Supplementary Information

Modelling and Analysis of Polarisation Characteristics in Lithium Insertion Electrodes Considering Charge Transfer and Contact Resistances

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Experimental

XRD Measurements

The crystal structures of $Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O_4$ (LAMO) were identified via powder X-ray diffraction (XRD) using an X-ray diffractometer (XRD-6100, Shimadzu Co. Ltd., Japan). An iron tube (wavelength: λ = 1.93579 Å) was used as the X-ray source, and the X-rays were monochromatised using a graphite monochromator. The tube voltage and current were 40 kV and 15 mA, respectively. The measurement range was 10° to 100° in 2θ, and the scan rate was 0.5° min^{-1}. The lattice constants were calculated using the least-squares method.

Electrode Preparation and Cell Fabrication

The diluted-LAMO electrode consisted of 20 wt% LAMO, 68 wt% Al_2O_3, 6 wt% acetylene black, and 6 wt% polyvinylidene fluoride (PVdF). To prepare the LAMO electrodes, a slurry was made by mixing LAMO, Al_2O_3, and acetylene black, and adding PVDF dissolved in N-methyl-2-pyrrolidone. This slurry was cast onto an aluminium foil, dried under vacuum overnight at 150 °C, and punched out to 2 cm^2 (diameter 16 mm). The loading weight of the electrodes was approximately 30 mg, with a thickness of approximately 100 µm. The electrochemical cell consisted of an LAMO electrode as the positive electrode, Li metal as the negative electrode, and 1 M $LiPF_6$ dissolved in an ethylene carbonate/dimethyl carbonate (3/7 by volume) solution as the electrolyte.

Construction of LAMO/LAMO Symmetric Cell

To prepare LAMO/LAMO symmetric cells, two identical diluted-LAMO electrodes with the same loading weight, thickness, reversible capacity, and polarisation were initially cycled in a cell with a Li metal electrode. One electrode was set to be fully oxidised, and the other fully reduced, before combining them into a single cell.

Electrochemical Measurements

To preliminarily confirm the electrochemical behaviours of the Li/LAMO and LAMO/LAMO symmetric cells, constant-current charge-discharge tests were performed using a battery cycler (Battery Laboratory System, Keisokuki Centre Co. Ltd., Japan). The cells were cycled at 0.1 mA cm^{-2} at 25°C.

To examine the electrochemical impedance spectroscopy (EIS) of the cell, a frequency response analyser (Solartron, SI1287A) was connected to a potentiostat (Solartron SI1287A), and a sinusoidal voltage with an amplitude of 10 mV was applied to the cell. The measurement frequency ranged from 100 kHz to 10 mHz, with 10 points measured per decade on a logarithmic scale.

For the steady-state polarisation measurements, the same instruments used for the EIS measurements were employed. A sinusoidal voltage with an amplitude of 1000 mV was applied to the LAMO/LAMO symmetric cells, and both the applied voltage and the output current were recorded using a data logger (NR-500, Keyence). The steady-state polarisation curves were analysed using data from the 10th cycle onwards, when the response current had stabilised.

Derivation of the Polarisation Equation of Lithium Insertion Electrodes

If the electrode kinetics of the Li insertion reactions follow the Butler-Volmer equation, the polarisation curve can be calculated using Eq. (S1).

$$j = j_0\left[exp\frac{(1-\alpha)F\eta}{RT} - exp\frac{-\alpha F\eta}{RT}\right] \qquad (S1)$$

In the region where the overpotential is sufficiently large ($\eta > 0.1$ V), one of the current components becomes negligibly small, so the Butler-Volmer equation simplifies to the Tafel equation below.

$$i_a = i_0 exp\frac{(1-\alpha)F\eta}{RT} \text{ and } i_c = i_0 exp\frac{-\alpha F\eta}{RT} \qquad (S2)$$

The exchange current density is expressed by the following equation using charge-transfer resistance:

$$j_0 = \frac{RT}{nFR_{ct}} \qquad (S3)$$

By substituting Eq. (S3) into Eq. (S2), the relationship between the activation overpotential and the current density due to the charge transfer reaction can be expressed as follows:

$$j = \frac{RT}{nFR_{ct}} exp\left(\frac{\alpha nF}{RT}\eta\right) \qquad (S4)$$

In addition to R_{ct}, lithium insertion electrodes involve a contact resistance R_{cont} between the active material and the current collector, which exhibits resistance polarisation behaviour. Since resistance polarisation follows Ohm's law, it can be expressed by Eq. (S5).

$$\eta_{cont} = j\,R_{cont} \qquad \text{(S5)}$$

The equivalent circuit of the lithium insertion electrodes comprises R_{cont} and R_{ct} connected in series. Therefore, the polarisation equation for the lithium insertion electrodes is obtained by summing both overvoltages.

