Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Sulfur Poisoning Pt and PtCo Anode and Cathode Catalysts in Polymer Electrolyte Fuel Cells Studied by Operando Near Ambient Pressure Hard X-ray Photoelectron Spectroscopy

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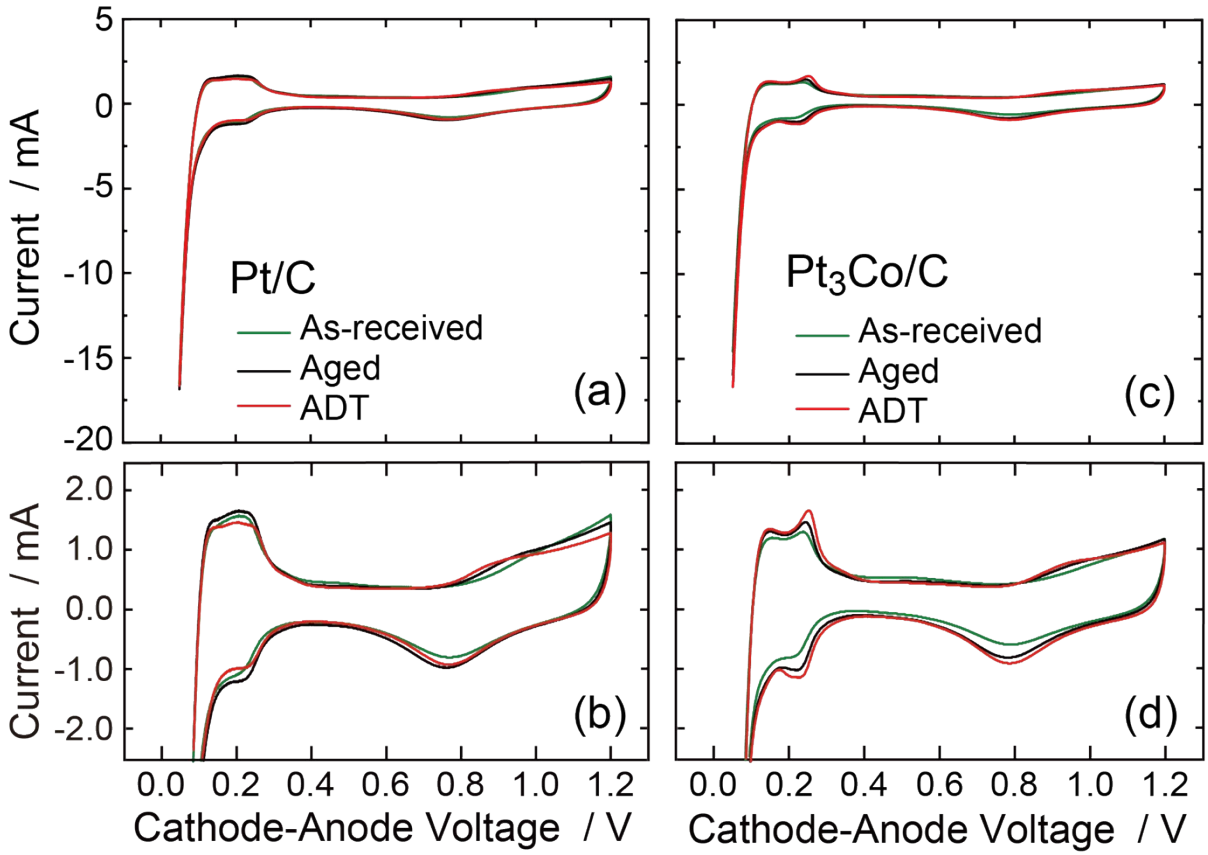

Figure S1. Typical CV curves of the cathode (a,b) Pt/C (2.6 nm) and (c,d) Pt_3Co/C (3.0 nm) electrodes for as-received, aged, and degraded (after ADT) MEA. (b) and (d) are just the magnified plots of (a) and (c), respectively.

