

Supplementary Information

of

“All-Solid-State Ion-Selective Electrodes with Redox-Active Lithium, Sodium, and Potassium Insertion Materials as the Inner Solid-Contact Layer”

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Detailed experimental conditions and setup

LiFePO₄ powder was synthesized by hydrothermal process¹ as follows: 10 mmol of LiOH·H₂O, 5 mmol of (NH₄)₂HPO₄, 1 mmol of L-ascorbic acid were dissolved in ion-exchanged water under N₂ atmosphere, and then 5 mmol of FeSO₄ was slowly added. The resultant aqueous solution was put into an autoclave, then it was sealed and heated at 170 °C for 12 h. After cooling to room temperature, the precipitated product in the solution was separated by filtration, washed with water, and dried under vacuum. The final product was annealed at 400 °C for 1 h in argon atmosphere. Na_{0.33}MnO₂ powders were prepared through a solid-state reaction. A pelletized mixture of 10 mmol of Mn₂O₃ (prepared by heating of MnCO₃ at 700 °C under air for 5 h) and 5 mmol of Na₂CO₃ powders was heated for 24 h at 800 °C in air to first prepare Na_{0.44}MnO₂. The Na_{0.44}MnO₂ powder was dispersed to be aged in 0.01 mol dm⁻³ NaNO₃ aqueous solution in air for 40 h, resulting in the formation of Na_{0.33}MnO₂.² The obtained product was washed with pure water and dried at 80 °C. Birnessite-type K_xMnO₂·nH₂O (*x* = ca. 0.3, *n* = ca. 0.4 due to its non-stoichiometry)³⁻⁵ was also obtained through a solid-state reaction as generally known. Powders of 6 mmol of K₂CO₃ and 12 mmol of Mn₂O₃ were mixed by wet ball milling in acetone, and the mixture was filtered, followed by heating the product for 24 h at 800 °C in air and rinsed with deionized water.

The synthesized insertion materials were thoroughly mixed with acetylene black (AB, Strem Chemicals Inc.), poly(vinylidene fluoride) (PVDF, Polysciences, Inc.) (8:1:1 w/w) dispersed in N-methyl-2-pyrrolidone solvent (Kanto Chemical Co., Inc.). AB and PVDF were added as conductive and binder agents, respectively, as broadly used in the research field of battery materials. Thus obtained black slurry was carefully dropped and casted onto a Pt disk electrode (1 mm in diameter) embedded in epoxy resin to ensure coverage of whole surface of the Pt disk. The cast slurry was dried for 1 day at room temperature to prepare the composite layer containing 80 wt% insertion materials an internal solid-contact layer. The Pt disk electrodes covered with thus formed composite layer were immersed for at least 1 day in aqueous solution containing 0.01 mol dm⁻³ alkali chloride as a conditioning process to equilibrate electrode potential and alkali content. After the conditioning, the electrodes of Pt/(insertion material) were washed with water and dried in a desiccator for 1 day.

As for ion-sensitive membrane, ionophores of 6,6-Dibenzyl-1,4,8,11-tetraoxacyclotetradecane, bis[(12-crown-4)methyl]-2-dodecyl-2-methylmalonate, and bis[(benzo-15-crown-5)-4-methyl]pimelate, that are commercially available from Dojindo Laboratories, Inc., were used for lithium, sodium, potassium ion electrodes, respectively. To prepare ion-sensitive

polymeric membranes, high molecular weight poly(vinyl chloride) (PVC, Wako Pure Chemical Industry, Ltd.), 2-nitrophenyloctylether (NPOE, Dojindo Laboratories), potassium tetrakis(4-chlorophenyl)borate (KTCBP, Dojindo Laboratories, Inc.), and tetrahydrofuran (THF, Kishida Chemical Co., Inc.) were employed as membrane matrix, plasticizer, lipophilic anion, and casting solvent, respectively.

