# Supporting Information:

# Lithium Metal Protected by Atomic Layer Deposition Metal Oxide for High Performance Anodes

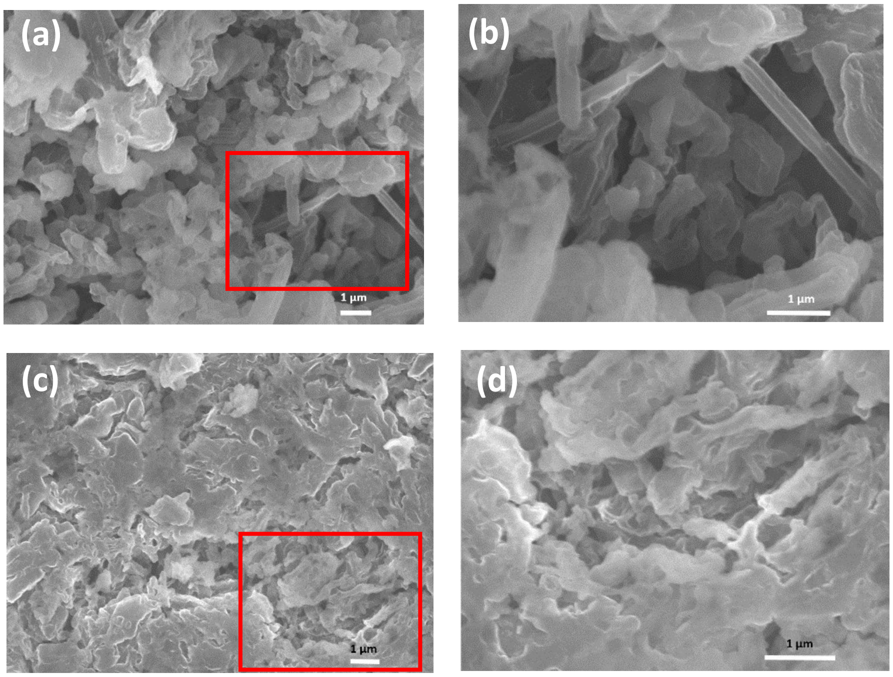

Figure S1. SEM images of Li surface in symmetric cell after 50 charge-discharge cycles. (a) Pristine Li (9,000 magnification). (b) Magnified view of region in red box in Figure S1a (20,000 magnification). (c) 4nm $Al_2O_3$ coated Li (9,000 magnification). (d) Magnified view of region in red box in Figure S1c (20,000 magnification).

Table S1: Atomic composition of Li coated with 10 and 20 ALD $Al_2O_3$ cycles prior to electrochemical cycling as measured by XPS.

| | Concentration (at%) | |
|---|---|---|
| Species | 10×$Al_2O_3$ Li | 20×$Al_2O_3$ Li |
| Al | 2.1 | 2.9 |
| Li | 44.0 | 41.7 |
| O | 39.2 | 35.3 |
| C | 14.5 | 19.5 |
| F | 0.1 | 0.6 |

