Near ideal synaptic functionalities in Li ion synaptic transistor using Li$_3$PO$_x$Se$_x$ electrolyte with high ionic conductivity

Revannath Dnyandeo Nikam$^{1,2}$, Myonghoon Kwak$^{1,2}$, Jongwon Lee$^{1,2}$, Krishn Gopal Rajput$^{1,2}$, Writam Banerjee$^{1,2}$ & Hyunsang Hwang$^{1,2}$*

All solid-state lithium-ion transistors are considered as promising synaptic devices for building artificial neural networks for neuromorphic computing. However, the slow ionic conduction in existing electrolytes hinders the performance of lithium-ion-based synaptic transistors. In this study, we systematically explore the influence of ionic conductivity of electrolytes on the synaptic performance of ionic transistors. Isovalent chalcogenide substitution such as Se in Li$_3$PO$_4$ significantly reduces the activation energy for Li ion migration from 0.35 to 0.253 eV, leading to a fast ionic conduction. This high ionic conductivity allows linear conductance switching in the LiCoO$_2$ channel with several discrete nonvolatile states and good retention for both potentiation and depression steps. Consequently, optimized devices demonstrate the smallest nonlinearity ratio of 0.12 and high on/off ratio of 19. However, Li$_3$PO$_4$ electrolyte (with lower ionic conductivity) shows asymmetric and nonlinear weight-update characteristics. Our findings show that the facilitation of Li ionic conduction in solid-state electrolyte suggests potential application in artificial synapse device development.

The recent advances in development of redox transistor such as lithium-ion synaptic transistor (LIST) to build an artificial neural networks exhibit tremendous advantages over the existing memristors technology$^{1–3}$. In a LIST device, the read and write operations are performed separately using a "gate electrolyte" to switch the channel conductance by injecting or extracting Li$^+$ ion from solid electrolyte or channel$^{1,2,4}$. The inserted or extracted ion from the channel changes the doping state through which multilevel conductance level can be achieved. However, the low ionic conductivity of currently available electrolytes creates nonlinear switching and retention issues in LIST devices. The ionic liquid based electrolytes shows better prospects to achieve some synaptic functionalities$^{5,6}$, However, the use of traditional liquid electrolyte limits the practical application of synaptic devices, and it forms lithium dendrites that affect its long-term stability$^4$. The use of solid-state electrolyte offers several advantages over liquid electrolytes such as better stability and low energy operation by reducing the switching energy. Recently, the polymer-based solid-state electrolyte, polyethylene oxide: lithium perchlorate (PEO: LiClO$_4$), has been proven to be capable of achieving excellent synaptic functionality owing to the high ionic conductivity of PEO substitute$^2$. However, the polymer-based solid-state electrolyte PEO: LiClO$_4$ is soluble in a commonly used lithographic solvent that complicates the creation of the top gate architecture. Therefore, these devices are always fabricated with a lateral gate architecture with gaps of several micrometers from a channel that induces a large electric double layer formation, which causes an adverse effect on ion migration reversibility. The lithium phosphate (Li$_3$PO$_4$) is the most well-known and studied lithium oxide solid electrolytes$^2$. The ionic conductivity of the pure Li$_3$PO$_4$ in bulk is relatively low at $10^{-7}$ S·cm$^{-1}$ and in thin film $10^{-8}$ S·cm$^{-1}$ $^8$. The nitrogen doping Li$_3$PO$_4$ was first reported by Bates et al. Experimental evidences confirm that nitrogen replaces the bridging oxygen (P-O-P) and nonbridging oxygen (P-O) in Li$_3$PO$_4$ and forms a cross link structure$^9$. Bates et al. suggested that cross linked structure between P and N atoms result a high ionic conductivity of up to $10^{-5}$ S·cm$^{-1}$ at 25 °C in micrometer scale thick LiPON film, it is sufficient to achieve high performance in large scale energy storage devices. It is worth to noting that scaling down the LiPON thickness to nm scale greatly reduces the ionic conductivity.

---

1Center for Single Atom-based Semiconductor Device, Pohang University of Science and Technology (POSTECH), Pohang, 790-784, Republic of Korea. 2Department of Material Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, 790-784, Republic of Korea. *email: hwanghs@postech.ac.kr
conductivity between $10^{-10}$ to $10^{-7}$ S·cm$^{-1}$ that hinders the applicability of LiPON in nanoscale electronic devices such as ionic transistor. Therefore, due to above mentioned LiPON limitation, alternative thin film electrolyte material with at least $10^{-6}$ S·cm$^{-1}$ ionic conductivity is highly desirable for nanoscale synaptic transistor. Apart from the nitridation (nitrogen doping) in Li$_3$PO$_4$, another scheme to increases the ionic conductivity in thin film is the isovalent substitution of oxygen (both bridging and apical oxygen) by anion such as S and Se but those result not yet verified experimentally. The theoretical study confirms that (S or Se) bridge with P that allow the fast Li$^+$ ion conduction because the S or Se forms the weak ionic bond with Li ion (Li–Se or Li–S)$.\text{12}$ It is still not fully understood the underlying mechanism behind this, but it is empirically proven without any doubt. In spite the recent advances in developing high Li$^+$ conducting electrolyte, in this study we have demonstrate Se doping in Li$_3$PO$_4$ electrolyte and develop a LIST device compatible Li$_3$PO$_x$Se$_x$ solid electrolyte.