To form an ion-sensitive membrane, ionophore, NPOE, PVC, and K-TCPB were dissolved in THF, and then the drops of the THF solution was placed on the electrode to cover the whole surface of the black composite electrode consisting of insertion material, AB, and PVDF. The solution cast on the electrode was dried to evaporate THF solvent in a desiccator for 1 day to form a transparent plasticized PVC membrane of which thickness is approximately 0.5 mm. Finally, we prepared the double-layer electrode, hereafter denoted as Pt/(insertion materials)/PVC, through simple drop-casting of the NMP slurry and THF solution. The membrane compositions are listed in **Table S1**. Additionally, Pt/PVC electrodes without the inner layer of insertion materials were prepared as typical direct contact electrodes for comparison of the performance. Prior to electrochemical measurement of the Pt/(insertion materials)/PVC and Pt/PVC electrodes, their conditioning by immersing in aqueous electrolyte solution containing 0.01 mol dm^{-3} of each alkali ion for overnight was also carried out to equilibrate electrode potential. We also prepared Pt/Li_xFePO₄ electrodes ($x = 1, 0.5, \text{ and } 0$) via electrochemical delithiation from LiFePO₄ composite formed on the Pt disk by applying constant potential of $-0.3, 0.25, \text{ and } 0.8 \text{ V vs. Ag/AgCl}$ for $x = 1, \text{ ca. } 0.5, \text{ and } = 0$ in Li_xFePO₄, respectively, to study relation between the Li content and electrochemical property of the Pt/Li_xFePO₄/PVC electrodes. For cyclic voltammetry measurement, the slurry of insertion materials prepared as described above was pasted on stainless steel mesh with diameter of 1 cm and dried, resulting in the formation of composite electrode on the mesh.

Electrochemical measurements of electrodes were performed at room temperature by using a three-electrode cell which consists of the prepared electrode, counter Pt wire electrode, and Ag/AgCl/sat.KCl reference electrode connected with a salt bridge contained saturated KCl or 0.1 mol dm^{-3} lithium acetate aqueous solution.

The potentiometric measurements for the electrodes were conducted in two-electrode configuration with potentiostat HZ-5000 (Hokuto Denko Corp., input impedance: $1 \times 10^{11} \Omega$). The potentiometric sensitivity was checked from potential vs. alkali metal ion activity plots by using different concentrations of alkali chloride salts solutions of LiCl, NaCl and KCl with pH 7.5 of 0.01

mol dm⁻³ Tris-HCl buffer solution. Ionic activities of test solutions were controlled by dropping aqueous solutions of various concentrations of chloride salts at room temperature. The extended Deby-Huckel equation⁶ was utilized to convert concentration of the targeted ion to activity. The selectivity coefficients of the electrodes to each alkali ion in the presence of several cations were determined by using the fixed interference method (FIM).⁷ The selectivity measurement was performed in 0.05 mol dm⁻³ Tris buffer aqueous solution of the targeted or interfering alkali chloride salts. The selectivity coefficient, $K^{\text{pot}}_{A,B}$, is calculated using following equation:

$$K^{\text{pot}}_{A,B} = (a_A / a_B)^{Z_A / Z_B} \quad (1)$$

where a_A and a_B , are activity of detection limit of targeted ion and interference ions denoted as A and B, and Z_A , and Z_B are valance number of A and B ions, respectively.

Cyclic voltammetry for the mesh electrodes of insertion materials used was examined in aqueous solutions containing targeted ions by dissolving 0.50 mol dm⁻³ alkali sulfate. Three cycles were recorded at the scan rate of 0.1 mV s⁻¹. To compare the potential polarization of electrodes, chronopotentiometry was conducted on Pt/PVC and Pt(insertion materials)/PVC electrodes in 0.1 mol dm⁻³ alkali chloride solution by applying a constant current of +1.0 nA for 300 s followed by – 1.0 nA current for another 300 s.⁸ Electrochemical alternating current (AC) impedance measurements were performed in 0.1 mol dm⁻³ alkali chloride electrolyte solution in the frequency range from 100 kHz to 10 mHz by adding a sinusoidal excitation signal (± 100 mV) at the open circuit potential. To test practical performance of Li⁺ ion sensing, the Pt/LiFePO₄/PVC electrode is examined to determine concentration of Li⁺ ion dissolved in commercially available natural mineral water for drinking, named “nerea” (actual producer: NEREA S.p.A). Additionally, to evaluate accuracy of determination of Li⁺ ion concentration by the electrode, the lithium concentration of the natural water was determined by using the inductive coupled plasma atomic emission spectrometry (ICP-AES, SPS3520UV, SII nanotechnology Inc.) as a conventional analytical method.

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Table S1. Compositions of the plasticized PVC membranes used for ISEs.

	Ionophore wt%	NPOE wt. %	PVC wt. %	K-TCPB wt. %
Li ⁺ ion-sensitive membrane	1.5	69.3	28.1	1.1
Na ⁺ ion-sensitive membrane	0.9	67.1	31.7	0.3
K ⁺ ion-sensitive membrane	0.9	65.5	33.3	0.3

