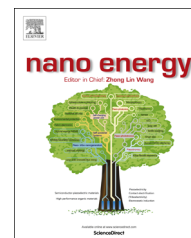




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RAPID COMMUNICATION

Highly porous piezoelectric PVDF membrane as effective lithium ion transfer channels for enhanced self-charging power cell



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Abstract

A self-charging power cell (SCPC) is a structure that hybridizes the mechanisms for energy conversion and storage into one process through which mechanical energy can be directly converted into electrochemical energy. A key structure of an SCPC is the use of a polyvinylidene fluoride (PVDF) piezo-separator. Herein, we have fabricated a piezoelectric β -form PVDF separator with a highly porous architecture by introducing ZnO particles. The electrochemical charge/discharge performance of this SCPC was greatly enhanced at lower discharge rates compared to highly stretched (high- β -content) or less porous PVDF membranes. The lower charge-transfer resistance of this well-developed porous piezo-separator is the main factor that

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facilitated the transport of Li^+ ions without sacrificing piezoelectric performance. This study reveals a novel approach for improving the performance of SCPCs.
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Introduction

Piezoelectric nanogenerators have been recently garnering substantial attention in a variety of energy conversion and storage applications because of their remarkable intrinsic properties, such as a rapid electromechanical effect and relatively high force generation following a small external stimulus [1–6]. Among them, polyvinylidene fluoride (PVDF) with a predominantly β -phase crystal structure is investigated as the most widely available piezoelectric polymer for practical energy-generating devices [7–9]. Research utilizing the piezoelectricity of β -phase PVDF has been recently expanding into sustainable and renewable energy sources that can simultaneously exhibit energy harvesting and storage abilities, which has been accomplished by integrating the polarized PVDF polymer into an electrochemical system such as lithium-ion secondary batteries and supercapacitors [2,10–14]. The hybridization of the two separate energy processes (i.e., mechanically harvesting energy created from a piezoelectric potential and storing electrochemical energy induced by ion migration) provides an innovative method of self-charging that can supply continuous power from the environment without the need for an external power source.

Rechargeable Li-ion batteries (LIBs), long positioned as an attractive power source in terms of energy storage, have aimed at maintaining their integrity over many charge/discharge cycles [15]. Thus, the introduction of a stabilized PVDF piezo-separator with the self-charging function as a replacement for the conventional polyethylene (PE) separator can be regarded as one of the most critical concerns required to maintain cell sustainability in LIBs. However, an important limitation exists concerning the practical application of a piezo-separator; the less- or non-porous structure of a PVDF piezo-separator causes ineffective migration of Li^+ ions from lithium transition metal oxide (e.g., LiCoO_2) to a counter electrode such as graphite, despite its self-charging capability through a mechanical-to-electrochemical process. Generally, to maximize piezoelectric performance as the means for self-charging, the PVDF film must have a high β -phase content, which can be achieved through uni- or biaxial stretching processes [16,17]. Unfortunately, these processes eliminate porosity within a PVDF membrane (Supporting information, S-1), which makes it difficult for the cells to charge and discharge galvanostatically, even at extremely low rates (Supporting information, S-2).

Thus, effective Li-ion transfer and outstanding piezoelectric output have become important considerations in the development of a β -phase PVDF piezo-separator with the self-charging feature. In this work, we focused on the design of a piezoelectric separator having well-defined porosity without sacrificing electrochemical performance. As the first step, we introduced ZnO particles to act as

nucleating agents to induce the formation of the piezoelectric β -form and impart good solubility in acidic solution [8]. Second, the amount of ZnO particles was optimized because they strongly affect the porosity and flexibility of the PVDF piezo-separator. A self-charging power cell (SCPC) fabricated with the optimized highly porous PVDF piezo-separator exhibited a charge/discharge profile (ca. 80% discharge capacity at 0.05 C) that was superior to that of a solution-cast PVDF separator without ZnO particles (ca. 10% at 0.05 C) or of a highly stretched commercial PVDF separator (0% at 0.05 C). This is an important advance in PVDF piezo-separator development toward improved electrochemical performance and self-charging. It was evaluated in a conventional battery model; the schematic diagram in Figure 1a shows the structure of the SCPC wetted with a carbonate-based electrolyte containing 1 M LiPF_6 salt. It used LiCoO_2 as the cathode (Figure 1b) and artificial graphite as the anode (Figure 1c) with a porous ZnO-free PVDF separator.

Experimental section

Fabrication of a highly porous PVDF separator

PVDF powder (Sigma-Aldrich, M_w ca. 534,000) was fully dissolved in *N,N*-dimethylformamide (DMF; Sigma-Aldrich, > 99.9%) solvent (10 wt%) at 23 °C. Then, ZnO particles (Alfa Aesar, 99.99%, avg. 200 nm size) with the same mass as the PVDF were added to the viscous PVDF solution. The PVDF/ZnO suspension was stirred at high speed and then treated in an ultrasonic bath for 1 h to provide a uniform dispersion. The mixture was then coated onto a glass substrate that had been previously cleaned with acetone; a razor blade provided a film of constant thickness. The coated mixture was dried at 60 °C in an oven to evaporate the solvent. Then the prepared thin film was carefully immersed in aqueous concentrated hydrochloric acid (37 wt%), etched for more than 12 h to completely eliminate ZnO particles, and washed several times with deionized water. Highly porous PVDF thin separators (30–40 μm thick) with well-constructed Li^+ paths were thus obtained. These separators were purged under an argon gas atmosphere for 1 h at room temperature before cell fabrication.

