

Supporting Information
for
Fluorinated Ethylene Carbonate as Electrolyte Additive for
Rechargeable Na Batteries

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Experimental

The reagent grade sodium metal, poly(vinylidene fluoride) (Wako Pure Chemical Industries, Ltd.), battery grade ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), vinylene carbonate (VC), NaClO₄ (containing ca. 100 ppm H₂O), NaPF₆, NaN(SO₂CF₃)₂ (Kishida Chemical Co., Ltd.), fluoroethylene carbonate (FEC), *t*-di fluoroethylene carbonate (DFEC) (Kanto Denka Kogyo Co., Ltd.) and commercially available hard-carbon (Carbotron P(J), Kureha Co.) (ref. 4) are used. All chemicals are handled in an Ar-filled glove box (whose dew point ranges from –85 to –70°C). The NaNi_{1/2}Mn_{1/2}O₂ was synthesized as we previously described (ref. 4). For the electrode preparation, hard-carbon (90 wt%) was mixed with PVdF binder (10 wt%) in *N*-methylpyrrolidinone. The obtained slurry was doctor-bladed onto Al or Cu foil. The NaNi_{1/2}Mn_{1/2}O₂ (80 wt%) and acethylene black (10 wt%) were mixed with PVdF (10 wt%) in *N*-methylpyrrolidinone, and thus obtained slurry was cast onto Al foil. The electrodes were dried at > 80°C in a vacuum prior to use. The coin-type cells (20 mm diameter, 3.2 mm thickness) with hard-carbon or NaNi_{0.5}Mn_{0.5}O₂, and excess Na metal electrodes, electrolyte, and a glass fiber filter (thickness: 0.38 mm, Toyo Roshi Kaisha, Ltd.) as a separator were fabricated in the glove-box.

The electrodes were observed by using a scanning electron microscope (SEM, S-5000, Hitachi), transmission electron microscope (TEM, 200 kV, H-9500, Hitachi), and X-ray photoelectron spectrometer (XPS, JPS-9010MC, JEOL) equipped with monochromatic Mg K α X-ray source with depth profiling by argon ion beam sputtering. The electrolyte solution within separator was analyzed by attenuated total reflection-Fourier transform infrared spectroscopy (ATR FT-IR, NICOLET6700, Thermo Scientific. Co. Ltd.).

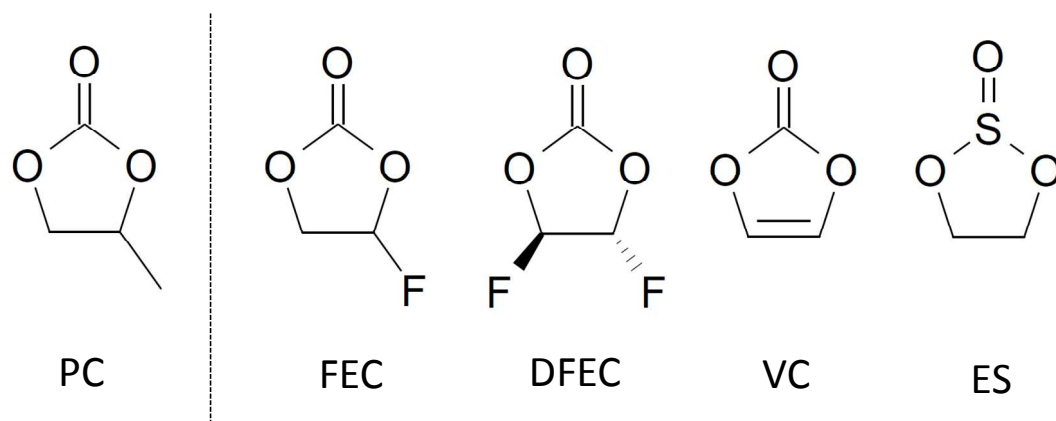


Figure S1. Molecular structures of electrolyte additives used in Na cells.