To the best of our knowledge, no study has clarified the influence of ionic conductivity of electrolyte on the synaptic property of LIST devices. Without a way to address the influence of ionic conductivity and develop high ionic conductive in thin film electrolyte, the LIST cannot function as an ideal synaptic device. Therefore, to enhance the practicality of employing LIST as an ideal synapse device, we devoted our study to develop a LIST compatible thin film electrolyte and systematically explore its effect on synaptic functionalities.

**Result and Discussion**

The synaptic device used in this study had a three-terminal configuration consisting of lithium cobalt oxide (LiCoO$_2$) as a channel, and ionic conductive material such as lithium phosphate (Li$_3$PO$_4$) or Se doped lithium phosphate (Li$_3$PO$_x$Se$_x$) as a solid state gate electrolyte. Figure 1(A,B) represents the simultaneous write-read operations. During the write operation, the program voltage pulse is applied to the gate electrolyte through the silicon.
smooth height surface with small pinnacles in its 3D topographic scan. Li3POxSex electrolyte shows the smooth surface with ~80 nm thickness as shown in Fig. 1(E).

gate voltage is swept to positive values, indicating the reversible switching of channel from high resistance (HRS) to low resistance (LRS) state. The transfer characteristics of the redox transistor show large memory windows of 1.63 V with a lower operation, whereas postsynaptic spike denoted as a read operation. In case of Li3PO4 consisted LIST device, each conductance change in channel were measured for 1 s as shown in Fig. 1(H,I).

The parameter used in simulation are listed in Table S1. It is worth noting that there is a significant difference in the positive and negative swept is minimal owing to the low ionic conduction of Li3PO4 electrolyte. The resultant device shows large memory windows of 1.63 V with a lower operating potential of ~2.48 V. The large hysteresis loop in the transfer curve is attributed by the higher Li+ ion transport through the Li3PO4Se electrolyte layer. The resultant device shows large memory windows of 1.63 V with a lower operating potential of ~2.48 V. The large hysteresis in Li3PO4Se electrolyte device associated with nonvolatile conductance change in LiCoO2 channel. The magnitude of on/off ratio in LIST devices is directly related to the ionic conductivity of the electrolyte. The transfer characteristics and the hysteresis loop behavior of the redox transistor can provide clear evidence on the influence of ionic conductivity of electrolyte. The transfer characteristics of as-fabricated redox transistors are measured by applying the varying gate bias at a sweep rate of 5 mV s−1 and a source-drain voltage of 0.4 V. In both devices, the channel current increases as the gate voltage is swept to negative values, while channel current decreases when the gate voltage is swept to positive values, indicating the reversible switching of channel from high resistance (HRS) state to low resistance state (LRS). Figure 1F shows the transfer characteristics of the Li3PO4 electrolyte. In the case of Li3PO4 electrolyte, the transfer curve clearly indicates that the hysteresis between the positive and negative sweep is minimal owing to the low ionic conduction of Li+ ions through the electrolyte. Additionally, the Li3PO4 electrolyte device shows the small memory windows of 1.13 V and high device operating potential of ~2.64 V. The transfer characteristics of the LIST device consisting of Li3PO4 electrolyte are shown in Fig. 1G. The large hysteresis loop in the transfer curve is attributed by the higher Li+ ion transport through the Li3PO4Se electrolyte layer. The resultant device shows large memory windows of 1.63 V with a lower operating potential of ~2.48 V. The large hysteresis in Li3PO4Se electrolyte device associated with nonvolatile conductance change in LiCoO2 channel. The magnitude of Li+ ion induced hysteresis in LIST devices is directly linked to the net ionic conduction through electrolyte layer and can be further explained qualitatively by measuring the volatile/nonvolatile memory behavior. To study the nonvolatile behavior in Li3PO4 electrolyte device, a series of presynaptic spikes (~1 V, 1 s) were applied to via electrolyte gate terminal and postsynaptic current change in channel was measured for 1 s as shown in Fig. 1(H,J). The presynaptic spike denoted as write operation, whereas postsynaptic spike denoted as a read operation. In case of Li3PO4 electrolyte device each presynaptic spike raises the channel conductance to certain value (denoted as read) as shown in Fig. 1(H). Due to the low ionic conduction through Li3PO4 electrolyte the Li ions no longer accumulate at channel-electrolyte interface and gradually diffuse back to channel, resulting in massive decay in channel conductance. The decay in channel conductance during read operation represent the volatile memory behavior that causes the shallow hysteresis in Li3PO4 electrolyte device as shown in Fig. 1(F). On the other hand, the Li3PO4 electrolyte device each presynaptic spike induces very steady change in channel conductance (denoted as read) as shown in Fig. 1(I).

The fast ionic conduction through Li3PO4Se electrolyte the Li ions no longer accumulate at the channel-electrolyte interface, resulting in steady state channel conductance change. The steady channel conductance change in Li3PO4Se electrolyte device depicted the nonvolatile memory behavior that causes the ionic hysteresis as shown in Fig. 1(G). The shallow hysteresis due to volatile conductance state or large hysteresis due to nonvolatile conductance state in LIST devices are governed by net moment of Li ion from channel to reservoir via electrolyte layer. To underpin our hypothesis, we have performed the theoretical simulation to calculate the real time Li+ ion concentration. More detailed description on the time dependent Li+ distribution simulation can be found in Supplementary Information (Section 1). To perform the simulation, we first obtained a real time discharge curve for both Li3PO4 and Li3POxSex electrolyte devices as shown in Fig. S1. Subsequently, we process the simulation by considering known device parameter such as thickness, ionic conductivity, area. Then we tune the various unknown parameter such as reaction rate, diffusion coefficient until a good fit is achieved for experimental data. Finally, we perform the simulation in real time mode to obtain the unknown concentration of Li+ ion in LiCoO2 layer. The parameter used in simulation are listed in Table S1. It is worth noting that there is a significant difference in Li+ ion concentration distribution in LiCoO2 layer was observed between Li3PO4 and Li3PO4Se electrolyte devices (Fig. S2). The high Li+ concentration in in LiCoO2 layer is clear evidence of a fast back diffusion of Li ion due to low ionic conduction in Li3PO4 electrolyte device.