Poling process to develop piezoelectric behavior

To electrically polarize the porous PVDF separator, aluminum (Al) metal was deposited on both sides of the separator using an E-beam evaporator; the thickness of the Al coating was ca. 500 μm . The treated separator was then poled at room temperature for 2 h in an electric field of 20 $\text{V } \mu\text{m}^{-1}$ to align the randomly organized β -form dipoles. No breakdown or fluctuation of the applied voltage occurred, indicating the stability of PVDF nanogenerators for poling process

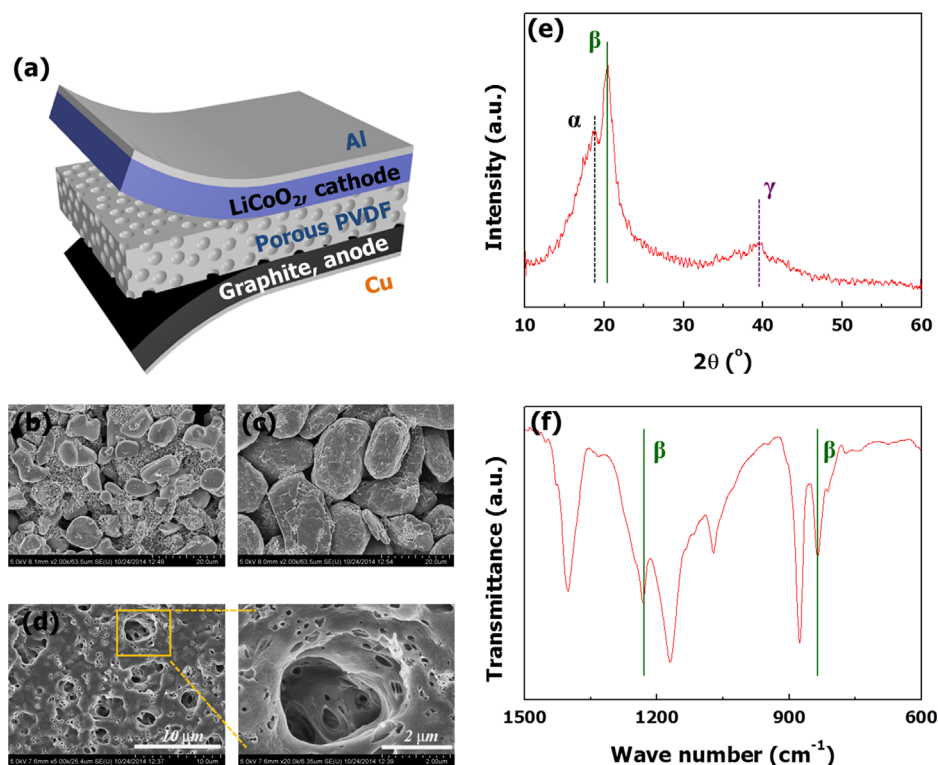


Figure 1 (a) Schematic diagram of an SCPC consisting of LiCoO₂ as the cathode, artificial graphite as the anode, and a porous PVDF piezo-separator. Morphological image of the cathode (b) coated on an Al sheet and the anode (c) coated on a Cu sheet. (d) PVDF surface image showing the amorphous macro- and mesoporous structure at low (left) and high (right) magnifications. (e) XRD pattern showing complete elimination of the ZnO particles and growth of the β -phase PVDF, which is supported by the observed FTIR-ATR peaks (f).

without any defect. The PVDF piezo-separator deposited with Al was sealed in the absence of electrolyte into a stainless steel 2016 size coin cell and the piezoelectric behavior of the poled PVDF separator was measured in a Faraday cage. The electrical potential output detected from the poled PVDF film was recorded with a Keithley 6514 Electrometer.

Structural characterization of the PVDF thin film

The surface morphology of the porous PVDF film was characterized using a Hitachi SU8010 scanning electron microscope (SEM). The crystalline phases present in the thin film were identified by Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) using an instrument equipped with a zinc selenide (ZnSe) crystal plate (Nicolet iS5 Spectrometer, Thermo Scientific) and by X-ray diffraction (XRD; X'Pert PRO, PANalytical B.V.) operating in continuous scanning mode with $10^\circ < 2\theta < 60^\circ$.