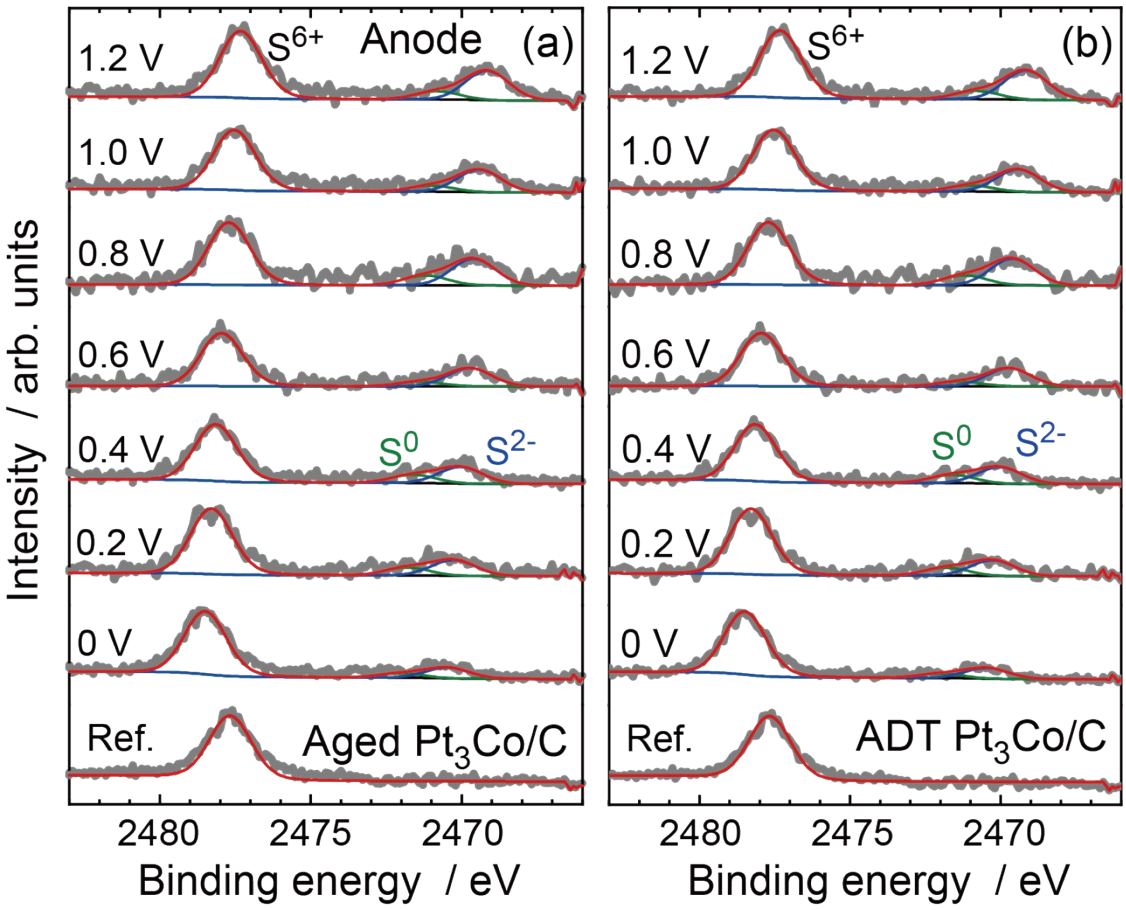

Figure S2. S 1s HAXPES at the anode Pt_3Co/C (3.0 nm) electrode with increasing the cathode-anode bias voltage from 0 to 1.2 V (a) before and (b) after ADT. At the anode, 4,000 Pa H_2O and 200 Pa H_2 gases were introduced, whereas N_2 (25 mL/min) flowed into the cathode. The cathode is grounded. The gray and red lines are the observed and fitted spectra, respectively.