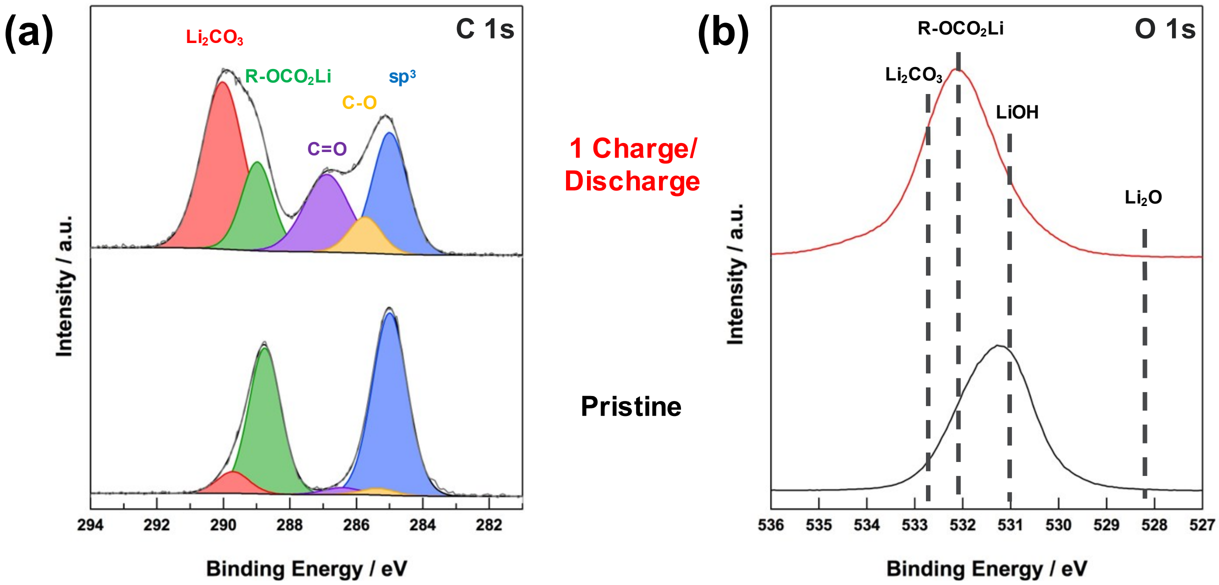

Figure S2. High-resolution XPS spectra for the (a) C 1s and (b) O 1s core levels. The bottom spectra show the surface speciation for the pristine ALD-coated Li (20x$Al_2O_3$), and the top spectra show the change in surface speciation after one discharge-charge cycle.