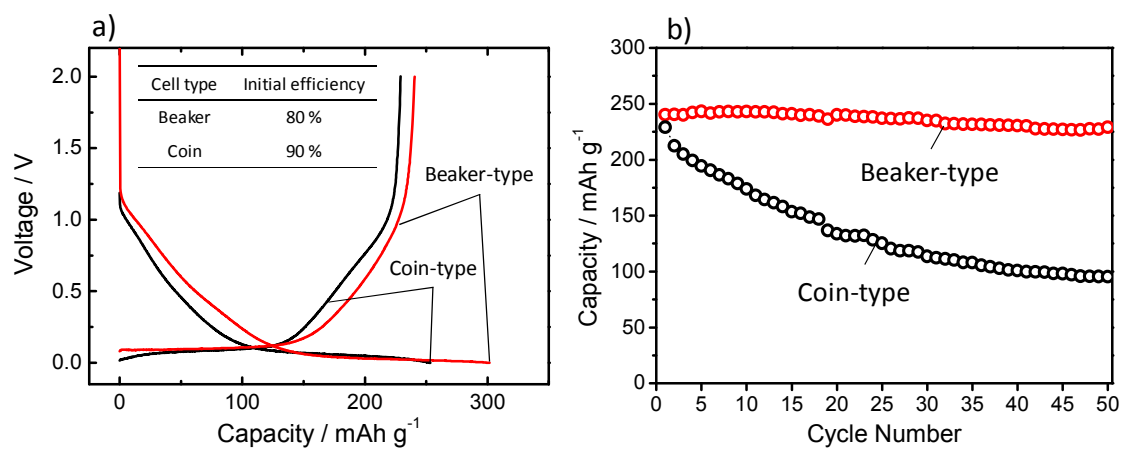


Figure S2. (a) The initial reduction/oxidation curves (inset: initial efficiency defined as $Q_{\text{oxidation}}/Q_{\text{reduction}}$) and (b) reversible capacity variation for hard-carbon electrodes in a 1 mol dm⁻³ NaClO₄ PC solution comparing results in beaker-type or coin-type Na cells at a rate of 25 mA g⁻¹.

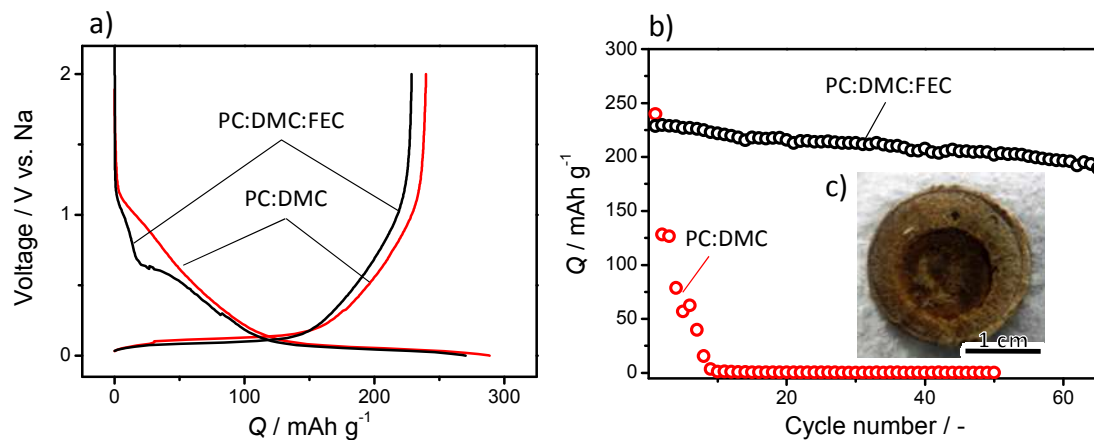


Figure S3. (a) The initial reduction/oxidation curves and (b) reversible capacity variation for hard-carbon on Al foil in 1 mol dm⁻³ NaClO₄ PC:DMC (1:1) solutions with and without 2 vol% FEC additive tested at a rate of – 25 and + 25 mA g⁻¹ in coin-type Na cells. (c) A photo of separator tested in the FEC-free PC:DMC after 50 cycles.