$$\eta = \eta_{ct} + \eta_{cont} = \frac{RT}{\alpha nF} \ln\left(\frac{nFR_{ct}}{RT} \times j\right) + R_{cont} \times j \qquad (1)$$

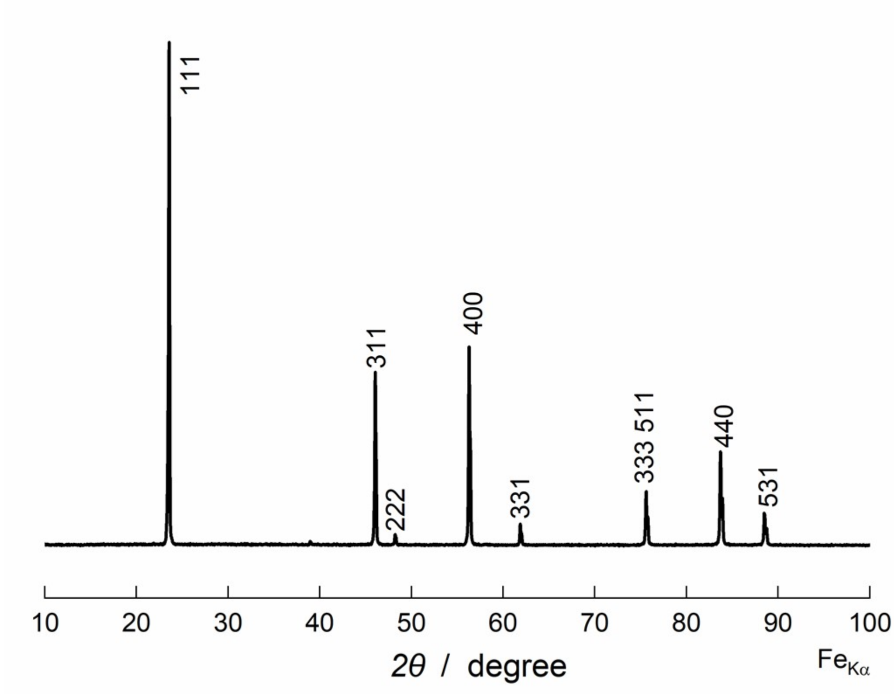

Fig. S1 Powder XRD pattern of LAMO.

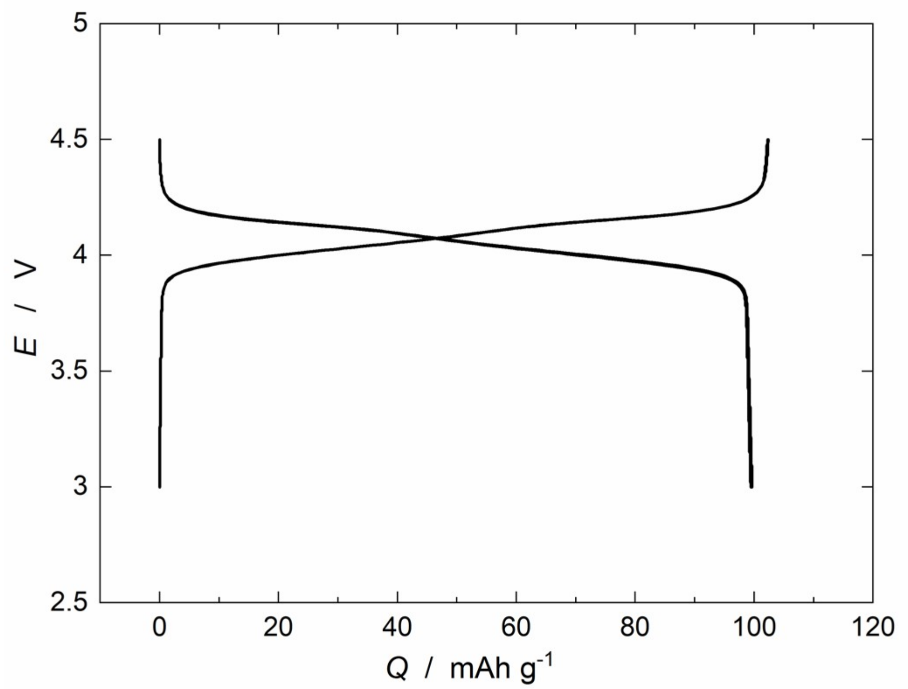

Fig. S2 Charge-discharge curves of a diluted-LAMO electrode tested in a cell with a lithium metal electrode. The cell was operated at a rate of 0.1 mA cm^{-2} at 25°C. The diluted LAMO electrodes comprised 20 wt% LAMO, 68 wt% Al_2O_3, 6 wt% acetylene black and 6 wt% PVdF.