Electrochemical analysis and cell design

Stainless steel 2016 coin full cells were employed with the poled PVDF porous separator exhibiting good wettability to the carbonate-based electrolyte. Cathodes were prepared by coating a slurry of LiCoO₂ (KD10, Umicore N.V.), 2 wt% Super P (Timcal Graphite & Carbon), and 2 wt% PVDF binder (KF7208, Kureha Corp.) on Al foil (15 μ m, Sam-A Aluminum

Co., Ltd.). Anodes were prepared by coating a mixture of artificial graphite (Sumitomo-AR, Sumitomo Corp.) with 2 wt% Super P and 5 wt% PVDF binder (KF9130, Kureha Corp.) on copper (Cu) foil (10 μ m, Iljin Materials). All electrodes were dried at 90 °C under vacuum after razor-blade coating. An electrolyte solution comprising 1 M LiPF₆ (water content ca. 10 ppm; Soulbrain MI) dissolved in ethylene carbonate (EC) and ethyl-methyl carbonate (EMC) (1:2 v:v) was dried with activated molecular sieves and filled into the cell before use. Cells were galvanostatically charged to 4.2 V and then discharged to 3.0 V at room temperature at a rate of 0.05 C for stabilization. A battery analyzer (BST8-WA, MTI Corp.) was used for observing electrochemical performance and monitoring self-charging effect during mechanical compressive deformation.

Electrochemical impedance measurement

The impedance spectra of cells in the discharged state were obtained by applying 10 mV ac amplitude in the frequency range of 500 kHz to 10 mHz. For comparison at the same voltage, cells were initially charged at 4.2 V and discharged at 3 V galvanostatically after sufficient time for aging/wetting, i.e., more than 12 h after cell fabrication. All measurements were carried out at room temperature using a potentiostat (VersaSTAT3, Princeton Applied Research) equipped with an electrochemical impedance spectroscopy (EIS) analyzer.

Results and discussion

Highly porous structure of β -form PVDF

The motivation for this work resulted from the inadequate electrochemical performance during which highly stretched non- or weakly porous PVDF films displayed relatively serious charge/discharge capacities due to the absence of channels that would effectively allow the flow of Li^+ ions within the PVDF film (Supporting information S-2). Mechanically uniaxial stretching of PVDF film isothermally at high temperature (e.g., 80 °C) is a well-known technique to increase the β -phase content and thereby greatly improve the piezoelectric properties [18,19]. However, increasing the β -polymorph content in this manner decreases porosity and interferes in the smooth movement of Li^+ ions when the high contents of β -phase PVDF film is used as a separator in lithium-ion secondary batteries. Thus, we focused on how to develop a PVDF membrane having a well-defined porosity without sacrificing its electrochemical performance while maintaining a predominant β -phase form to exhibit piezoelectric characteristic. To simultaneously achieve these requirements, we uniformly dispersed ZnO particles in the viscous PVDF solution, which served several purposes: the ZnO particles acted as nucleating agents to provide the solution-cast PVDF film with a high β -phase content, and the uniform dispersion and facile removal of the particles by etching in acid solution did not damage the PVDF base film and provided well-defined Li^+ paths through the porous structure of the PVDF film. SEM images (Figure 1d) show many random holes well interconnected within the PVDF spherulitic crystal structure, indicating complete etching of the ZnO particles; XRD patterns (Figure 1e) show the growth of the β -phase PVDF and no peak signals corresponding to ZnO particles (Supporting Information S-3). The characteristic peaks at 840 and 1280 cm^{-1} observed in the FTIR-ATR spectrum also confirmed the formation of the β -phase in the ZnO-absent PVDF separator (Figure 1f).

Basic mechanism for the SCPC

Piezoelectric properties were observed for the highly porous Al-coated PVDF separator when it was sealed in a stainless steel 2016 coin cell in the absence of liquid electrolyte. The piezoelectric voltage output of the PVDF film was proportional to the externally applied force: the measured mean values were 2.31 V at 141 mJ, 3.84 V at 282 mJ, and 6.21 V at 423 mJ (Figure 2a). The proportional response occurs because stress applied mechanically along a polarization axis increases strain in the porous PVDF film to generate a temporary flow of free electrons in the piezoelectric field, which results in a higher potential output. The average potentials were higher than those recently reported for other PVDF piezo-separators [2,11,12,14]. These enhanced values are attributable to a geometric strain effect induced by the highly porous structure of the PVDF that contributed to better alignment of dipoles and considerable displacement under external impact [8]. The piezoelectric potential profiles of this porous nanogenerator were also measured under periodic external compressive forces to confirm the piezoelectric polarities. The two potential outputs of the

device shown in Figs. 2b and c indicate that this porous PVDF separator demonstrated complete piezoelectric behavior with two opposite polarizations and maintained its stable polarization (i.e., behavior with no distinct degradation) under a constant compressive force (here, an external force of 353 mJ was applied). The bottom plot of each figure shows the features of the output signal generated during one mechanical compression cycle (i.e., a gradual decrease to the base voltage after apparent peak). The positive and negative output signals were respectively detected with the two opposite connections, indicating the authentic piezoelectric polarities in this porous PVDF piezoseparator.