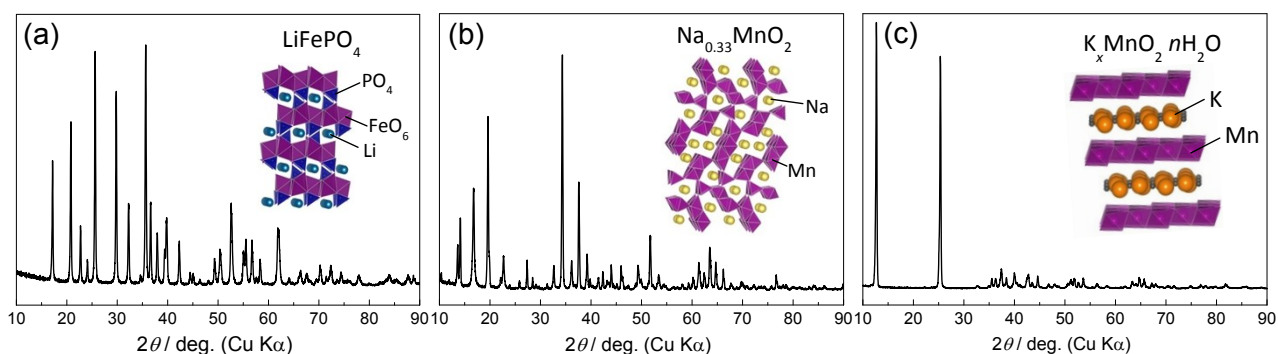


Figure S1. Powder XRD patterns and schematic illustrations of the crystal structures of alkali insertion materials used in this study. (a) LiFePO_4 , (b) $\text{Na}_{0.33}\text{MnO}_2$, and (c) $\text{K}_x\text{MnO}_2 \cdot n\text{H}_2\text{O}$.

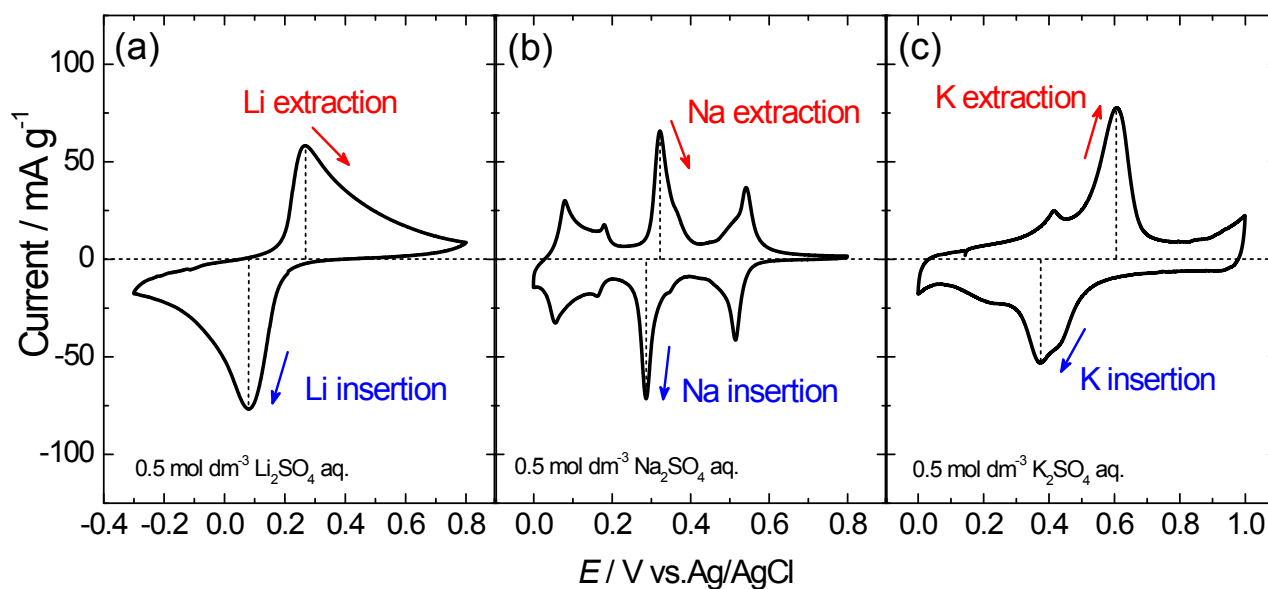


Figure S2. Cyclic voltammograms of composite electrodes of (a) LiFePO_4 , (b) $\text{Na}_{0.33}\text{MnO}_2$, and (c) $\text{K}_x\text{MnO}_2 \cdot n\text{H}_2\text{O}$ in $0.5 \text{ mol dm}^{-3} \text{ A}_2\text{SO}_4$ ($\text{A} = \text{Li}, \text{Na}, \text{and K}$) aqueous solution at a scan rate of 0.1 mV/s .

Table S2. Comparison of logarithm of selectivity coefficients, $\log K^{\text{pot}}_{A,B}$ of three types of electrode configurations of Li^+ , Na^+ , and K^+ ion-selective electrode, the Pt/(insertion materials), DCE-type Pt/PVC, and Pt/(insertion materials)/PVC electrodes determined by the FIM.