In order to underpin the ionic conduction phenomenon in Li3PO4 and Li3POxSex electrolytes, we extend our study to understand their bonding structure. Numerous studies predicted the influence of bonding structure in Li3PO4 electrolyte on Li ion mobility14. The Li3PO4 electrolyte comprises of PO4 tetrahedral unit, each of which is bonded to other tetrahedras through bridging oxygen (P–O–P)15. Two outer oxygen atoms in PO4 tetrahedral unit have ionic bond with two Li atom denoted as a non-bridging oxygen (Li+…O–P). The remaining one oxygen atom in PO4 tetrahedral unit form the π bond with central phosphorous atom denoted as a non-bridging oxygen (O=Li)x16. The Li atoms have the...
freedom to migrate to the empty π bonded oxygen atom site (and the π bond moves to the vacated Li site), which constitutes the most basic form of ion transport. Due to the high electronegativity of oxygen atom forms the strong electrostatic interaction with Li atom (Li$^+$…O–P) as a result lack of intrinsic mobile Li vacancies in Li$_3$PO$_4$ and thereby decreases its ionic conductivity$^{14,17}$. More specifically, changing the bonding structure by substituting non-bridging oxygen (Li$^+$…O–P) and bridging oxygen (P–O–P) by nitrogen or isovalent anion would result in a reduction of the overall electrostatic interaction with Li$^+$. This weak electrostatic interaction destabilizes the Li$^+$, result in formation of extrinsic Li vacancies in doped Li$_3$PO$_4$ and thereby increases its ionic conductivity$^{11,18}$. Additionally, isovalent anion substitution of in Li$_3$PO$_4$ causes disordered Li-ion sublattice that provide more stable Li interstitial sites thereby contribute high ionic conductivity$^{19,20}$.

In order to further confirm the chemical composition and nature of the chemical bonding in Li$_3$PO$_4$ and Li$_3$PO$_{x}$Se$_y$ electrolytes, high resolution X-ray photoelectron spectroscopy (XPS) was performed and are shown in Fig. 2. Prior to the XPS analysis, both Li$_3$PO$_4$ and Li$_3$PO$_{x}$Se$_y$ samples were etched up to 10 nm to avoid the effect of surface oxidation. The initial XPS survey scan confirmed the presence of Li, P, O, Se and C in Li$_3$PO$_4$ and Li$_3$PO$_{x}$Se$_y$ samples respectively (Figs. S3 and S4). The XPS core peak spectra of O 1$s$ for Li$_3$PO$_4$ electrolyte is shown in Fig. 2A. The O 1$s$ spectra deconvoluted into the three distinct peaks attributed respectively to non-bridging oxygen (P=O) at 531.5 eV, non-bridging oxygen (Li$^+$…O–P) at 532.5 eV, and bridging oxygen (P–O–P) at 532.8 eV. The obtained fitted by Gaussian–Lorentzian XPS curves for O 1$s$ region are consistent with previously reported results on Li$_3$PO$_4$ electrolyte$^{21}$. The non-bridging oxygen (Li$^+$…O–P) and bridging oxygen (P–O–P) are the chemical reactive site toward elemental doping such as Se. The Li$_3$PO$_{x}$Se$_y$ electrolyte was obtained by selenization of Li$_3$PO$_4$ due to partial replacement of oxygen species in Li$^+$…O–P and P–O–P bonds.