A coin full cell comprising LiCoO_2 as the cathode and artificial graphite as the anode, with a carbonate-based electrolyte, was fabricated to investigate the self-charging effect of the cells containing the porous PVDF piezoseparator (Supporting information, S-4). The typical self-charging profile for this cell consisted of three processes (Figure 3a): (1) a periodic compression region that shows a self-charging profile with no external current input, (2) a galvanostatic discharge region, and (3) a subsequent equilibrium region at the open-circuit voltage (V_{oc}). When a compression energy or force of 282 mJ [potential energy (E)= mgh ; here, m (mass of the object) was 288 g, g (acceleration due to gravity) was 9.8 m s^{-2} , and h (height) was 100 mm] was applied to the coin cell at a frequency of 1 Hz, the voltage of the cell increased from 1.2 to ca. 1.4 V over 200 s. After completing the self-charging stimulus, the cell was galvanostatically discharged at a constant current of 0.01 mA (0.05 C) to 1.185 V, when the discharge capacity required to return to the original potential (1.2 V) initiating self-charging was ca. 0.4 μAh . Then, the cell voltage typically increased to the equilibrium voltage, V_{oc} . The magnitude of the piezopotential and the self-charging of the device were directly proportional to the magnitude of the external impact. The two curves shown in Figure 3b illustrate the correlation between mechanical stress and piezo properties. When two mechanical forces having different potential energies of 141 and 282 mJ impacted the surface of the cell at a frequency of 1 Hz, the device was self-charged to 1335 and 1400 mV, respectively, after 200 s. Galvanostatic discharge was carried out at a constant 0.01 mA current (here, the discharge capacity at a potential energy of 141 mJ after self-charging was ca. 0.18 μAh), and a higher applied mechanical force enhanced the self-charging effect of the cell. When a constant force of 141 mJ was applied at a frequency of 1 Hz (Figure 3c), the increase in the potential generated from the isomechanical energy remained stable and the behavior was replicated over the two cycles shown. The cell that incorporated this porous PVDF piezo-separator was self-charged even under the stimulus of finger pressure, despite the hard stainless steel casing. Figure 3d shows that the self-charging effect enhanced by finger pressure almost reached the value obtained with an impact potential energy of 141 mJ (equivalent to dropping from a height of ca. 50 mm). The highest mechanical force gave the greatest voltage enhancement of ca. 400 mV and the discharge capacity of ca. 3.04 μAh , confirming the proportional relationship between self-charging and the magnitude of the externally applied mechanical force. Figure 3e shows the stability of the PVDF piezoseparator itself after mechanically shocking the device: no