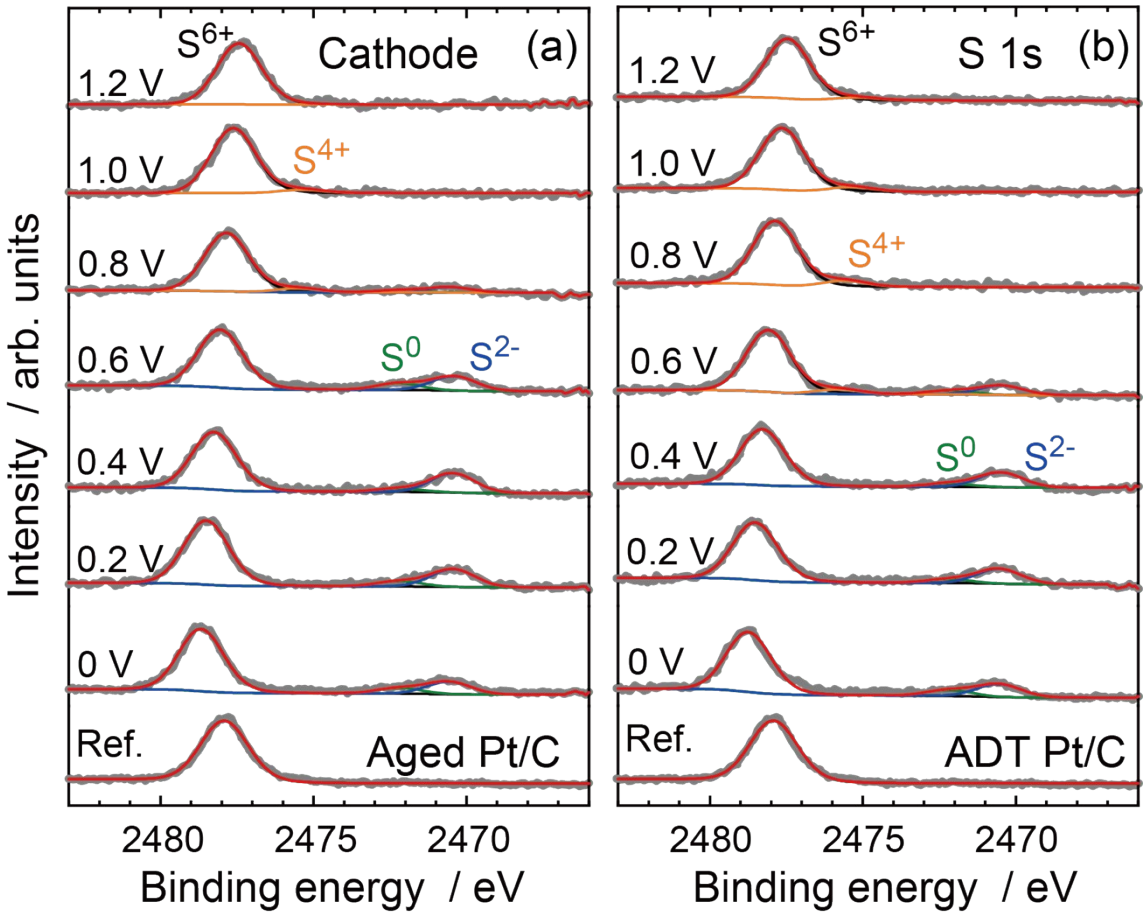

Figure S3. S 1s HAXPES at the cathode Pt/C (2.6 nm) electrode with increasing the cathode-anode bias voltage from 0 to 1.2 V (a) before and (b) after ADT. At the cathode, water vapor (4,000 Pa) from water bath (50°C) was introduced into the measurement chamber, whereas hydrogen gas (H_2, 99.99999%, 15 mL/min) was fed into the anode. The cathode is grounded. The gray and red lines are the observed and fitted spectra, respectively.