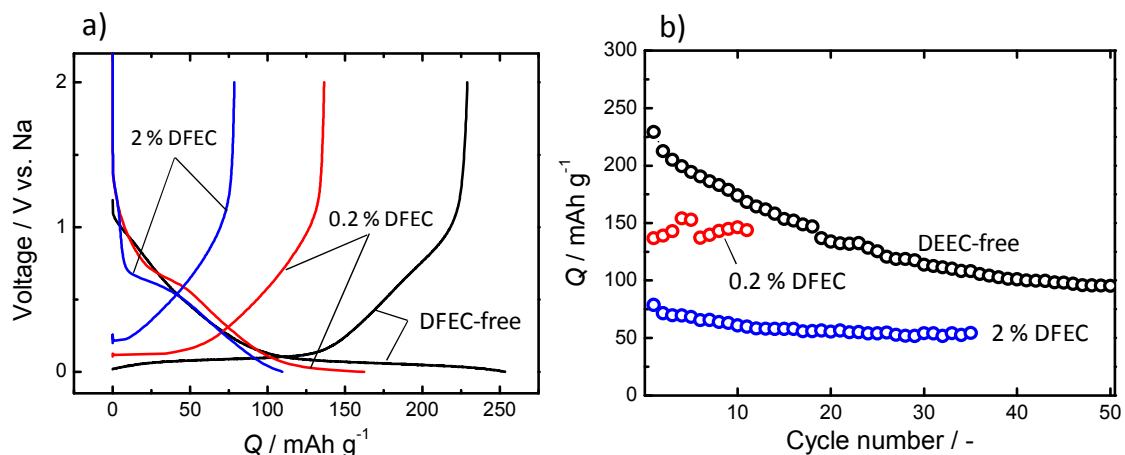


Figure S4. (a) The initial reduction/oxidation curves and (b) reversible capacity variation for hard-carbon electrodes in 1 mol dm⁻³ NaClO₄ PC solutions with and without 0.2 and 2 vol% DFEC examined at a rate of - 25 and + 25 mA g⁻¹ in coin-type Na cells.

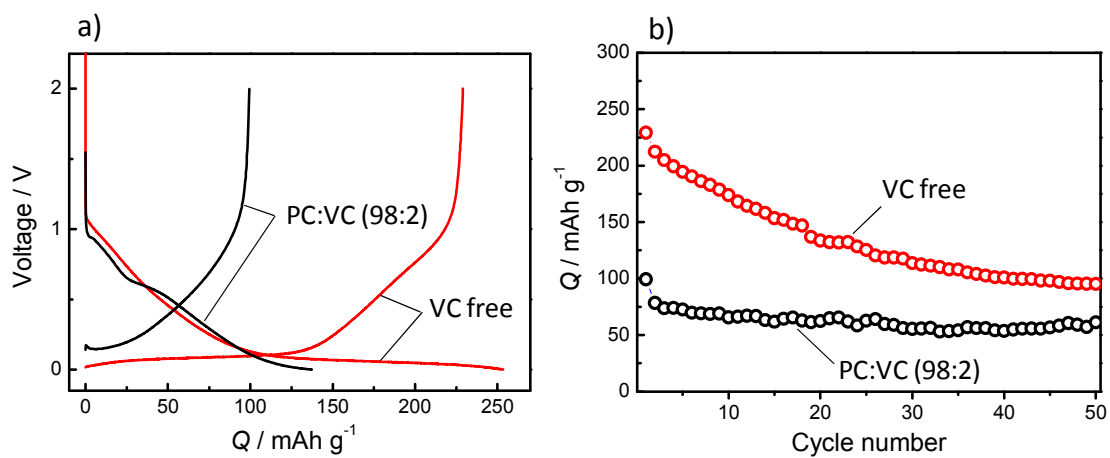


Figure S5. (a) The initial reduction/oxidation curves and (b) reversible capacity variation for hard-carbon electrodes in $1 \text{ mol dm}^{-3} \text{NaClO}_4$ PC solutions with and without 2 vol% VC examined at a rate of -25 and $+25 \text{ mA g}^{-1}$ in coin-type Na cells.