Figure 2. Chemical structural analysis of as fabricated Li$_3$PO$_4$ and Li$_3$PO$_{x}$Se$_y$ electrolytes using high resolution core level XPS (A) O 1$s$ core spectra in Li$_3$PO$_4$ (B) O 1$s$ core spectra in Li$_3$PO$_{x}$Se$_y$ (C) Li 1$s$ core spectra in Li$_3$PO$_4$ (D) Li 1$s$ core spectra in Li$_3$PO$_{x}$Se$_y$ (E) P 2$p$ core spectra in Li$_3$PO$_4$ (F) P 2$p$ core spectra in Li$_3$PO$_{x}$Se$_y$ (G) Se 2$p$ core spectra in Li$_3$PO$_4$ (H) Se 2$p$ core spectra in Li$_3$PO$_{x}$Se$_y$ (I) Model chemical structutre of Li$_3$PO$_4$ electrolyte and (J) Model chemical structutre of Li$_3$PO$_{x}$Se$_y$ electrolyte.
by Se. The XPS core peak spectra of O 1s for Li₃POₓSex electrolyte is depicted in Fig. 2B. In Li₃PO₄, electrolyte the peak of non-bridging oxygen at 531.5 eV is remain unchanged, clearly indicating (P=O) conserved during selenization of Li₃PO₄. During selenization, we notice the major changes in non-bridging oxygen (Li—…—O—O) and bridging oxygen (P—O—P) sites. The selenization process greatly reduces the intensity second peak at 532.5 eV that was associated with non-bridging (Li—…—O—P) chemical environment. This indicates a substitution of an oxygen atom by a selenium atom at non-bridging site to form (Li—…—Se—P) bonds. The third peak located at 533.05 eV is associated with bridging (P-Se-P) chemical environment. The up shift of this peak during selenization is believed to be due the replacement of P-O-P bond by P-Se-P bond. The XPS core spectra of Li 1s for Li₃PO₄ electrolyte is shown in Fig. 2C. The peak position of Li 1s located at 56.59 eV is due the highly polarized bonding between Li and O (Li-O) and it indicating single form of chemical environment of Li at the non-bridging site (Li—…—O—P). The spectra of Li 1s for Li₃PO₄, electrolyte is depicted in Fig. 2D and decomposed into two distinct peaks. The reduced intensity of 56.59 eV peak clearly indicating reduction of non-bridging oxygen site (Li+…—O—P). The newly generated downshifted peak at 55.87 eV due to the formation of low polarized non-bridging selenium site (Li+…—Se—P). Furthermore, to know the chemical environment of P in Li₃PO₄, electrolyte the P 2p slow scan peak were deconvoluted into two set of peaks by considering the spin orbital split doublet P 2p₁/₂ and P 2p₃/₂ as shown in Fig. 2E. The first peak observed at 133.94 eV is due is the characteristics of a PO₄²⁻ tetrahedral chemical environment. Note that the peak at 133.94 is the combination of doublets 2P₁/₂ and 2P₃/₂. The peak observed at 134.83 eV reveals the existence of bridging P-O-P bond surrounded by a lithium chemical environment. To further confirm the chemical state of P in Li₃PO₄, electrolyte, we extend our XPS analysis into P 2p regions as shown in Fig. 2F. The XPS core spectra of Li₃PO₄, electrolyte in P 2p region clearly shows that the peak intensity of P 2p₁/₂ (133.94 eV) and P 2p₃/₂ (134.84 eV) are reduced due appearance of new peaks at 139.57 eV, 140.26 eV due to formation of (PSe₃)³⁻ and PSe₇⁻ chemical species. The XPS scan in the Se 2p region (Fig. 2G) shows no signal that clearly indicating the absence of Se in Li₃PO₄, electrolyte. We believe that the selenization process allow to replace the highly polarized bridging oxygen (P—O—P) and non-bridging oxygen (Li+…—O—P) sites Li₃PO₄, electrolyte. Interestingly, we found the remarkable change in Se 2p region of Li₃PO₄, electrolyte (Fig. 3H). The two distinct peaks at 162.06 eV, 166.56 eV are associated with (PSe₃)³⁻ and P-Se-P chemical environment. The fractional elemental percentage in Li₃PO₄ and Li₃PO₄, electrolytes obtained from XPS are listed in Tables S2 and S3. Finally, based on our XPS analysis result, we propose the model structures for Li₃PO₄ and Li₃PO₄, electrolytes as shown in Fig. 2(I,J). In case of Li₃PO₄, the PO₄³⁻ link to another PO₄³⁻ thorough bridging oxygen (P—O—P) and three oxygen on each tetrahedral denoted as apical oxygen or non-bridging oxygen site (Li+…—O—P). In Li₃PO₄, the substitution of bridging oxygen (P—O—P) by Se stabilizes the Li vacancy by forming bridging selenium (P—Se—P) site. Also, the selenization Se substitution for a tetrahedral O in PO₄³⁻ stabilizes a Li inferential ion by forming apical selenium or non-bridging selenium site (Li+…—O—P).

To demonstrate the effect of ionic conductivity of electrolytes on the stability of finely spaced conductance state and their symmetry, LIST device was operated by sending several programmed voltage pulses to the gate electrolyte. The “write” operation consists of 40 down pulses (−1 V, 2 s with space 2 s) and 40 up pulses (+1 V, 2 s with space 2 s). The “read” operation is performed at 1 s right after each successive voltage pulse by applying a small 0.5 V DC bias to the source-drain terminal. As shown in Fig. 3A, when the negative voltage pulse (potaentiation) is applied to the gate electrolyte, an Li⁺ ion starts to move from the LiCoO₂ channel to the Si reservoir through the Li₃PO₄ electrolyte. The extracted Li⁺ ion from the channel changes the doping state in LiCoO₂, and the channel conductance gradually switches off up to certain pulses. Subsequently, a further increase in the negative voltage pulse on the gate electrolyte results in a sudden increase in channel conductance. The zoom in view shows that the conductance change per pulse (ΔG) is more massive and unstable indicating high volatility. Similarly, when a series of identical positive pulses (depression) is applied to the same device, a sudden decrease in channel conductance is observed up to a certain pulse, and the subsequent channel conductance becomes saturated. This behavior of abruptness and saturation in channel conductance is due to the accumulation of Li⁺ ion at channel electrolyte interface, which is governed by low ionic conduction in Li₃PO₄ electrolyte. In contrast, Li₃PO₄, based LIST device exhibit symmetric analog conductance change (Fig. 3B). The zoom in view shows the stable and nonvolatile conductance change. The high nonvolatility in Li₃PO₄, based LIST device is governed by the high ionic conduction through electrolyte layer. As a result of fast ionic conduction through Li₃PO₄, electrolyte the Li ions no longer accumulate at the channel electrolyte interface, resulting in analog channel conductance change. Figure 3(C,D) show the schematic of the interionic switching mechanism of Li₃PO₄ and Li₃PO₄, electrolytes, respectively. As shown in Fig. 3C, Li₃PO₄ electrolyte based LIST device exhibit least Li⁺ ion migration from LiCoO₂ channel to Si reservoir. The nonlinear switching behavior in Li₃PO₄ consisted LIST devices arises due to the low Li⁺ ion migration from LiCoO₂ channel to Si reservoir through Li₃PO₄ electrolyte. The overall electrochemical reactions involving Li⁺ ions migration in LiCoO₂/Li₃PO₄/Si are as follows:

$$LiCoO_2+\text{(1—x)}e^- \leftrightarrow Li_{1-x}CoO_2 + (1—x)Li^+$$  \hspace{1cm} (1)

$$Li_3PO_4 + x_1Li^+ + x_2e^- \leftrightarrow Li_{1-x}Li_3PO_4$$  \hspace{1cm} (2)

$$Si + x_1Li^+ + x_2e^- \leftrightarrow Li_{3-x}Si$$  \hspace{1cm} (3)