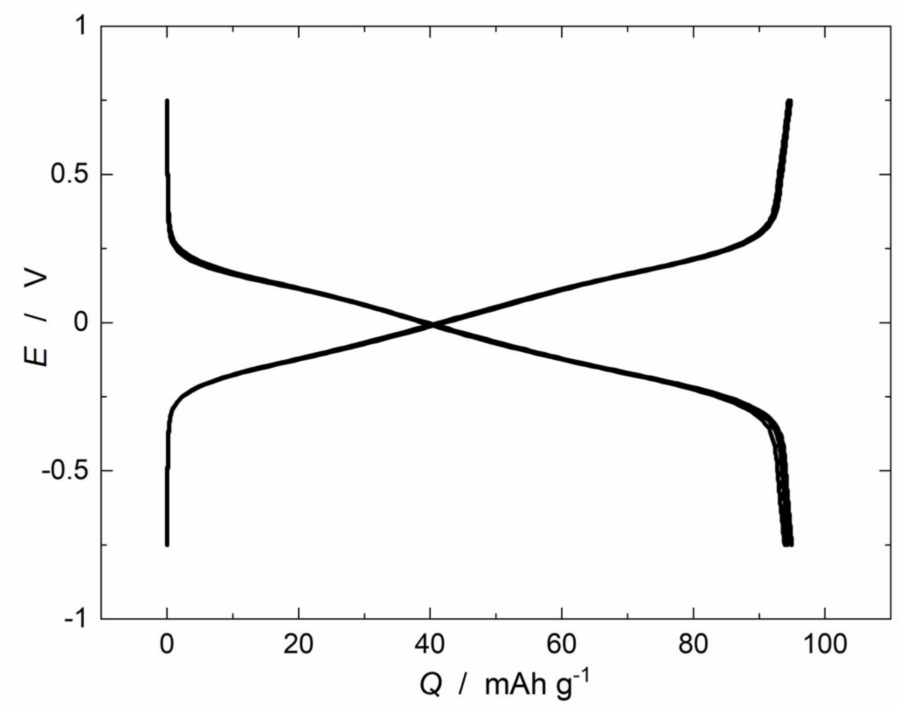

Fig. S3 Charge-discharge curves of a LAMO/LAMO symmetric cell operated at a rate of 0.1 mA cm^{-2} at 25°C. The symmetric cell comprised two identical diluted-LAMO electrodes with loading weights of 35.9 mg and 34.2 mg, and thicknesses of 105 μm and 102 μm, respectively. The diluted LAMO electrodes consisted of 20 wt% LAMO, 68 wt% Al_2O_3, 6 wt% acetylene black and 6 wt% PVdF.