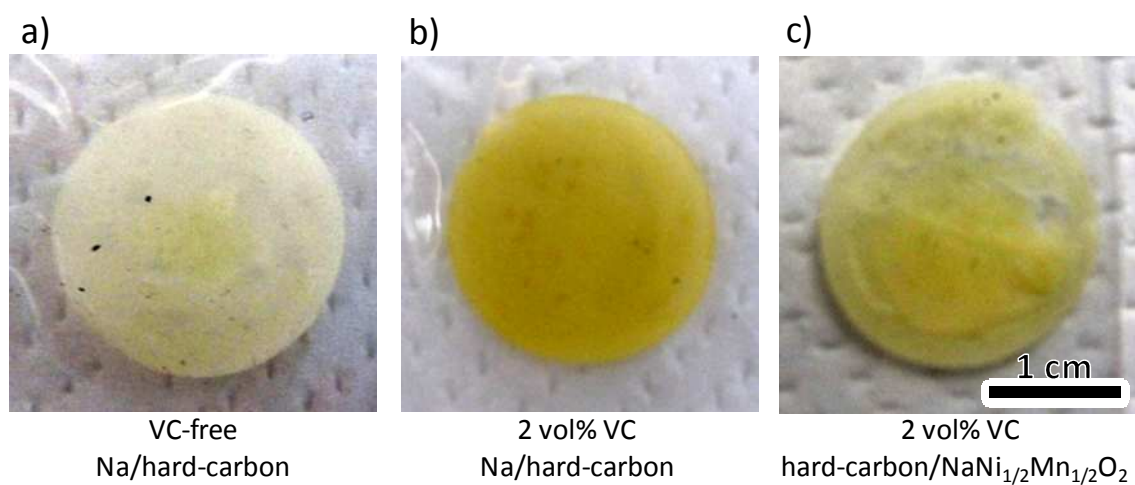


Figure S6. Photographs of the used glass-separators in coin-type cells of Na//hard-carbon (half cell) configuration with 1 mol dm⁻³ NaClO₄ in a) PC and b) PC:VC (98:2 volume) and c) hard-carbon//NaNi_{1/2}Mn_{1/2}O₂ (Na-ion full cell) configuration with the 2 vol% VC solution after the first galvanostatic cycle.