The electrochemical reaction (1) and (3) are happened in channel and reservoir layer. The electrochemical reaction (2) is related to transport of Li⁺ ions through Li₃PO₄ electrolyte and it is most important step in LIST device because it determines how fast Li⁺ ions are transported toward Si reservoir and ultimately it determines the switching behavior of channel. It is well known fact that relatively low ionic conductivity of Li₃PO₄ thin film inherit it applicability in nano-batteries and nanoscale electronic devices. Previous experimental evidences
predicted that the low ionic conductive electrolyte result in a Li accumulation at cathode/electrolyte interface. Those accumulated Li directly affect the reversible intercalation in LiCoO2. In Li3PO4 consisted LIST device the nonlinear switching behavior associated with accumulation Li ion at channel/electrolyte interface. During potentiation the Li ion start to extract from channel LiCoO2 channel as a result conductance gradually increases. Due to low conduction through Li3PO4 extracted Li ion accumulated at channel/electrolyte interface. (D) Schematic of interionic switching dynamics for Li3PO4 consisted LIST device. The fast ionic conduction associated with presence of extrinsic Li ion vacancies and interstitial configurations in Li3PO4-Se, that allow the uniform Li+ ion migration between LiCoO2 to Si reservoir. Consequently, Li+ gets accumulated at channel/electrolyte interface. (E) Temperature dependent EIS measurements for Li3PO4 and Li3POxSex electrolytes, respectively. EIS measurement was performed at a test frequency region varying from 0.1 Hz to 1 MHz, using two terminal cells consisting of a sandwiched electrolyte layer between the top and bottom Pt electrodes. The dots are the measured data and the lines are the fitted data using the equivalent circuit model. (F) Arrhenius plots of the ionic conductivity of the Li3PO4 and Li3POxSex electrolytes (G) Activation energy for Li+ ion migration in Li3PO4 electrolyte. (H) Activation energy for Li+ ion migration in Li3POxSex electrolyte.
To improve the synaptic functionalities, we replace the conventional Li₃PO₄ electrolytes with Li₃POₓSex. The interionic switching mechanism in Li₃POₓSex consisted LIST device depicted in Fig. 3(D). The linear switching in Li₃POₓSex consisted LIST device is associated with fast Li ionic conduction from LiCoO₂ channel to Si reservoir through Li₃PO₄Sex electrolyte. The XPS analysis confirm that selenization process allow the substitution of bridging oxygen (P–O–P) by Se that stabilizes the Li vacancy by forming bridging selenium (P–Se–P) site. Also, the selenization Se substitution for a tetrahedral O in PO₄³⁻ stabilizes a Li inferential ion by forming apical selenium or non-bridging selenium site (Li⁺…O–P). The stable Li ion vacancy and interstitial allow the fast Li ion motion that result in high ionic conductivity in Se doped Li₃PO₄.

To further confirm the effect of Se-substitution on the ionic conductivity and activation energy of electrolytes, a temperature dependent electrochemical impedance spectroscopy (EIS) tests were performed at a test frequency region varying from 0.1 Hz to 1 MHz using two terminal cells consisting of a sandwiched electrolyte layer (200 nm) between the top and bottom Pt electrodes. A detail description about device fabrication for EIS analysis is discussed in experimental section. The thickness and surface analysis of as deposited electrolytes was confirmed with atomic force microscopy (AFM), as shown in Fig. S5 of the Supporting Information. Figure 3(E) show the EIS spectra of Li₃PO₄ and Li₃POₓSex electrolytes. The obtained EIS spectra of each electrolyte were appropriately fitted using the standard circuit model (Fig. S6). The fitted EIS data with model circuit clearly shows that the ionic conduction in all electrolytes is modeled by two parallel circuit elements (i.e., constant phase element (CPE) and resistance (R₀)) in the high and medium frequency regions. The CPE is used to analyze a capacitor; R₀ used to model an ionic resistance and W₀ analyze the polarization of the electrode electrolyte interface. The small semicircle EIS spectra of Li₃POₓSex electrolyte-Pt electrode. The model circuit consists of one additional elements Rₚ represent the contact resistance. The ionic conductivity of electrolytes is calculated by the equation $\sigma = \frac{d}{(R_{\text{cor}} A)}$, where $\sigma$ (S cm⁻¹) is the ionic conductivity; d (cm) is the thickness; R (Ω) is the resistance; and A (cm²) is the area of device. The CPE spectra for Li₃PO₄, (Fig. 3E) clearly show that the large semicircle is associated with more substantial ionic resistance. For Li₃PO₄ electrolytes, we measured an ionic conductivity of 1.2 × 10⁻⁷ S/cm. However, it should be noted that the small semicircle EIS spectra of Li₃POₓSex (Fig. 3E) indicates low ionic resistance, which results in high ionic conductivity of 2.0 × 10⁻⁵ S/cm. Ionic conductivity has been reported to increase by substituting chalcogenide anion, and accordingly, we observed a dramatic increase in ionic conductivity in Li₃POₓSex electrolytes. We have additionally compare the thin film ionic conductivity of our designed electrolyte with previously reported electrolyte matrial and presented in Table S4. The activation energy of Li₃PO₄ and Li₃POₓSex electrolytes were determine using Arrhenius plot of the ionic conductivity as shown in (Fig. 3F). The activation energies calculated by using the relation $\sigma T = A \exp\left[-\frac{E_a}{kT}\right]$, where $\sigma$ is the ionic conductivity, T is temperature, A is a pre-exponential factor, Ea is the activation energy, and k is the Boltzmann constant. The plots of ln($\sigma$) vs 1000/T were used to extract the value of activation energy by linearly fitting to the experimental data. From Arrhenius method, the activation energies determined to be 0.356 and 0.253 eV for Li₃PO₄ and Li₃POₓSex electrolytes, respectively. The experimental determined activation energy for ion migration are schematically shown in Fig. 3(G,H). In order to reveal the effect of the Se doping on switching property, we further tune structure of Li₃POₓSex by changing the Se content. The detailed description on Se content dependent switching behavior of Li₃POₓSex consisted LIST device can be found in Section 5 of Supplementary Information. At low Se content (0.13%) nonlinear switching with high channel conductance reveal the accumulation of Li⁺ ion at electrolyte/channel interface due low ionic conduction through electrolyte (Fig. S7). Another remarkable observation is that when Se content is high (0.52%) saturation in channel conductance was observed, indicating the formation of barrier layer by unreacted Se.