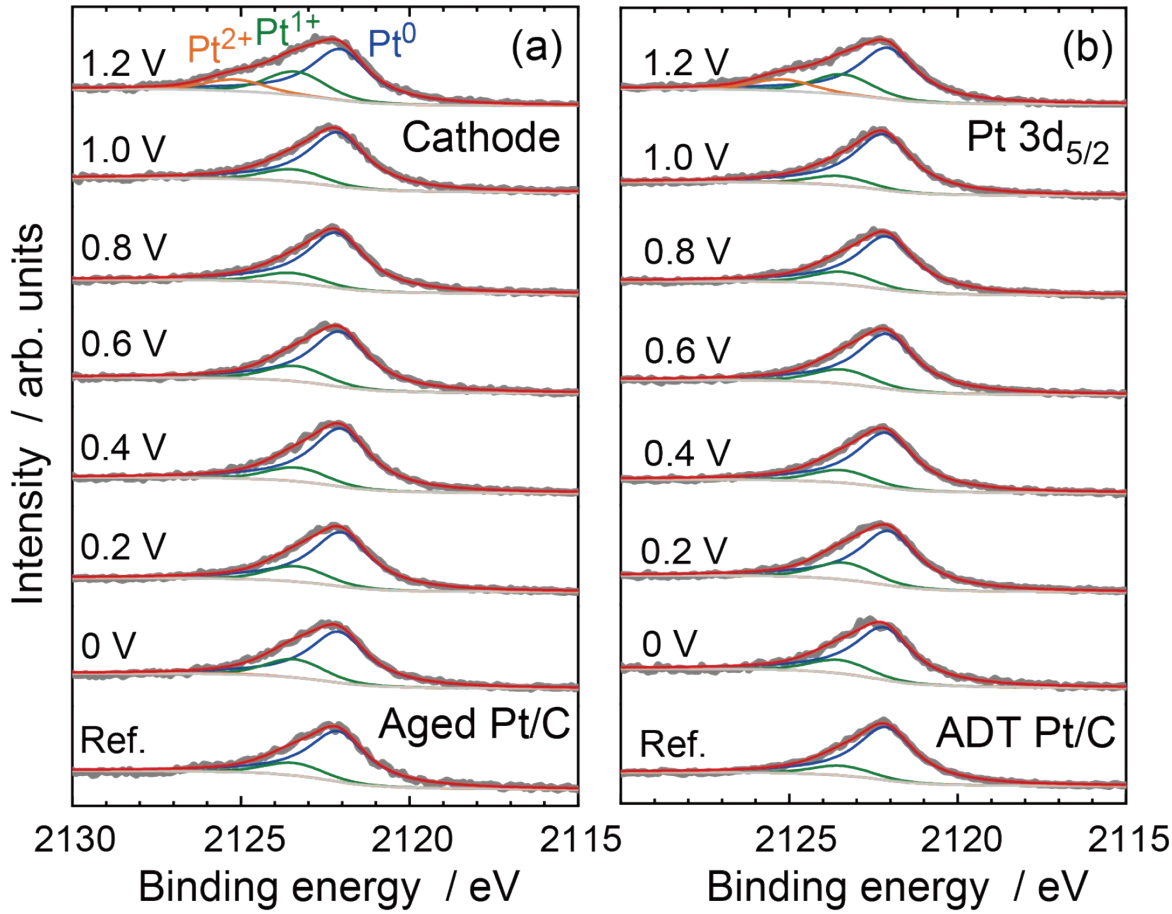

Figure S4. Pt $3d_{5/2}$ HAXPES at the cathode Pt/C (2.6 nm) electrode with increasing the cathode-anode bias voltage from 0 to 1.2 V (a) before and (b) after ADT. At the cathode, water vapor (4,000 Pa) from water bath (50°C) was introduced into the measurement chamber, whereas hydrogen gas (H_2, 99.99999%, 15 mL/min) was fed into the anode. The cathode is grounded. The gray and red lines are the observed and fitted spectra, respectively.