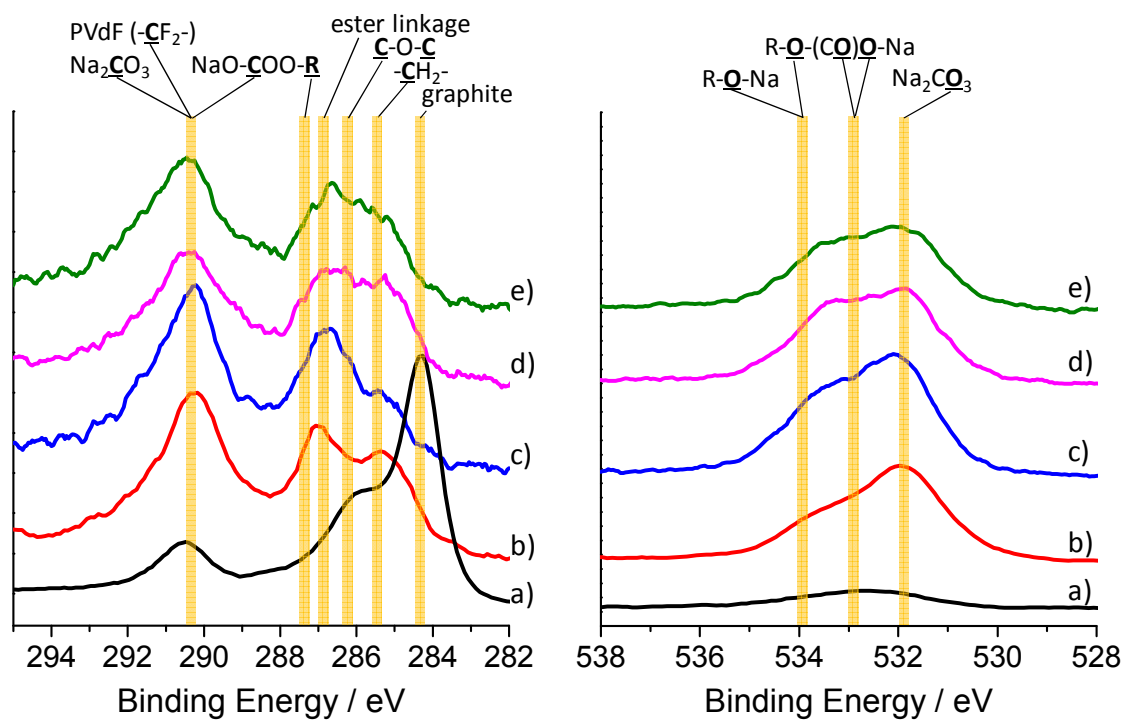


Figure S7. (left) C 1s and (right) O 1s X-ray photoelectron spectra for hard-carbons: a) pristine and hard-carbon electrodes after the first galvanostatic cycle test in 1 mol dm⁻³ NaClO₄ PC b) without and with c) 0.5, d) 2, and e) 10 vol% FEC addition in Na cells.

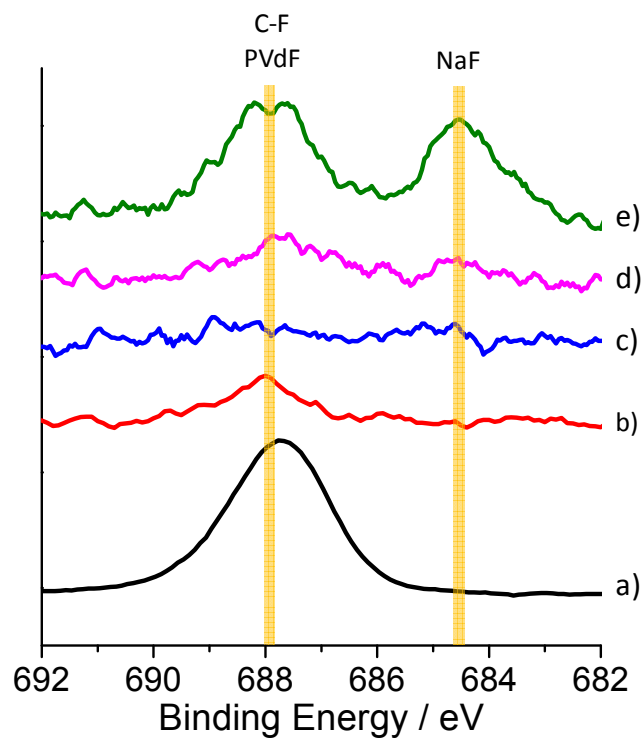


Figure S8. F 1s XPS spectra for hard-carbons: a) pristine and hard-carbon electrodes after the first galvanostatic cycle test in 1 mol dm⁻³ NaClO₄ PC b) without and with c) 0.5, d) 2, and e) 10 vol% FEC addition in Na cells.