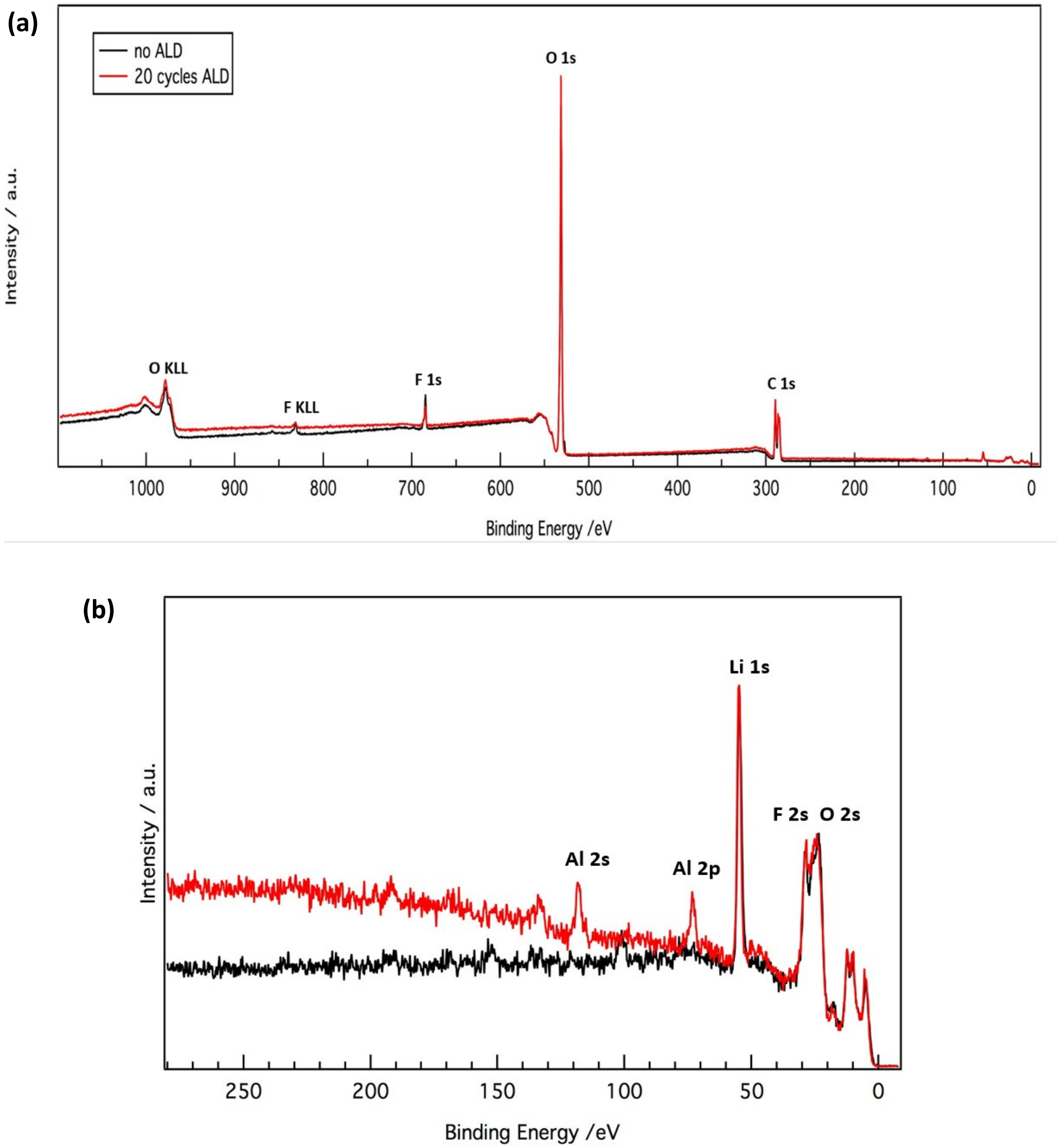

Figure S3. XPS spectra of bare Li and 20×$Al_2O_3$ Li after 10 stripping/plating cycles. Signals taken from the center of the electrodes. (a) In the range of 0-1100 eV after 10 stripping/plating cycles. (b) In the range of 0-280 eV after 10 stripping/plating cycles.

Table S2 Elemental concentration for uncoated Li and 20 ×$Al_2O_3$ coated Li after 10 discharge-charge cycles by XPS

| | Concentration (at%) | |
|---|---|---|
| Species | Uncoated Li | 20 × $Al_2O_3$ Li |
| Al | 0.0 | 1.1 |
| Li | 36.6 | 31.4 |
| O | 34.9 | 36.3 |
| C | 26.7 | 30.1 |
| F | 1.7 | 1.1 |