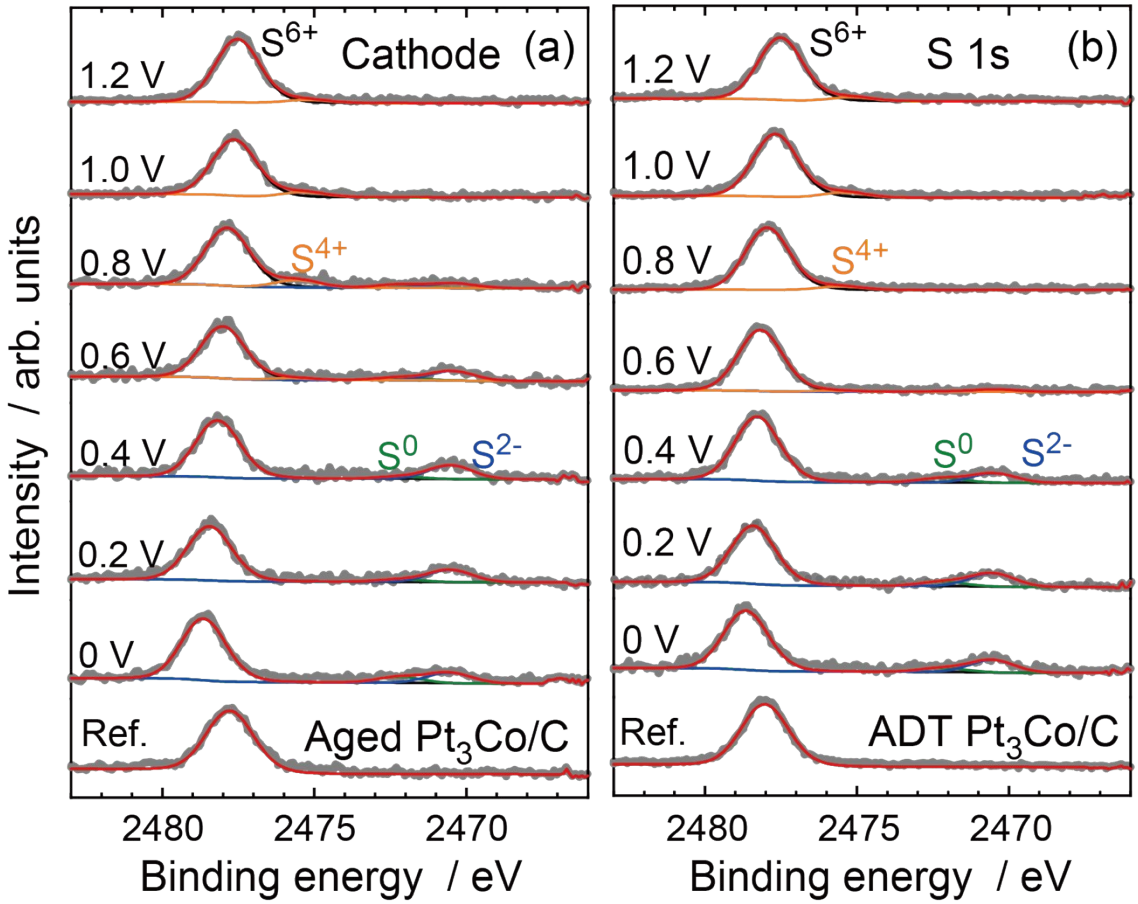

Figure S5. S 1s HAXPES at the cathode Pt_3Co/C (3.0 nm) electrode with increasing the cathode-anode bias voltage from 0 to 1.2 V (a) before and (b) after ADT. At the cathode, water vapor (4,000 Pa) from water bath (50°C) was introduced into the measurement chamber, whereas hydrogen gas (H_2, 99.99999%, 15 mL/min) was fed into the anode. The cathode is grounded. The gray and red lines are the observed and fitted spectra, respectively.