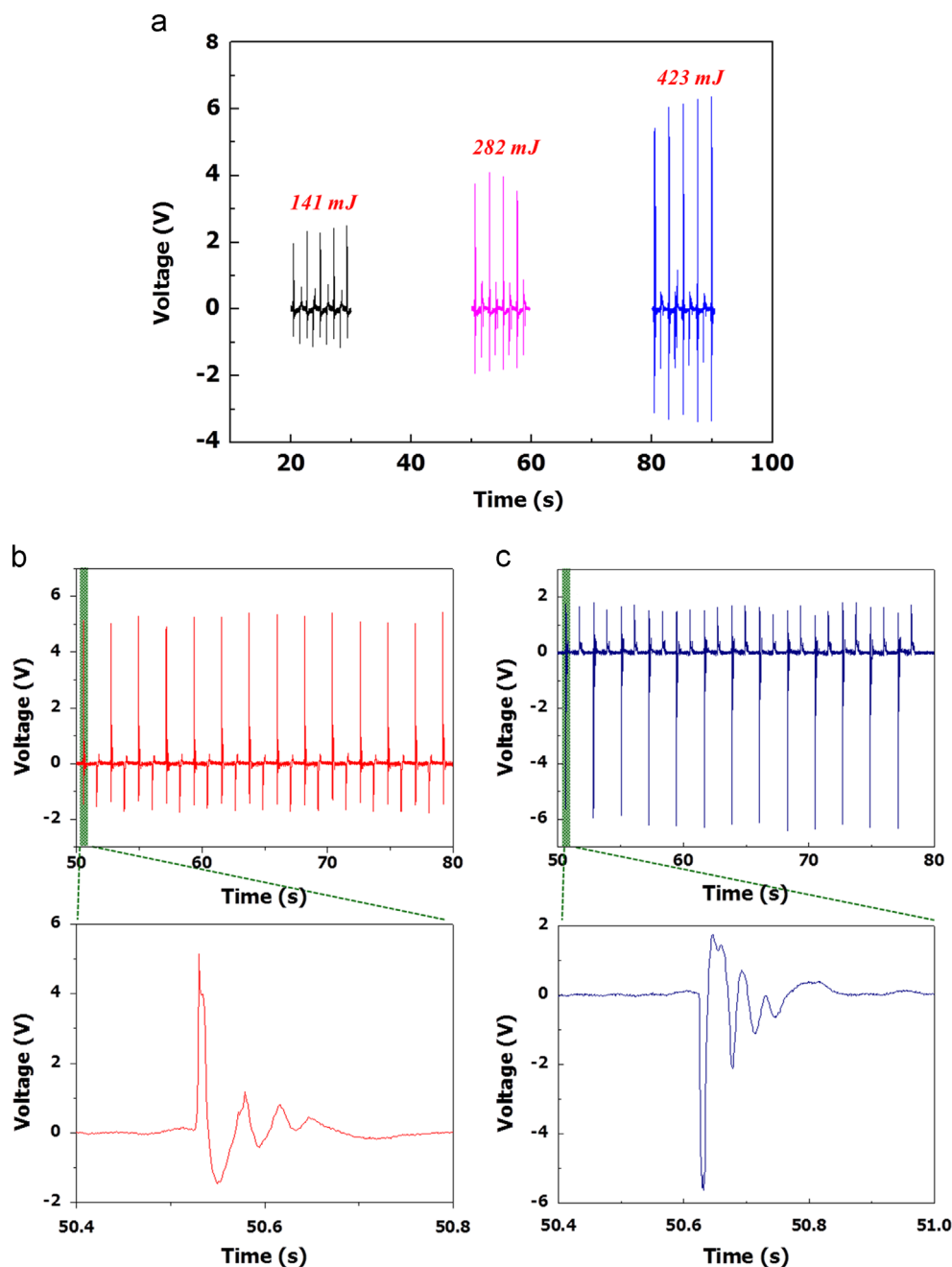


Figure 2 (a) Periodic piezoelectric voltage output of the porous PVDF piezo-separator under externally applied forces of 141, 282, and 423 mJ in the absence of electrolyte. The magnitude of the voltage peak is proportional to the applied mechanical force. (b and c) Characteristic piezoelectric signals obtained in the two opposite polarizations for an externally applied force of 353 mJ. The lower graphs show the voltage output generated during one mechanical compression cycle and confirm the piezoelectric behavior of the porous PVDF separator.

fluctuations occurred within the working potential range for ca. 3000 s at a constant charge and discharge rate of 0.01 mA, indicating that the piezoelectric separator was not damaged or degraded by the mechanical stress.

The direction of the piezoelectric field generated by mechanical compression makes the PVDF piezo-separator maintain a positive piezopotential at the LiCoO_2 surface and a negative piezopotential at the graphite surface because of close contact between the cathode and the anode. This piezoelectric field enables solvated Li^+ ions to easily

migrate or transfer from the positive to the negative electrode through the porous PVDF piezo-separator, providing electron flow within the system. Accordingly, the working mechanism of the SCPC is an electrochemical process operated with the driving force induced from the piezoelectric potential of the β -phase PVDF separator. As illustrated in the schematic diagram of the [Figure 4](#), three major reaction states associated with self-charging are working within the piezoelectric-driven electrochemical system: the initial state is an electrochemically stabilized