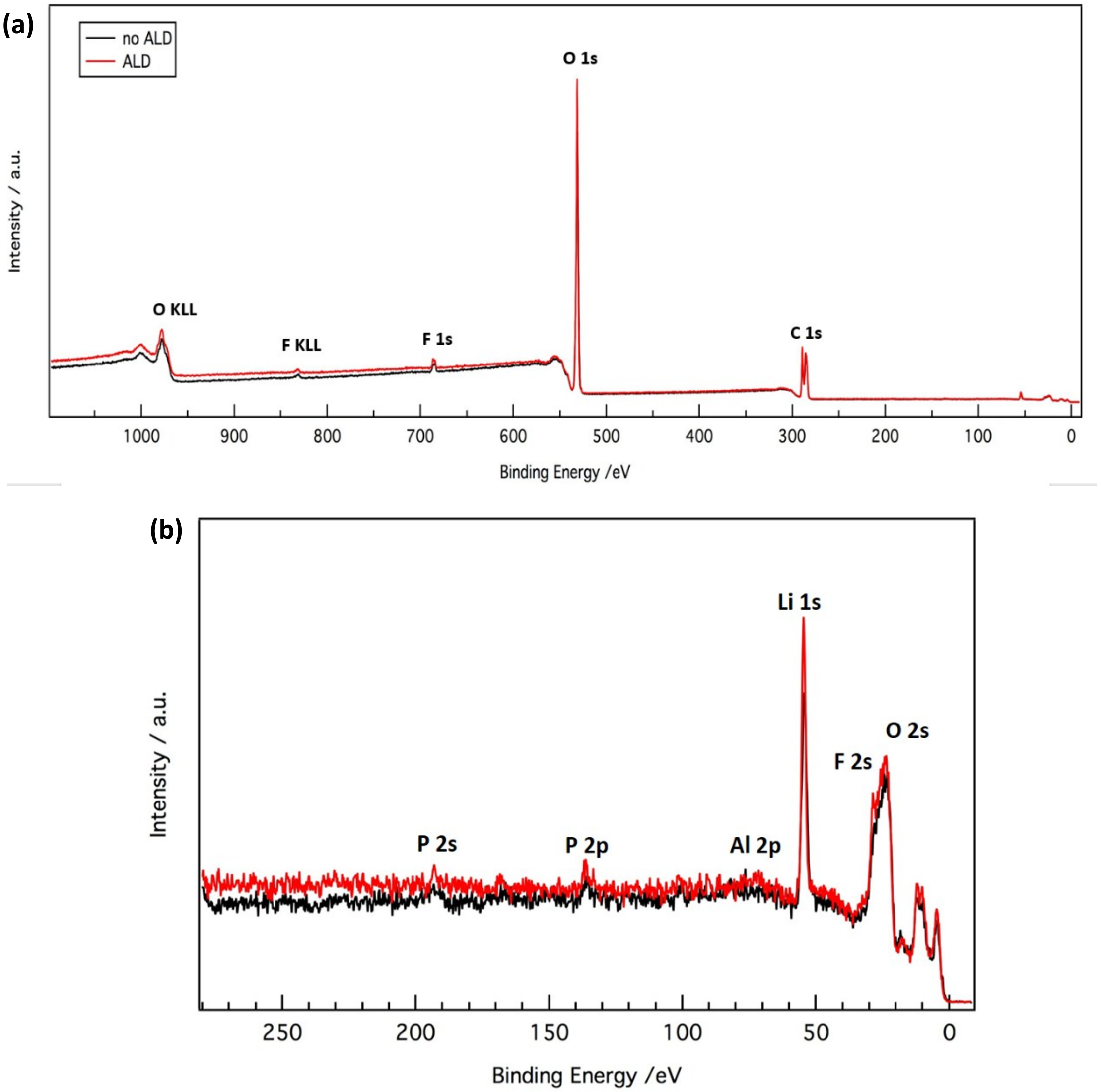

Figure S4. XPS of bare Li and 20×$Al_2O_3$ Li after 50 stripping/plating cycles. Signals taken from the center of the electrodes in the range of: (a) 0-1100 eV after 50 stripping/plating cycles; (b) 0-280 eV after 50 stripping/plating cycles.

Table S3 Concentration of elements for uncoated Li and 20 ×$Al_2O_3$ coated Li after 50 discharge-charge cycles by XPS

| | Concentration (at%) | |
|---|---|---|
| Species | Uncoated Li | 20 × $Al_2O_3$ Li |
| Al | 0.0 | 0.0 |
| Li | 32.0 | 31.2 |
| O | 35.7 | 36.8 |
| C | 31.1 | 30.9 |
| F | 1.1 | 0.9 |