	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Pt/PVC for Li^+	-	-2.6	-2.8	-4.0	-4.3
Pt/ LiFePO_4	-	-2.5	-2.7	-3.4	-3.6
Pt/ LiFePO_4 /PVC	-	-2.5	-2.8	-4.6	-4.7
	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Pt/PVC for Na^+	-3.6	-	-2.1	-4.8	-4.2
Pt/ $\text{Na}_{0.33}\text{MnO}_2$	-1.5	-	-2.0	-3.3	-2.6
Pt/ $\text{Na}_{0.33}\text{MnO}_2$ /PVC	-3.7	-	-2.1	-5.2	-4.6
	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Pt/PVC for K^+	-2.9	-3.1	-	-3.6	-3.7
Pt/ K_xMnO_2	-1.1	-1.1	-	-1.3	-1.5
Pt/ K_xMnO_2 /PVC	-3.3	-3.0	-	-3.3	-3.6

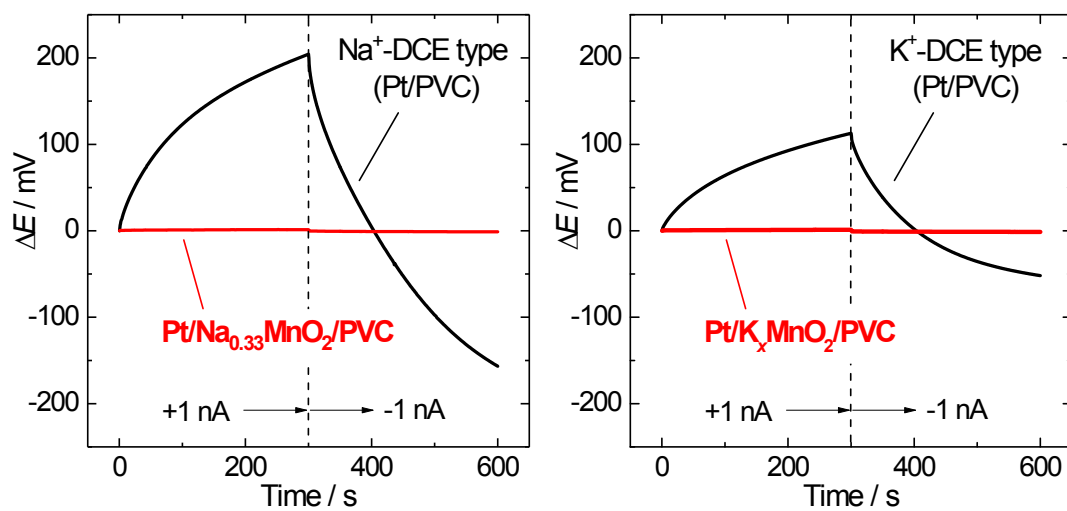


Figure S3. Chronopotentiograms of sodium and potassium ion selective electrodes; the DCE type, Pt/PVC, and Pt/(insertion materials)/PVC at reversal constant current of +1.0 and – 1.0 nA for 0 – 300 and 300 – 600 s, respectively, in 0.1 mol dm⁻³ NaCl or KCl aqueous solution.