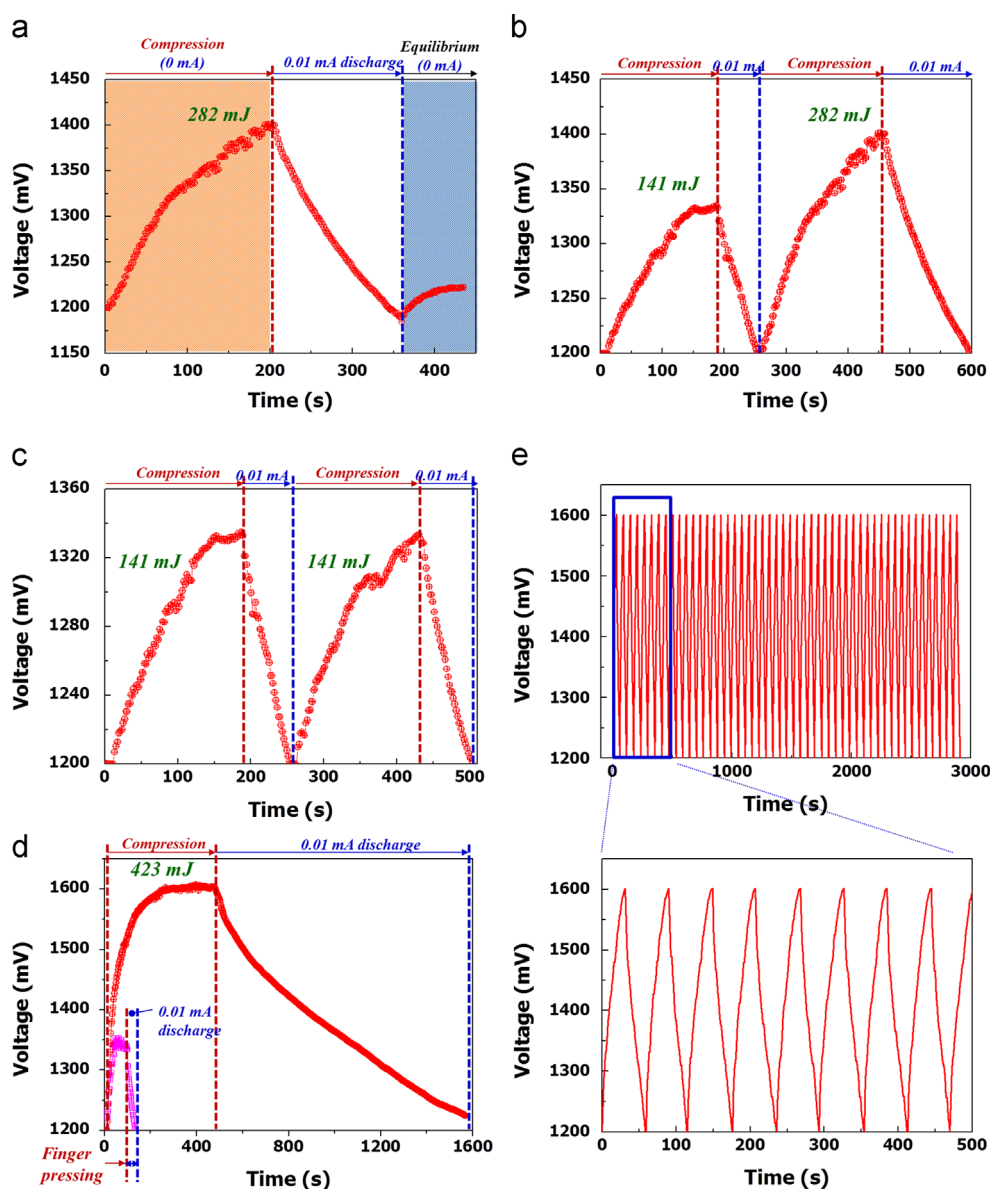


Figure 3 (a) A typical self-charging profile comprising three regions: a compression region inducing self-charging over an initial 200 s when continuous mechanical compression of 282 mJ was applied at 1 Hz to the cell, a galvanostatic (0.01 mA) discharge region immediately following the self-charging, and an equilibrium region with no current input. (b and c) Two self-charging cycles with different and identical applied forces, respectively. (d) Comparison of self-charging behavior obtained using two different compression methods: finger pressure, which is similar to an applied mechanical force of 141 mJ, and a high mechanical force of 423 mJ, which gave the greatest voltage increase of ca. 400 mV. (e) Galvanostatic charge/discharge profile within the self-charging range of 1.2–1.6 V. The expanded lower profile shows the behavior over 500 s, which confirmed that no damage occurred to the porous PVDF piezo-separator.

region that is present before external compression is applied; in this state, the all electrode materials are wetted with liquid electrolyte and the PVDF piezo-separator only acts as an insulator to prevent electrical short between the cathode and the anode (Figure 4a). The second state is a self-charging region in which the piezoelectric field created by the PVDF piezo-separator forms along the z-axis from the cathode side of the system when compressive impact is applied to the cell surface. The piezoelectric potential of the porous PVDF separator causes Li^+ ions to migrate from the cathode to the anode through ion-conducting separator and electrolyte, resulting in the incorporation of Li^+ ions

into the anode electrode. An electron takes the same pathway to maintain charge neutrality (Figure 4b); this migration represents complete conversion of mechanical energy into electrochemical energy. The final state is a force-releasing region in which small amounts of Li^+ ions diffuse backwards in the direction opposite their initial flow to reach balanced distribution when the external stimulus, which was the driving force for the unidirectional movement of Li^+ ions from cathode to anode, is removed (Figure 4c). Subsequently, the delithiated cathode and lithiated anode system that were self-charged from the piezoelectric field are electrochemically restabilized. Note

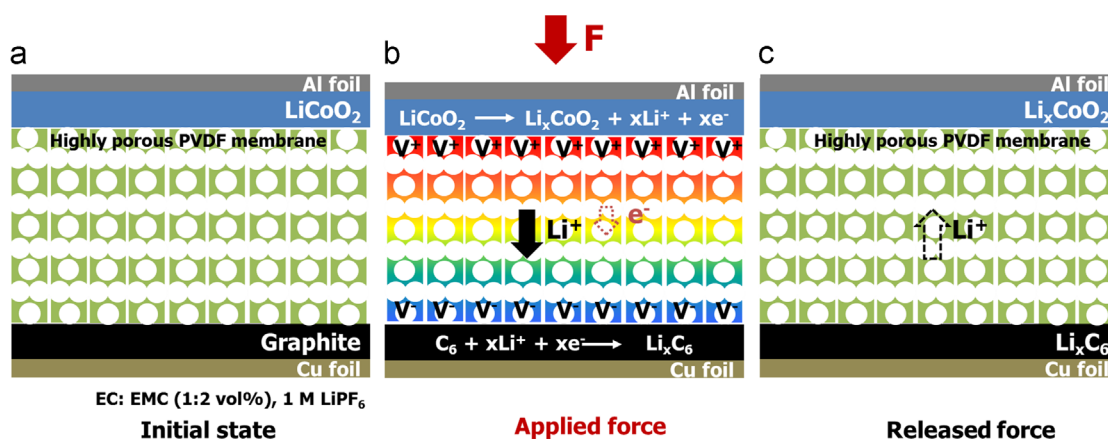


Figure 4 Schematic self-charging mechanism induced by a porous PVDF piezo-separator in Li-ion secondary batteries. (a) Initial state before the application of compressive strain in which the piezo-separator is wetted by the electrolyte. (b) With the applied external force, the PVDF piezo-separator generates positive and negative piezoelectric potentials at the cathode and the anode, respectively. The piezoelectric field generated up and down in the system drives the migration of Li⁺ ions through the porous piezo-separator from the cathode to the anode with accompanying electron transfer. (c) After removing the applied force, the device reaches the equilibrium V_{oc} , which drives the diffusion of Li⁺ ions backwards because of the disappearance of the piezoelectric field.