In neuromorphic computing, the endurance of neural hardware is defined using long-term potentiation (LTP) and long-term depression (LTD), which are essential for stable neuromorphic computations. As shown in Fig. 4A, the endurance in Li₃POₓSex-based redox transistor was studied by triggering the LTP and LTD functionalities using an alternate set of 90 identical voltage pulses (±1.5 V, 1 s) with 1 s space. The detail explanation about pulse scheme used for both potentiation and depression are schematically explained in Fig. S8. During the endurance test, channel conductance was reversibly switched between 2.1 to 40.6 nS with the number states representing the good LTP and LTD behaviors, contributing to the high on/off ratio of 19. Moreover, we observed that the device shows negligible degradation of up to 720 write-read cycles, which contribute to good stability of the device. The tendency to preserve the linearity and symmetric weight update during LTP and LTD in a synapse device decides its learning accuracy. To confirm the linearity and symmetric weight update in Li₃POₓSex-based redox transistor, we condensed the LTP and LTD together, as shown in Fig. 4B.

The symmetric weight update between the two consecutive potentiation and depression in a synaptic device is defined by the asymmetric ratio as

$$AR = \frac{\max G_p(n) - \max G_d(n)}{G_p(40) - G_d(40)} \text{ for } n = 1 \text{ to } 40$$

For an ideal device, the asymmetric ratio is zero. The analyzed asymmetric ratio for Li₃POₓSex-based redox transistor is 0.15, which is considerably lower than that of the recently reposted synaptic transistors (Table 1). The nonlinearity characteristics shows direct impact on pattern recognition accuracy when the synaptic device is employed in neuromorphic hardware. Here, nonlinearity calculations are performed using the previously reported weight update formula²⁶:
\[
G = \left\{ \begin{align*}
(G_{\text{LRS}}^\infty - G_{\text{HRS}}^\infty) \times W + G_{\text{HRS}}^\infty & \quad \text{if } \alpha \neq 0 \\
G_{\text{HRS}} \times \left( \frac{G_{\text{HRS}}}{G_{\text{HRS}}} \right)^W & \quad \text{if } \alpha = 0
\end{align*} \right.
\]

Where, \(G_{\text{LRS}}\) and \(G_{\text{HRS}}\) are the low and high resistance state. The \(\alpha\) denote the nonlinearity factor that controls the potentiation or depression. For an ideal device, a perfectly linear and symmetric conductance change occurs, which represents the nonlinearity factor value \((\alpha_p = \alpha_d = 1)\). The nonlinearity factor values obtained from the fitted LTP and LTD curves were 1.33 and \(-0.34\) for potentiation and depression, respectively. Finally, to compare the performance of Li\(_3\)PO\(_x\)Se\(_y\)-based redox transistor with other synaptic three-terminal transistor devices, we plotted the nonlinearity values obtained from this study and previous studies\(^{28-31}\) (Fig. 4C). In particular, this study shows near ideal and symmetric weight update as compared to previously reported ionic transistor, which paves the path of using high ionic conductive electrolyte in future synaptic devices.

Finally, we simulated the artificial neural network of LIST devices using the experimentally determined conductance change value (\(\Delta G\)) and linearity of weight update. To further understand the effect of \(\Delta G\) on image...
recognition accuracy, we extracted the average weight change value $\Delta G$ as a function of thickness of electrolytes (Fig. 5(A,B)). The effects of linearity and symmetric conductance update of LIST device on the pattern recognition accuracy of a model of a neural network were estimated using multilayer perception based on the Modified National Institute of Standards and Technology dataset.

In the neural network simulation model, the first input, second hidden, and third output layers were composed of 780, 250, 125, and 10 neurons, respectively. All neurons in each layer were fully connected to each other through synapses, as shown in Fig. 5(C) which shows the results of pattern recognition by LIST devices. In the Li$_3$PO$_x$Se$_y$-based LIST device, which exhibits the best synapse performance, the recognition accuracy was significantly improved by 91.01% (Fig. 5(D)). The performance comparison between this study and previously reported synaptic transistors is presented in Table 1.