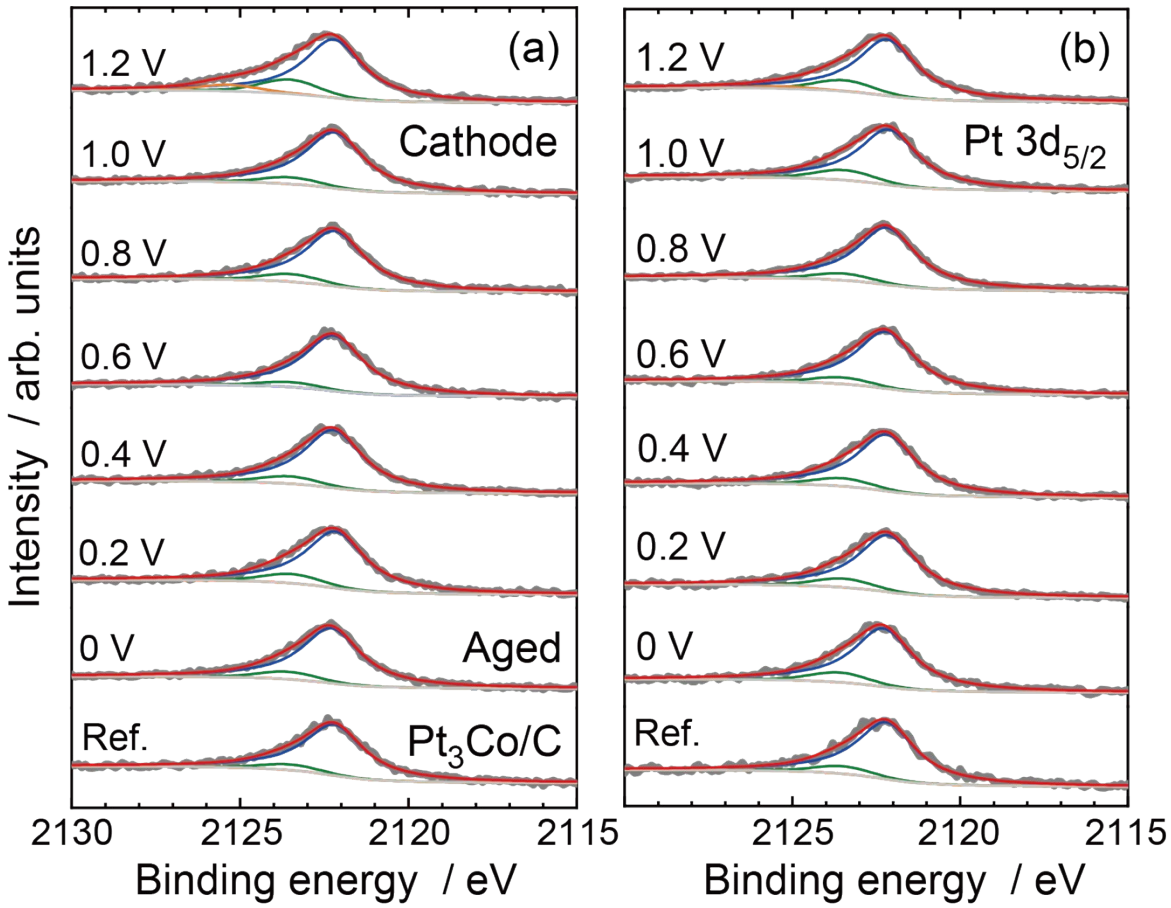

Figure S6. Pt $3d_{5/2}$ HAXPES at the cathode Pt_3Co/C (3.0 nm) electrode with increasing the cathode-anode bias voltage from 0 to 1.2 V (a) before and (b) after ADT. At the cathode, water vapor (4,000 Pa) from water bath (50°C) was introduced into the measurement chamber, whereas hydrogen gas (H_2, 99.99999%, 15 mL/min) was fed into the anode. The cathode is grounded. The gray and red lines are the observed and fitted spectra, respectively.