that the piezopotential of the porous PVDF enables an effective redox reaction in the system, i.e., oxidation or delithiation ($\text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$) at the cathode and reduction or lithiation (C_6 (graphite) + $x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C}_6$) at the anode. Another important consideration is that electrons may flow within the inner system without external circuit to neutralize the Li⁺ cationic charge and maintain the net charge balance; this is a completely different mechanism from the typical charge/discharge system of LIBs in which the flow of electron is only available through an external circuit. In the general concept regarding energy-storage of Li-ion chemistries, the travel of electrons through the inner cell system can be mainly related to a safety issue due to the possibility of an internal short-circuit resulting from the thermally abusive condition [20–22]. However, in the self-charging cell, electron flow through the PVDF piezo-separator is at the micro- or milli-ampere level and never leads to thermal side reaction during mechanical stimulus. Furthermore, the high melting point (T_m) of PVDF reduces the risk of cell degradation. The existence of an electron leakage mentioned in several literatures also supports the possibility of a reversible electron transfer through inner system [23,24]. The recovery profile shown in Figure 3e demonstrates the stability of the SCPC toward electron transfer through the inner electrochemical system.

Electrochemical properties of the porous PVDF piezo-separator

As noted above, electrochemical performance is crucial in considering self-charging nanogenerators for use in practical lithium-ion secondary battery applications. A PVDF piezo-separator, even with the self-charging capability described in the previous section, may have only limited applications if cell performance were diminished in the presence of the piezo-separator. Porosity is the most important characteristic that controls the effective migration of Li⁺ ions within the

electrochemical system. Most conventional or solution-cast PVDF films (Supporting information S-1, S-2) have non- or less-porous architectures, which prevent the movement of Li⁺ ions even if the film has a high β -polymorph content or a piezoelectric contribution that leads to self-charging. Thus, providing a porous structure to the PVDF separator without a serious loss of β -content with its aligned dipole configuration is beneficial in terms of the simultaneous satisfaction of both self-charging and electrochemical performance. The normalized capacity (Q) of a coin full cell consisting of two electrodes (LiCoO₂ and graphite), a PVDF separator, and a liquid carbonate-based electrolyte (Figure 5a) illustrates the significant difference in initial performance when a weakly porous and highly porous PVDF piezo-separator was used, respectively. The enhancements in Q at the current rate of 0.05 C for charging (Q_c) and discharging (Q_d) (i.e., 84.6 and 73.6%, respectively) were much larger than that of a typical solution-cast PVDF film made without the ZnO particle treatment. The PVDF piezo-separator whose porosity was well-defined by the ZnO particles (PVDF_{w.p}) had an outstanding Q_d of ca. 82%, while the less porous separator (PVDF_{wo.p}) had a Q_d of only ca. 8% because of high ohmic resistance (or I-R drop) and serious overpotential. Except for the initial irreversible capacity accompanying large Li loss over three cycles at 0.05 C, the PVDF_{w.p} coulombic efficiency gradually increased, averaging > 98%, during cycling regardless of the current rate (Figure 5b). The normalized discharge profile (Q'_d) based on the initial discharge capacity (the bottom plot of Figure 5b) exhibited there can be a possibility of capacity fading due to the large I-R drop and concentration polarization normally detected at high rates: Q'_d was ca. 85% at 0.3 C compared with ca. 95% at 0.05 C. This is still a great improvement over conventional solution-cast PVDF_{wo.p}, which suffers from a difficult charge/discharge process. Such porosity-induced behavior, which is related to the resistance to inhibit ionic conductivity of Li⁺ ions, is also supported by the results of EIS over the frequency range of 500 kHz to 10 mHz (Figure 5c). The impedance of PVDF_{w.p} was