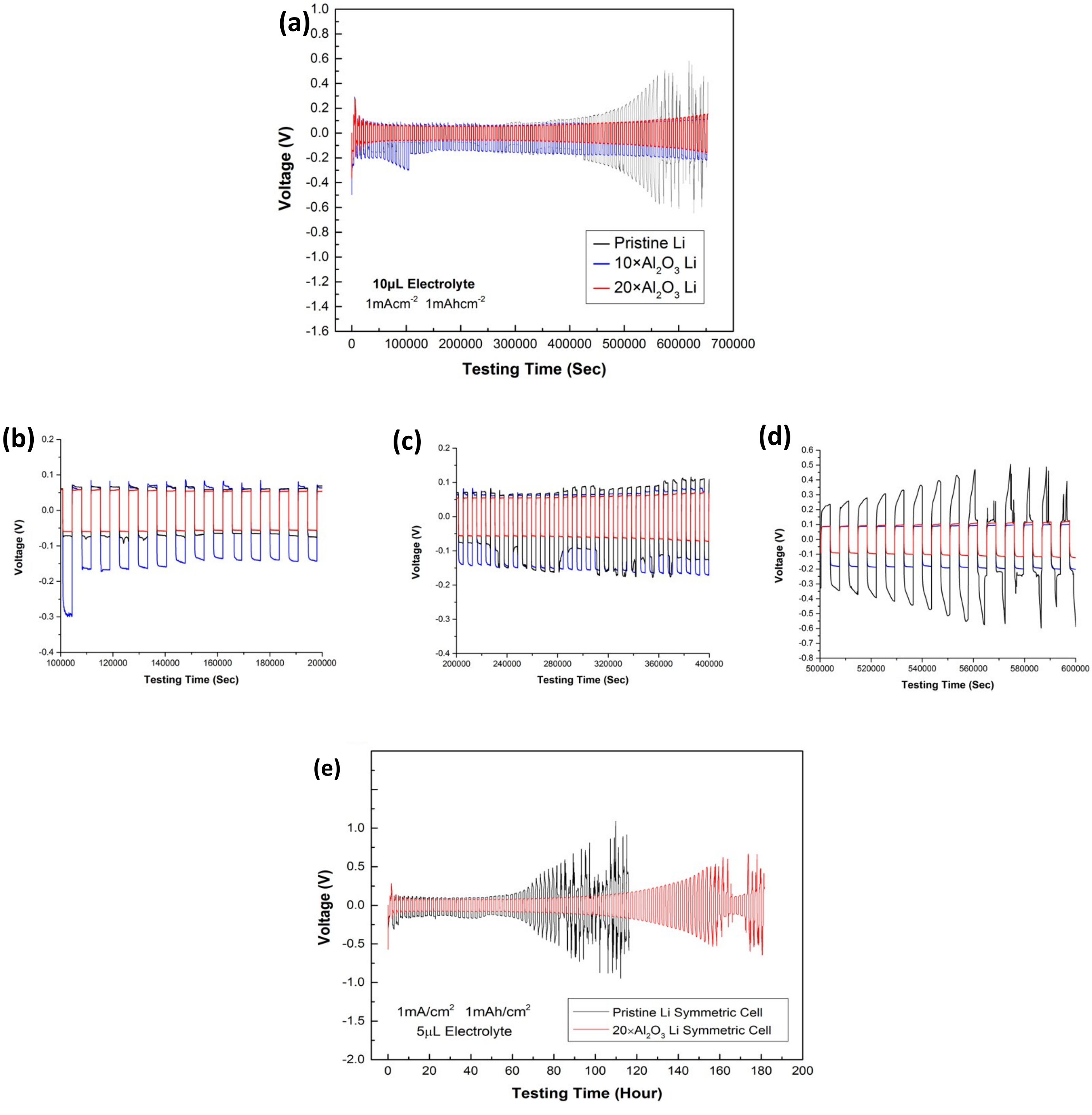

Figure S5. (a) Symmetric cell tests in 10 μL carbonate electrolyte at current density of 1 mA/cm$^2$ with capacity of 1mAh/cm$^2$. (b-d) Detailed voltage profile in different time range. (e) Symmetric cell tests using 5 μL carbonate electrolyte at current density of 1 mA/cm$^2$ with capacity of 1mAh/cm$^2$.

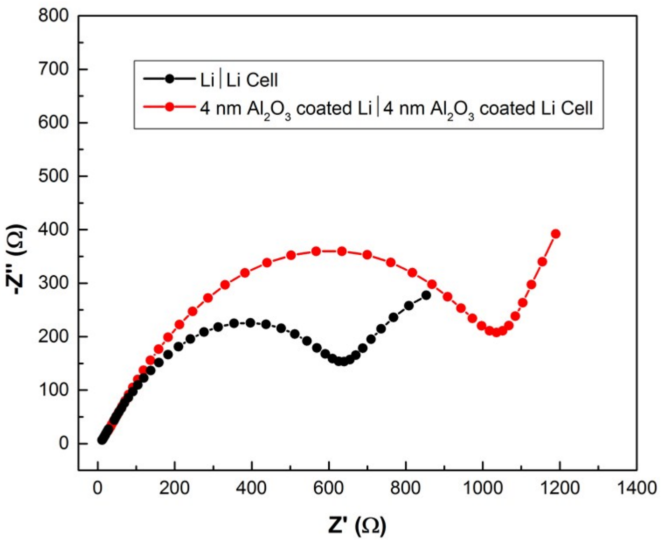

Figure S6. EIS of symmetric cells with 5 μL carbonate electrolyte before cycling (fresh cells).

**Fitting EIS data:** the slope of the incline line at low frequency is the Warburg coefficient (σ). The smaller of Warburg coefficient value, the steeper of the slope.[1] The coefficient can be expressed below,[2]

$$\sigma = \frac{RT}{\sqrt{2D_{\mathrm{Li}}}n^2F^2SC}$$

where R is the ideal gas constant, T is the thermodynamic temperature, F is the Faraday constant, n is the valence, $D_{\mathrm{Li}}$ is the diffusion coefficient of the Li ions in the cathode, C is the concentration of the $Li^+$ ions and S denotes the contacting area between the active material particles and the electrolyte. The slope of the uncoated Li-Cu is smaller than the $Al_2O_3$ coated Li-Cu cells, which means that the σ for uncoated Li is smaller, thus lithium ion conductivity is better with a larger $D_{\mathrm{Li}}$.

**Calculation of Li thickness:** the amount of Li stripped and plated when a Li/Li symmetric cell is discharged and charged at 1 mA/cm$^2$ to a capacity of 1 mAh/cm$^2$

In the discharge process, the amount of Li stripped from the anode is

$$\frac{1mAh/cm2 * 6.94g/mol * 6.24e18/Coul * 3.6Coul/mAh}{0.53g/cm3 * 6.022e23/mol} = 4.88\mu m$$

In the charge process, the amount of Li plated back to the anode side is also:

$$\frac{1mAh/cm2 * 6.94g/mol * 6.24e18/Coul * 3.6Coul/mAh}{0.53g/cm3 * 6.022e23/mol} = 4.88\mu m$$

Therefore, Li moved in the discharge and the charge process is both ~5 µm.

## References

1. G. Zhou, D.-W. Wang, L.-C. Yin, N. Li, F. Li and H.-M. Cheng, *ACS Nano*, 2012, **6**, 3214-3223.
2. N. Takami, A. Satoh, M. Hara and T. Ohsaki, *J. Electrochem. Soc.*, 1995, **142**, 371-379.