarization potential at 10 mV by a potentiostat (Biologic, VSP), respectively. The initial and steady-state values of contact resistance were determined by impedance measurements (10 mHz to 200 kHz) shortly before and after the potentiostatic polarization.

Calorimetry. Thermal behaviors of electrolytes were investigated by using differential scanning calorimeter (Mettler-Toledo, DSC823^o). The PVA-CN-containing electrolyte was thermally scanned twice up to 70 °C at 5 °C min^{-1} under nitrogen atmosphere to trace its gelation process. The reference electrolyte was tested in the same manner for comparison. All samples were injected into aluminium hermetic pans in a dry room. Also, thermal properties of cathodes were investigated



from 40 °C to 300 °C at 10 °C min⁻¹ (TA instruments, Q100). Cathode samples obtained from full cells fully charged at 4.2 V were transferred into a high-pressure cylindrical vessel in a dry room.

Battery cells. 750 mAh pouch-type full cells were constructed with a porous polyethylene separator (Asahi, NH616). Cathodes were prepared by mixing LiCoO₂ (Umicore, KD 10) with 2 wt.% carbon black (Super-P) and 3 wt.% polyvinylidene fluoride (PVDF) (Kureha, KF1000). Anodes were prepared by slurring natural graphite (Sodif, DAG-87) with 1.5 wt.% styrene-butadiene rubber (SBR) (Zeon, BM400B) and 1 wt.% carboxy-methyl cellulose (CMC) (Daichi, BSH12). The slurries were coated onto aluminium foil for cathodes or copper foil for anodes, followed by drying at 80 °C under vacuum. Cells were galvanostatically charged to 4.2 V at room temperature and then potentiostatically charged at 4.2 V when current reached 5% of charging current. Then, they were discharged to 3 V galvanostatically. A battery tester (BaSyTec, CTS-LAB) was used for cycling charge and discharge.

Thickness. Thickness of fully charged pouch cells was measured at 80 °C every minute for 3 days by a thickness recording reader (Mitutoyo, DP-1 VR).

First-principles density functional calculations. The Vienna Ab-initio Simulation Package (VASP) was used with the energy cut-off of 400 eV for the plane-wave basis set^{19–22}. The Perdew-Burke-Ernzerhof-type gradient-corrected exchange-correlation potential was employed for the electrons exchange-correlations²³. The polymer chain structure was modeled by the periodically repeated unit cell along the chain axis.

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Author contributions

Y.-S.K.: the first finding, synthesis and physicochemical and electrochemical analysis of organogel electrolytes. Y.-G.C.: gelation of various electrolytes and preparation of monolithic gels. D. O. and N.P.: first-principles density functional calculations and related writing. H.-K.S.: project planning and leading, data analysis and writing.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

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