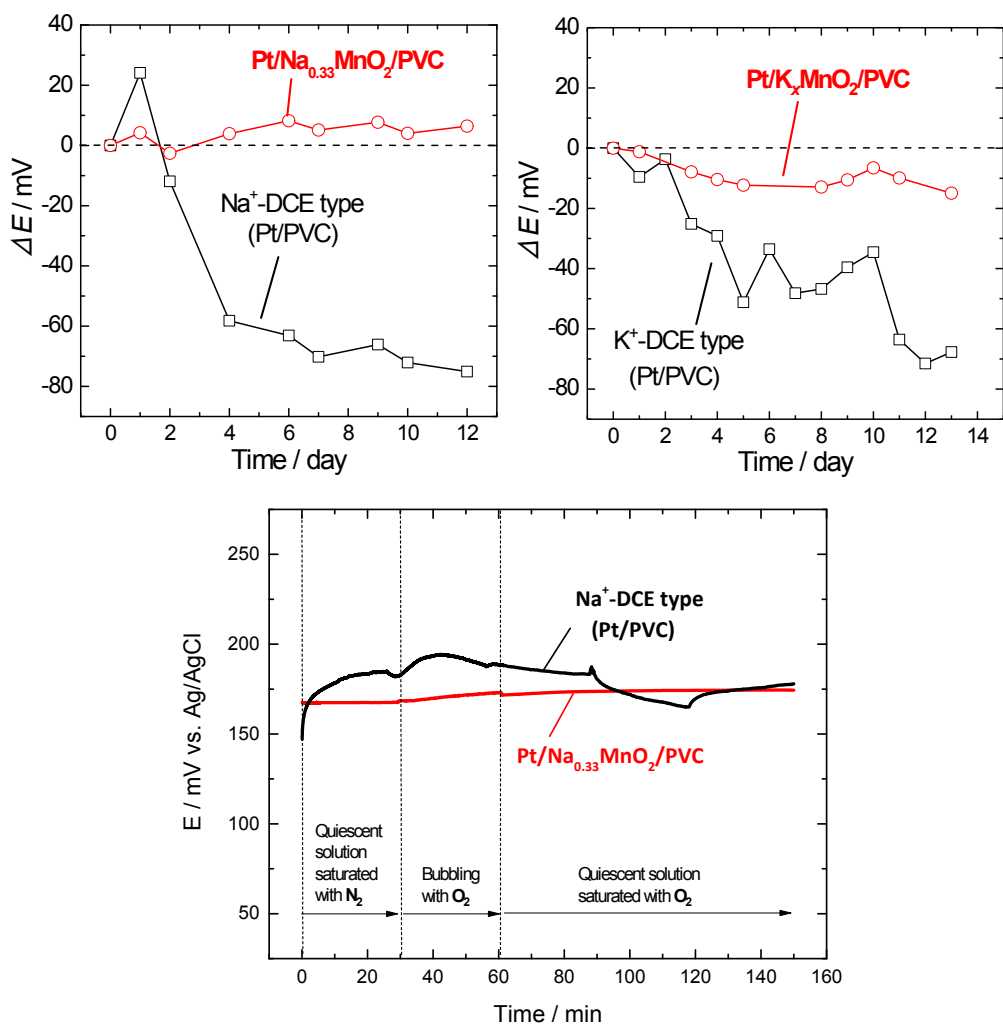


Figure S4. (top) Long-term potential stability of the Na⁺-ion and K⁺-ion selective electrodes; DCE type Pt/PVC and Pt/(insertion materials)/PVC in 0.01 mol dm⁻³ NaCl or KCl aqueous solution. (bottom) Dependence of response potential on N₂ and O₂ saturation in a 0.01 mol dm⁻³ NaCl aqueous solution for the Na⁺-ISEs; Pt/PVC and Pt/Na_{0.33}MnO₂/PVC electrodes.

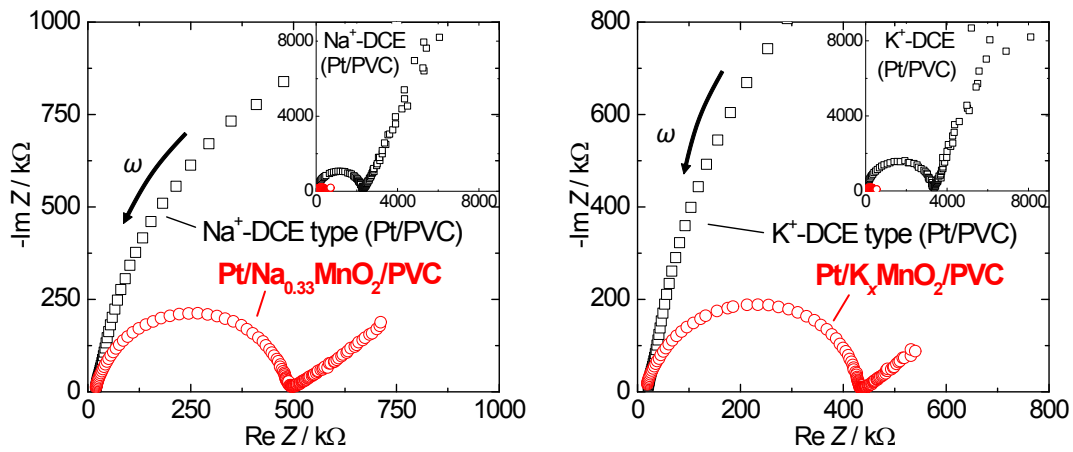


Figure S5. Nyquist plots of Na⁺-ion and K⁺-ion selective electrodes comparing the DCE type Pt/PVC and Pt/(insertion materials)/PVC electrodes.

