

Supplementary Material

for

**An all-solid-state thin-layer laminated cell for calibration-free coulometric
determination of K⁺**

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1. Conductometric titration of the aqueous solution of tetraethylammonium chloride

Figure S1 shows the results of conductometric titration of tetraethylammonium chloride (TEACl) with sodium tetraphenylborate (NaTPhB). TEA⁺ forms a precipitate with TPhB⁻ in the aqueous phase, and the resulting ionic composition of the aqueous phase alters the conductivity. A flexion point appeared upon the addition of ~18 cm³ of the NaTPhB solution, which was an equivalent point. The titration was performed four times, and the correction factor of the TEACl aqueous solution was evaluated to be 0.901 ± 0.01.

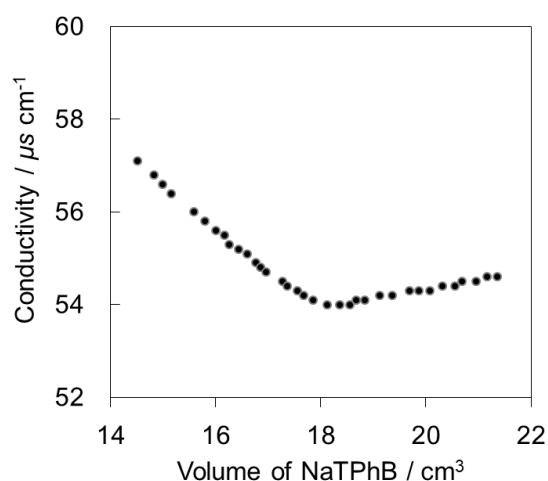


Fig. S1. Conductometric titration of tetraethylammonium chloride (TEACl) with sodium tetraphenylborate (NaTPhB). The TEACl aqueous solution (1 mmol dm⁻³, 20 cm³) was titrated with an aqueous solution of 1 mmol dm⁻³ NaTPhB.

2. Cyclic voltammetry for investigating the transfer of tetraethylammonium ions (TEA⁺) in the thin-layer laminated cell

Figure S2 shows the dependence of the peak current on the scan rate with respect to the transfer of TEA⁺ in the thin-layer laminated cell. The peak current increased proportionally to $\nu^{1/2}$, indicating the control of the peak current by the diffusion of TEA⁺ in the aqueous phase. The peak potentials varied in the 84–132 mV range, suggesting the existence of a small resistance in the peak current, which was attributed to solution resistance in the NPOE membrane and charge-transfer resistances at the boundary interfaces (Ag/AgCl-E, W–NPOE interface, PEDOT-PEG:TFPB/carbon-E).

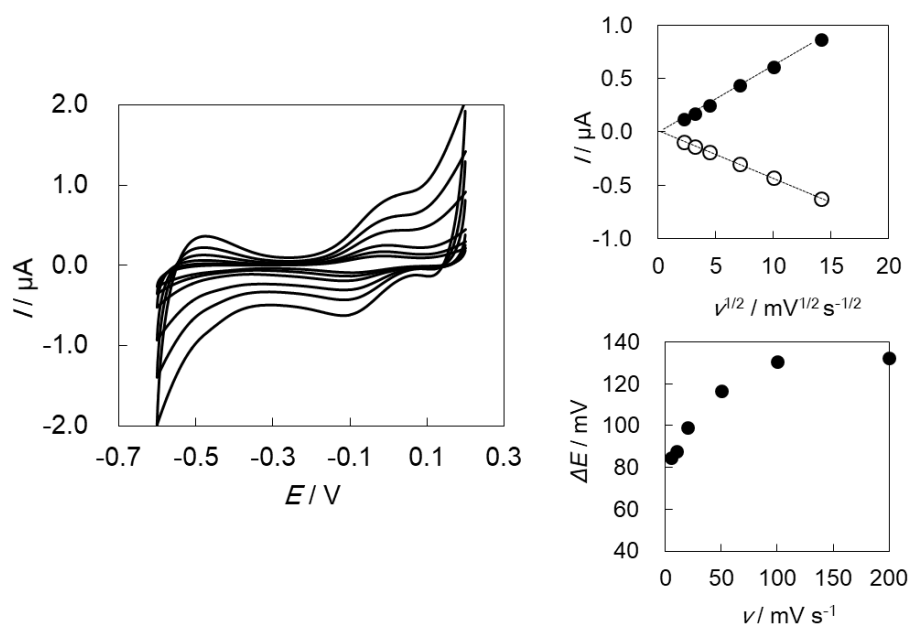


Fig. S2. Scan rate dependence of voltammograms corresponding to the transfer of TEA⁺ in the thin-layer cell. Scan rates of 5, 10, 20, 50, 100, and 200 mV s⁻¹ were employed. The sample was a 0.89 mm³ aqueous drop containing 50 μmol dm⁻³ TEACl and 0.01 mol dm⁻³ MgCl₂.

2. Peak currents corresponding to the transfer of Na⁺ in the thin-layer laminated cell

Figure S3 shows the peak currents acquired in the absence of K⁺. The peak current at -0.05 V was dependent on the concentration of Na⁺ in an aqueous solution (Fig. 9) and on the concentration of valinomycin (Fig. S3). Therefore, the peak currents could be attributed to the valinomycin-assisted transfer of Na⁺.

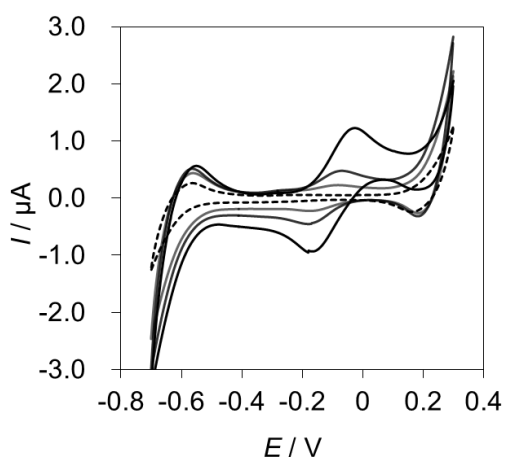


Fig. S3. Voltammograms corresponding to the transfer of Na⁺ facilitated by various concentrations of valinomycin (0, 2, 5, and 10 mmol dm⁻³). Each sample was a 0.89 mm³

aqueous drop containing 10 mmol dm^{-3} NaCl. A scan rate of 20 mV s^{-1} was employed.