### Conclusion

To summarize, we explored the effect of electrolyte ionic conductivity on the synaptic functionalities in LIST devices. We demonstrated that the substitution of chalcogenide such as Se in oxide-based Li$^+$ ion electrolyte enhances the ionic conductivity to $2.0 \times 10^{-6}\, \text{S/cm}$. The resultant LIST device consisted of high ionic conductive Li$_3$PO$_x$Se$_y$ electrolyte, which exhibits excellent synaptic properties with multiple conductance states at a very low threshold voltage ($V_{\text{th}} = -2.48\, \text{V}$) and ultralow channel conductance level (40 nA). This LIST device demonstrates symmetric analog switching with a near ideal asymmetric ratio (0.12) and good linearity with nonlinearity $1.33/-0.34$ for weight increase /decrease.

### Materials and Methods

#### Material synthesis.

100 nm of LiCoO$_2$ was used as the channel material. It was controllably grown on a 500 nm SiO$_2$/Si substrate through reactive sputtering using an LCO target. The nonstoichiometric composition in LiCoO$_2$ was controlled by the amount of oxygen during deposition. All LiCoO$_2$ samples used in this study were deposited by flowing 1 sccm O$_2$ and 30 sccm Ar using a sputtering power of 100 W at 5 mTorr pressure. The solid-state Li$_3$PO$_4$ and Li$_3$PO$_x$Se$_y$ were used as electrolytes. The electrolyte layers were prepared through reactive sputtering using a 2-inch Li$_3$PO$_4$ target, whereas Li$_3$PO$_x$Se$_y$ was deposited under Se flux from the Se target. This was followed by the deposition of high-quality 30 nm Si reservoir layer.

#### Device fabrication.

Initially, various dimensions of source-drain windows were defined on the SiO$_2$/Si substrate through photolithography, followed by the deposition of 60 nm pure Pt metal through reactive sputtering and the lift-up process. Then, various dimensions of channel windows were defined on the source-drain pad through photolithography. A 100 nm nonstoichiometric Li$_{1-x}$Co$_2$ channel layer was deposited on the predefined channel windows through reactive sputtering using the LCO target. After the deposition of LiCoO$_2$, the lift-up process was performed using acetone to form a LiCoO$_2$ channel. Post liftoff, a second lithography step was performed to define the channel windows.

![Figure 5. Handwritten image recognition simulation using Li$_3$PO$_4$ and Li$_3$PO$_x$Se$_y$-based redox transistor parameters.](image-url)
performed to define the gate electrolyte windows. In the final step, Li₃PO₄ or Li₃POₓSex electrolyte, Si reservoir and Pt metal was deposited on predefined gate electrolyte windows followed by liftoff process.

**Device fabrication for EIS.** For EIS measurement Pt/Li₃PO₄/Pt and Pt/Li₃POₓSex/Pt sandwiched-cell structure was used. The 100 nm Pt metal deposited on glass substrate as bottom contact electrode. Subsequently, fixed area shadow mask were placed on redeposited bottom electrode and thereafter Li₃PO₄ and Li₃POₓSex electrolytes with ~200 nm thickness were deposited by magnetron sputtering. Finally, the 100 nm Pt metal was deposited as top contact electrode. The active device area used in this study is 0.20 cm². The deposited thickness of each electrolyte was controlled by deposition time and it is confirmed by surface analysis technique such as AFM measurement. The result of surface analysis by AFM are shown in Fig. S5 of the Supporting Information.

**Electrical measurement.** The measurement of synaptic characteristics was performed in a three-point probe station using a semiconductor parameter analyzer (Agilent B1500) with a waveform generator/ fast measurement unit (WGFMU). B1530A WGFMU was used to apply the program voltage pulses for the read and write operations. The conductance of the channel was read using a programmed read pulse using a small DC voltage of 0.5 V between each programming operation to avoid voltage drop in the gate electrolyte.

Received: 30 July 2019; Accepted: 26 November 2019;
Published online: 11 December 2019