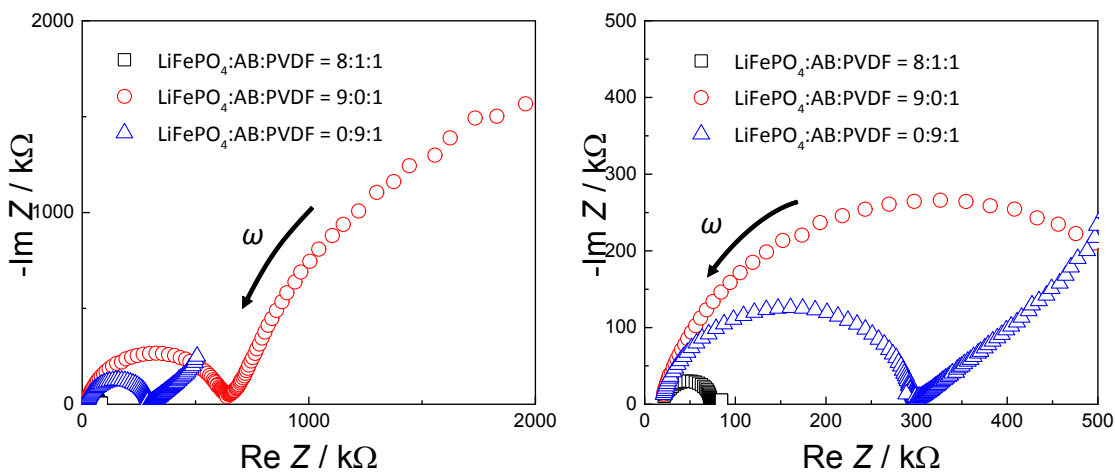


Figure S6. Nyquist plots of Li⁺-ion selective electrodes; the Pt/AB-PVDF/PVC (blue), Pt/LiFePO₄-PVDF/PVC (red), and Pt/LiFePO₄-AB-PVDF/PVC (black) electrodes in 0.1 mol dm⁻³ LiCl aqueous solution.