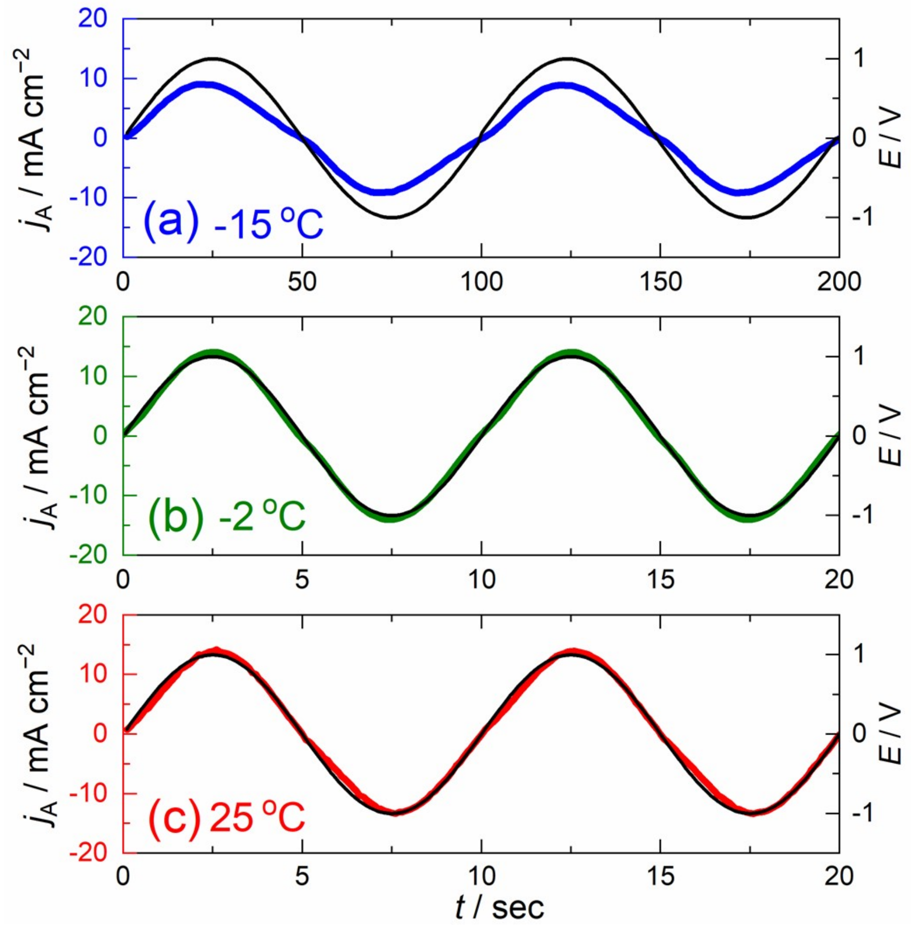

Fig. S4 Applied voltage and output current for polarisation measurements of the LAMO/LAMO symmetric cell at (a) −15°C, (b) −2°C and (c) 25°C. The frequency of the applied voltage was (a) 10 mHz and (b, c) 100 mHz.

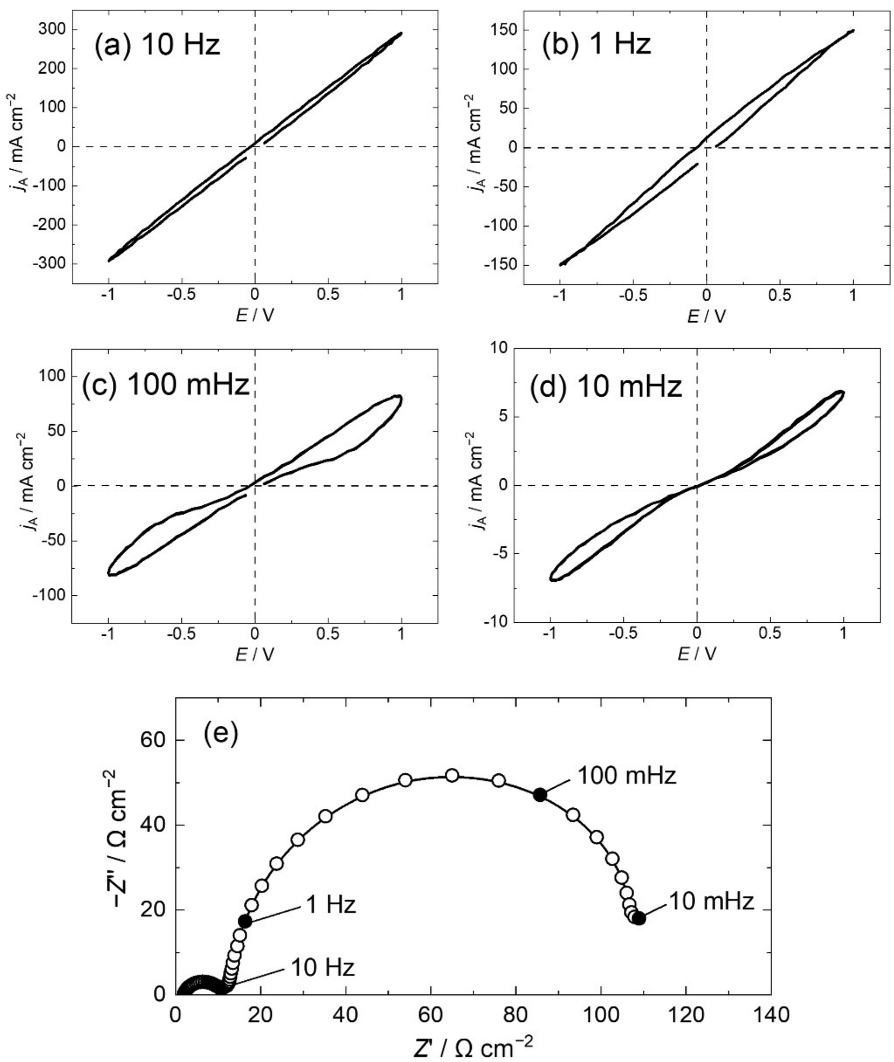

Fig. S5 (a-d) Steady-state polarisation curves and (e) Nyquist plots of the LAMO/LAMO symmetric cell at −5°C. The frequency of applied voltage was (a) 10 Hz, (b) 1 Hz, (c) 100 mHz and (d) 10 mHz.