**References**

1. Fuller, E. J. et al. Li-Ion Synaptic Transistor for Low Power Analog Computing. *Advanced Materials* **29**, 1604310 (2017).
2. Yang, C.-S. et al. All-Solid-State Synaptic Transistor with Ultralow Conductance for Neuromorphic Computing. *Advanced Functional Materials* **28**, 1804170 (2018).
3. Fuller, E. J. et al. Parallel programming of an ionic floating-gate memory array for scalable neuromorphic computing. *Science* **364**, 570 (2019).
4. Zhu, J. et al. Ion Gated Synaptic Transistors Based on 2D van der Waals Crystals with Tunable Diffusive Dynamics. *Advanced Materials* **30**, 1800195 (2018).
5. Huang, H.-Y. et al. Electrolyte-Gated Synaptic Transistor with Oxygen Ions. *Advanced Functional Materials* **29**, 1902702 (2019).
6. Li, Y. et al. Low-Voltage, CMOS-Free Synaptic Memory Based on LiXTiO2 Redox Transistors. *ACS Applied Materials & Interfaces* **11**, 38982–38992 (2019).
7. Ivanov-Shitz, A. K., Kireev, V. V., Mel’nikov, O. K. & Demianets, L. N. Growth and ionic conductivity of ~Li₃PO₄. *Crystallography Reports* **46**, 864–867 (2001).
8. Bates, J. B. et al. Electrical properties of amorphous lithium electrolyte thin films. *Solid State Ionics* **53-56**, 647–654 (1992).
9. Bates, J. B. et al. Fabrication and characterization of amorphous lithium electrolyte thin films and rechargeable thin-film batteries. *Journal of Power Sources* **43**, 103–110 (1993).
10. Xiong, X. et al. Electrochemical performance of lithium intercalation compounds of LiₓP1–ₓGexS5I for All-Solid-State Ion Gated Synaptic Transistors. *Journal of Materials* **27**, 5324–5331 (2015).
11. Ong, S. P. et al. Phase stability, electrochemical stability and ionic conductivity of the Li10±xMP2X12 (M = Si, Ge, Sn, Al or P, and x = 0, 0.5 or 1) family of superionic conductors. *Energy & Environmental Science* **6**, 148–156 (2013).
12. Pan, L. et al. Revisiting the ionic diffusion mechanism in Li3PS4 via the joint usage of geometrical analysis and bond valence method. *Journal of Materials Chemistry C* **5**, 688–695 (2019).
13. Domenico, C. A., Roitman, G. & Cedeno, G. A first-order Mott transition in LixCoO2. *Nature Materials* **3**, 627 (2004).
14. Larzon, R., W. & Day, D. E. Preparation and characterization of lithium phosphorus oxynitride glass. *Journal of Non-Crystalline Solids* **88**, 97–113 (1986).
15. Becke-Arghiri, M. Phosphorus and its Compounds, Bd. 1: Chemistry, von J. R. Van Wazer. Interscience Publishers, New York-London 1958. I. Aufl., XIII, 954 S., geb. $ 27.50. *Angewandte Chemie* **73**, 552–552 (1961).
16. Xu, Y.-N., Ching, W. Y. & Chiang, Y.-M. Comparative studies of the electronic structure of LiFePO4, FePO4, Li3PO4, LiMnPO4, LiCoPO4, and LiNPO4. *Journal of Applied Physics* **95**, 6583–6585 (2004).
17. Unuma, H., Komori, K. & Sakka, S. Electrical conductivity and chemical durability in alkali-silicate oxynitride glasses. *Journal of Non-Crystalline Solids* **95-96**, 913–920 (1987).
18. Wang, B., Kwak, B. S., Sales, B. C. & Bates, J. B. Ionic conductivities and structure of lithium phosphorus oxynitride glasses. *Journal of Non-Crystalline Solids* **183**, 297–306 (1995).
19. Zhang, Z. et al. New horizons for inorganic solid state ion conductors. *Energy & Environmental Science* **11**, 1945–1976 (2018).
20. Lui, J. et al. Sulfide Solid Electrolytes for Lithium Battery Applications. *Advanced Energy Materials* **8**, 1800933 (2018).
21. Wang, B. et al. Atomic layer deposition of lithium phosphates as solid-state electrolytes for all-solid-state microbatteries. *Nanoletters* **25**, 504007 (2014).
22. Pfeutzenber, B., Parquet, B., Martinez, H., Letellier, M. & Lavasseur, A. Investigation of the local structure of LiPO thin films to better understand the role of nitrogen on their performance. *Solid State Ionics* **186**, 29–36 (2011).
23. Du, Y. A. & Holzwarth, N. A. W. Mechanisms of S⁺[$\text{Li}^{+}][\text{Si}^{4+}][\text{S}^{-}]$ diffusion in crystalline $\text{Li}_n\text{SiS}_{2n+2}$. Chemistry of the atomic layer. *Journal of Materials Chemistry* **23**, 414 (2017).
24. Kraf, M. A. et al. Inducing High Ionic Conductivity in the Lithium Superionic Argyrodites Li₆+xP1–xGexS5I for All-Solid-State Batteries. *Journal of the American Chemical Society* **140**, 16330–16339 (2018).
25. Jang, J., Park, S., Berr, G. W., Hwang, H. & Jeong, Y. Optimization of Conductance Change in Pr1–xCaMnO3-Based Synaptic Devices for Neuromorphic Systems. *IEEE Electron Device Letters* **36**, 457–459 (2015).
26. Jang, J., Park, S., Jeong, Y. & Hwang, H. ReRAM-based synaptic device for neuromorphic computing. In: 2014 IEEE International Symposium on Circuits and Systems (ISCAS) (ed.)(eds) (2014).
27. Go, J. et al. W/WO3-x based three-terminal synapse device with linear conductance change and high on/off ratio for neuromorphic application. *Applied Physics Express* **12**, 026503 (2019).
28. Lee, J., Lim, S., Kwak, M., Song, J. & Hwang, H. Understanding of proton induced synaptic behaviors in three-terminal synaptic device for neuromorphic systems. *Nature Nanotechnology* **30**, 2533–2539 (2019).
29. van de Burgt, Y. et al. A non-volatile organic electrochemical device as a low-voltage artificial synapse for neuromorphic computing. *Nature Materials* **16**, 414 (2017).
30. Yang, C. S. et al. A Synaptic Transistor based on Quasi-2D Molybdenum Oxide. *Advanced Materials* **29**, 1700906 (2017).
Acknowledgements
This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2018R1A3B1052693)

Author contributions
R.D.N. conceived the idea, analyzed results and wrote the manuscript. M.K. performed the neural network simulation; J.L.; K.G.R.; and W.B. contributed to discussion throughout the project; H.H. supervised the project and reviewed the manuscript. All authors discussed the results and contributed to the final manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41598-019-55310-8.

Correspondence and requests for materials should be addressed to H.H.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2019