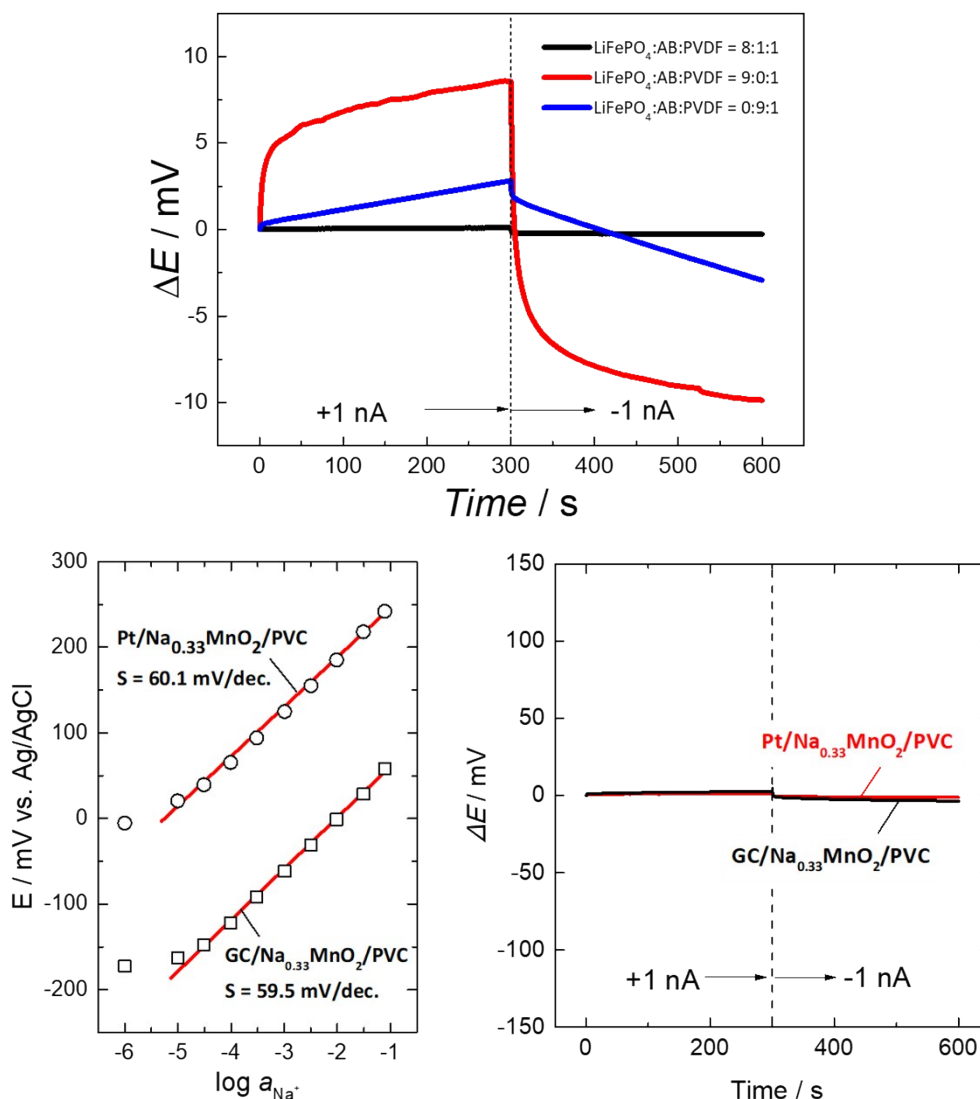


Figure S7. (upper) Chronopotentiograms of Li⁺ ion selective electrodes; the Pt/AB-PVDF/PVC (blue), Pt/LiFePO₄-PVDF/PVC (red), and Pt/LiFePO₄-AB-PVDF/PVC (black) electrodes at reversal constant current of +1.0 and – 1.0 nA for 0 – 300 and 300 – 600 s, respectively, in 0.1 mol dm⁻³ LiCl aqueous solution. (bottom) Dependence on electrode bed; (bottom left) logarithm of sodium ion activity vs. electrode potential plots obtained in 0.01 M Tris-HCl buffered solution at pH = 7.5 and (bottom right) chronopotentiograms of the Pt/Na_{0.33}MnO₂/PVC and GC/Na_{0.33}MnO₂/PVC electrodes at reversal constant current of +1.0 and – 1.0 nA for 0 – 300 and 300 – 600 s, respectively, in 0.1 mol dm⁻³ NaCl solution.

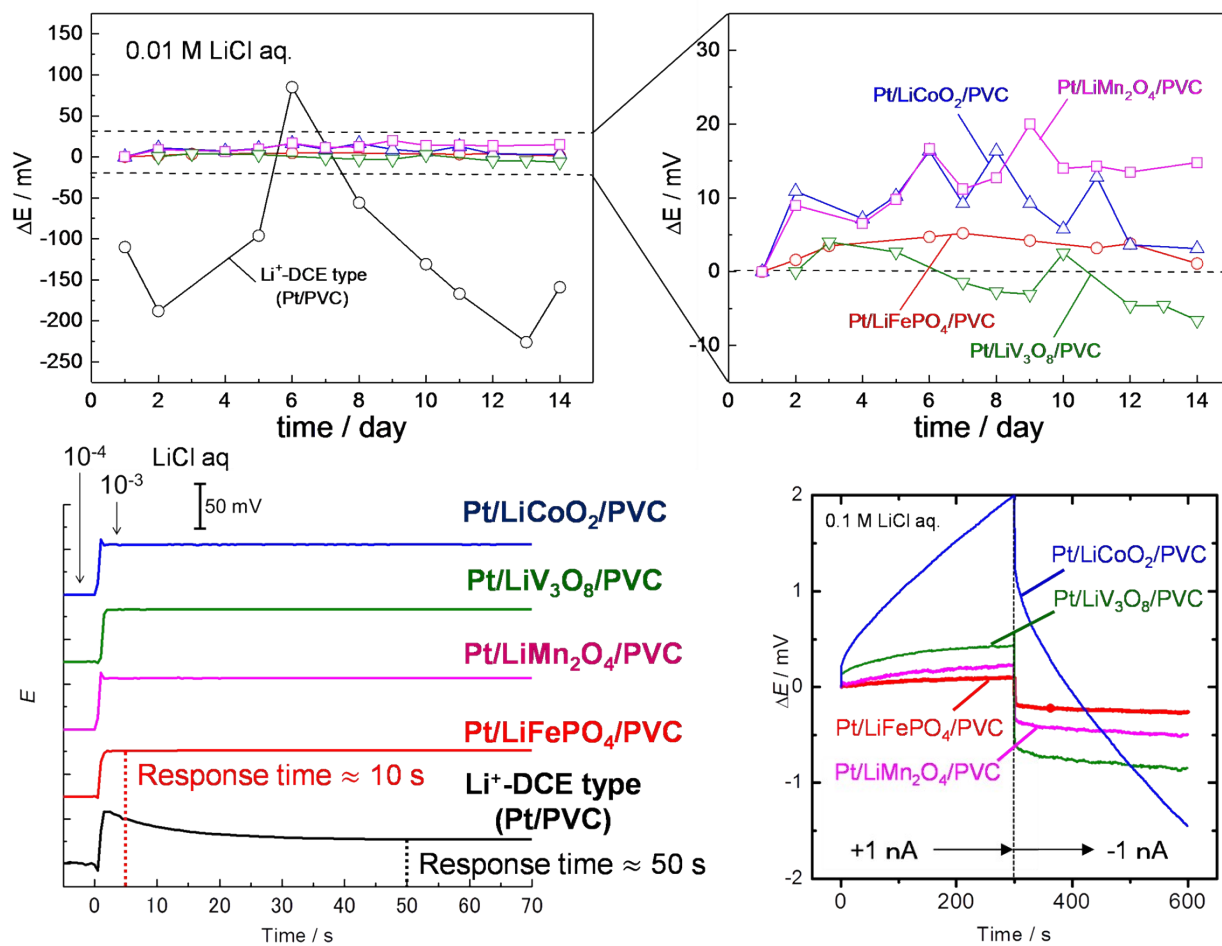


Figure S8. Long-term potential stability, response time, and chronopotentiograms of Li^+ -ion selective electrodes; Pt/PVC and four different Pt/(Li insertion materials)/PVC electrodes.