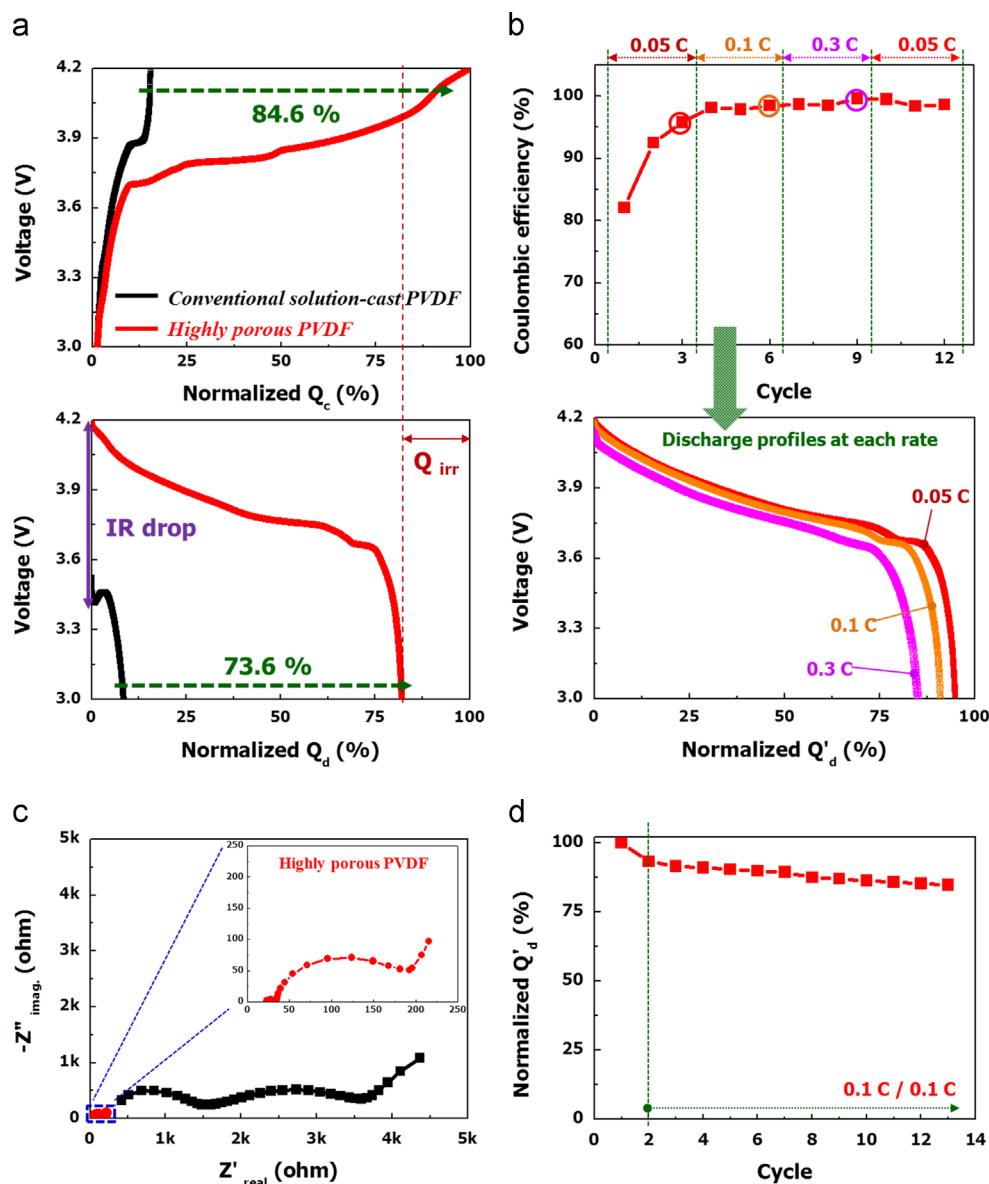


Figure 5 (a) Normalized initial charge (Q_c , upper plot) and discharge capacity (Q_d , lower plot) at a current rate of 0.05 C for a solution-cast low-porosity PVDF piezo-separator (black line, PVDF_{wo.p.}) and a highly porous PVDF piezo-separator (red line, PVDF_{w.p.}). (b) Coulombic efficiency of PVDF_{w.p.} as a function of current rate; the sequence follows three steps per C rate (here, the charge/discharge current at each step is the same); the discharge profile at the third cycle of each C rate is detailed on the bottom plot. (c) Nyquist plots of the impedance measured at a discharged potential of ca. 3.1 V; PVDF_{wo.p.} has serious solution and charge-transfer resistance (R_{ct}) compared with the impedance of PVDF_{w.p.} plotted in the inset. (d) Calendar life of the porous piezo-separator at 23 °C. The discharge capacity (Q'_d normalized on the basis of the initial discharge capacity) was monitored in the constant current charge/discharge mode (0.1 C) after an initial low current (0.05 C) was used in the first cycle to stabilize the electrode system.

significantly lower than that of PVDF_{wo.p.}; the charge-transfer resistance (R_{ct}) of the cathode and anode in the cell with PVDF_{w.p.} in the discharged state (3.1 V) was ca. 200 Ω , while PVDF_{wo.p.} had an R_{ct} of ca. 3000 Ω , which is more than 10 times higher than that of PVDF_{w.p.}. This unfavorable result for the PVDF_{wo.p.} piezo-separator is consistent with the serious capacity fading detected in the initial charge/discharge profiles shown in Figure 5a; the less porous structure is the main reason for the large impedance because it interferes with the effective mobility of Li^+ ions within the cell. The

calendar life of the porous piezo-separator at 23 °C (Figure 5d) shows that it maintained a stable discharge capacity at ca. 92% and a coulombic efficiency >98% during continuous charge/discharge processes at a rate of 0.1 C when the initial large irreversible capacity was excluded.

Conclusions

We investigated a highly porous PVDF film as an effective piezo-separator for enhanced SCPCs. The well-defined

porous structure stabilized the device, reduced charge transfer resistance, and prevented serious capacity decay, simultaneously enabling a self-charging effect induced by the piezopotential. Our strategy suggests a practical research direction for SCPCs utilizing the piezoelectric characteristics of predominantly β -phase PVDF, which enables direct conversion of mechanical energy into electrochemical energy without an external electrical source. In contrast to the conventional PVDF piezo-separator, which suffers from substantial capacity loss, the cells using the highly porous PVDF separator described herein were tuned to render them completely immune to electrochemical defects. Critical advantages exist over previous approaches to the application of PVDF piezo-separators in LIBs. This study, based on a porous architecture of β -phase PVDF, suggests a useful approach to overcome some serious limitations of current state-of-the-art SCPCs.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2015.01.006>.

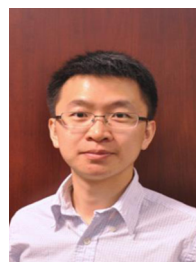
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