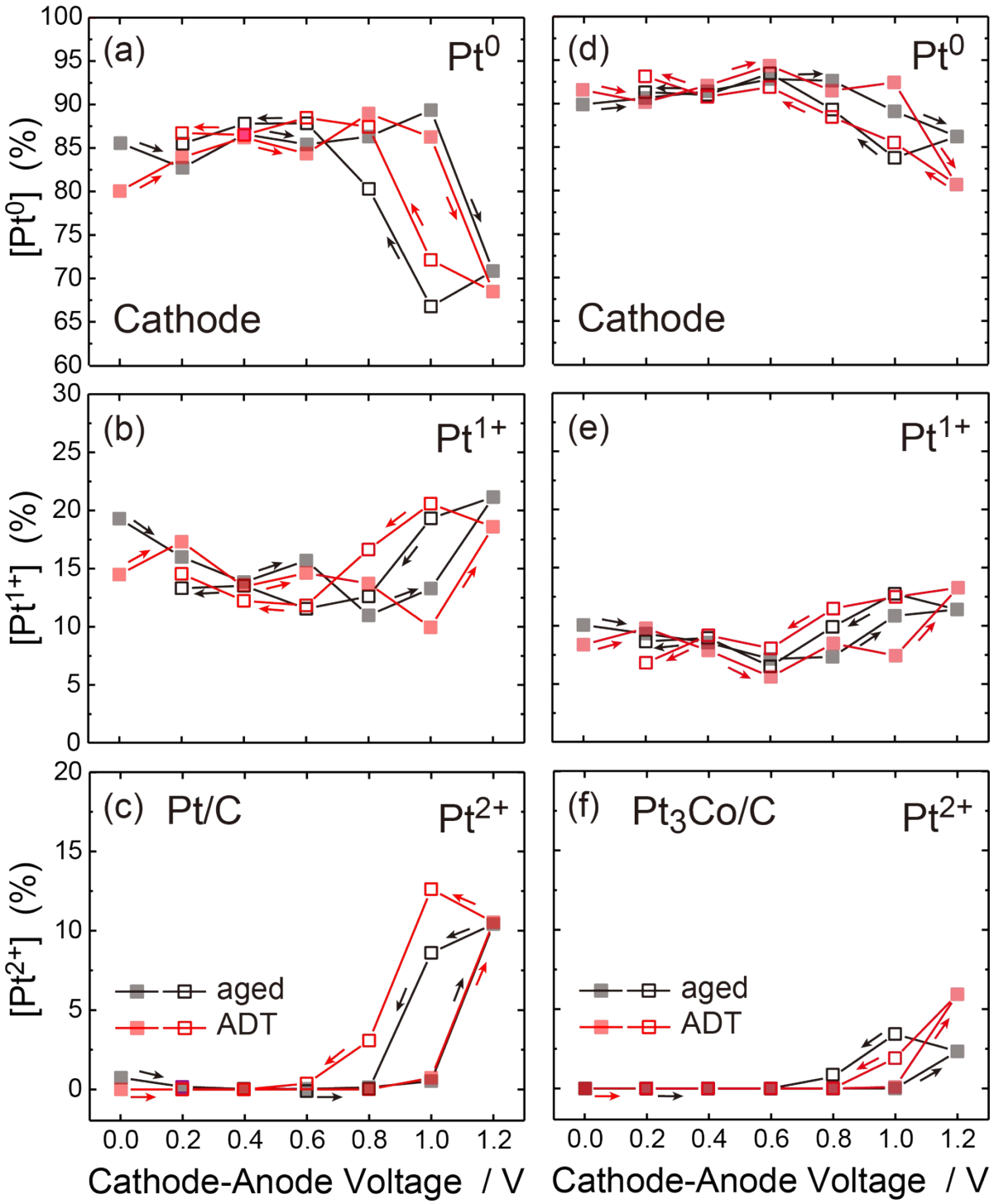

Figure S7. Component ratios of (a,d) Pt^0, (b,e) Pt^{1+}, and (c,f) Pt^{2+} in the Pt/C (a,b,c) and Pt_3Co (d,e,f) cathode electrodes before (black) and after (red) ADT, with increasing (light filled) and decreasing (open) the cathode-anode bias voltage, evaluated from the Pt $3d_{5/2}$ HAXPES given in Figures S3 and S5.