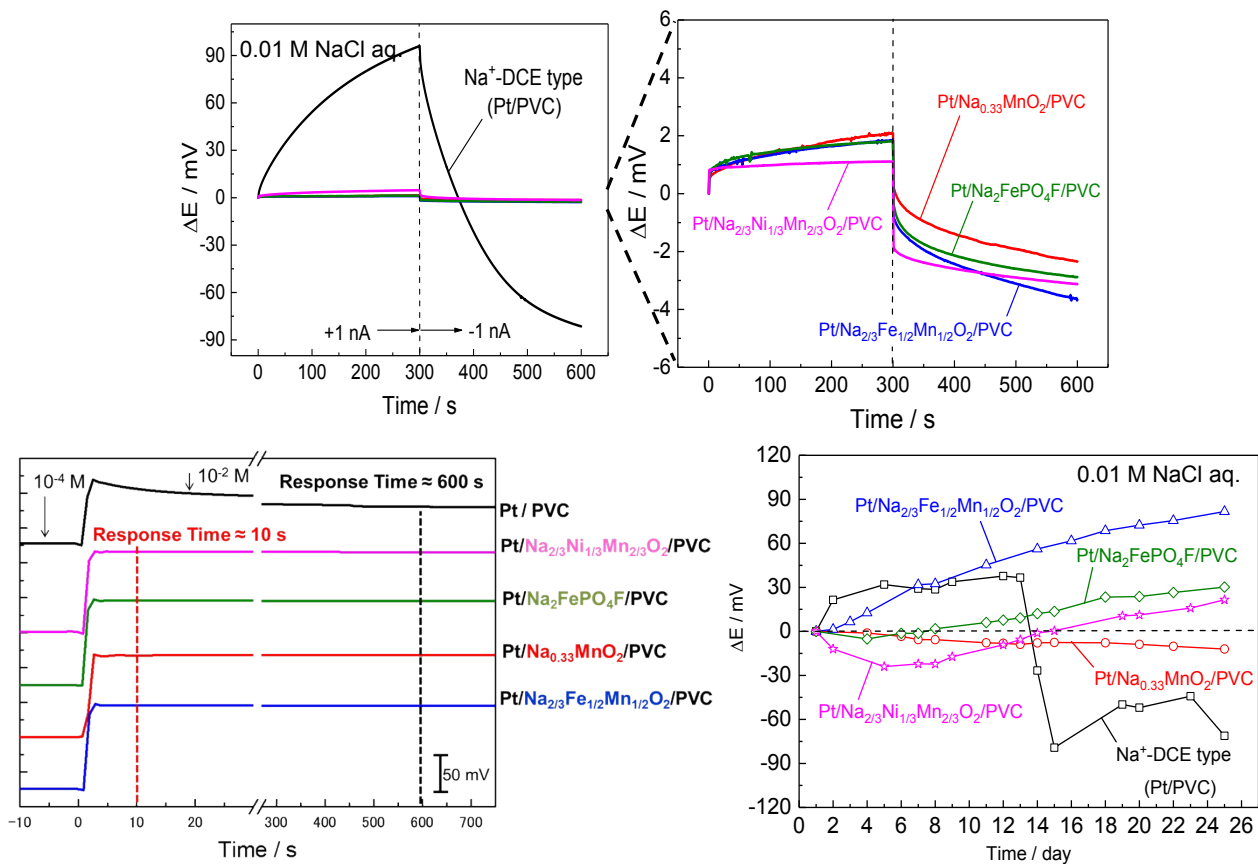


Figure S9. Chronopotentiograms, response time, and long-term potential stability of Na^+ -ion selective electrodes; Pt/PVC and four different Pt/(Na insertion materials)/PVC electrodes.

Table S3. Determination of lithium concentration contained in the mineral water measured by using the five Pt/LiFePO₄/PVC electrodes and ICP-AES analysis for comparison.

Electrode Lot #	Obtained Li ⁺ concentration in mineral water samples (ppm)	Electrode performance as slope (mV/dec.) in the calibration at RT
# 1	11.8	59.0
# 2	12.1	58.6
# 3	11.8	58.2
# 4	11.8	57.4
# 5	13.5	56.2
Ref. ICP-AES	11.8	