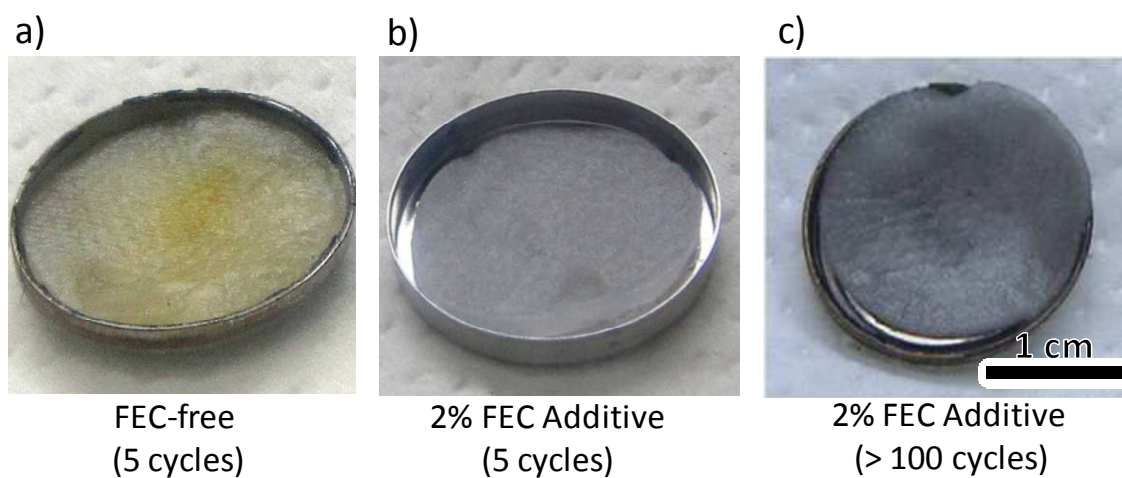


Figure S9. Photographs of the used glass-separators in coin-type cells of Na//hard-carbon cell with $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ in a) PC after 5 cycles, and b) PC:FEC (98:2 in volume) after b) 5 and c) 133 cycles.

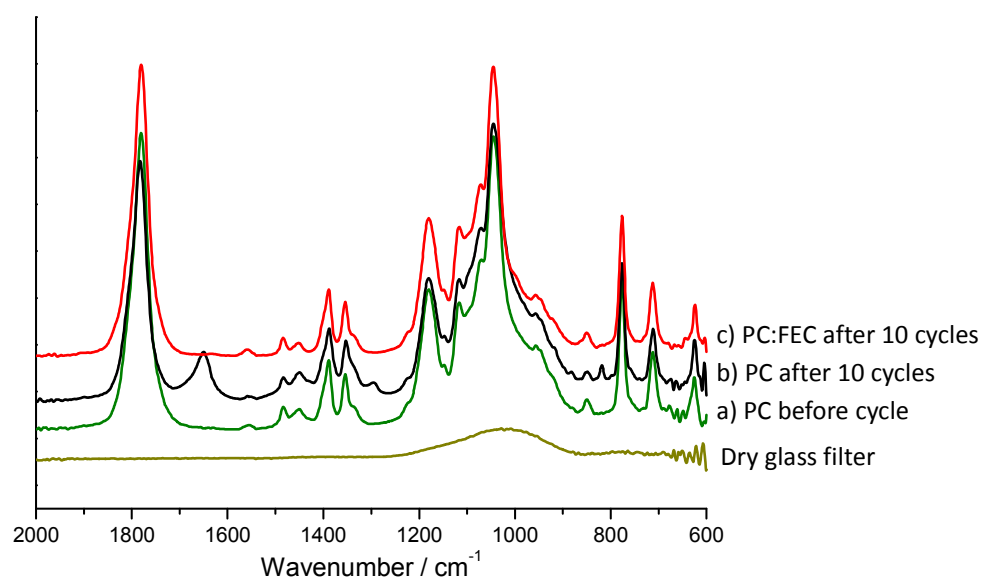


Figure S10. FT-IR spectra of the electrolyte solutions held in glass-separators a) before and after electrochemical tests in coin-type cells of Na//hard-carbon cell with 1 mol dm⁻³ NaClO₄ in b) PC after 10 cycles, and c) PC:FEC (98:2 in volume) after 10 cycles. Arrows indicate the peaks of decomposition products such as sodium alkoxides and/or sodium alkyl carbonates. A result of pristine glass-separator without any electrolyte solutions is shown for comparison.

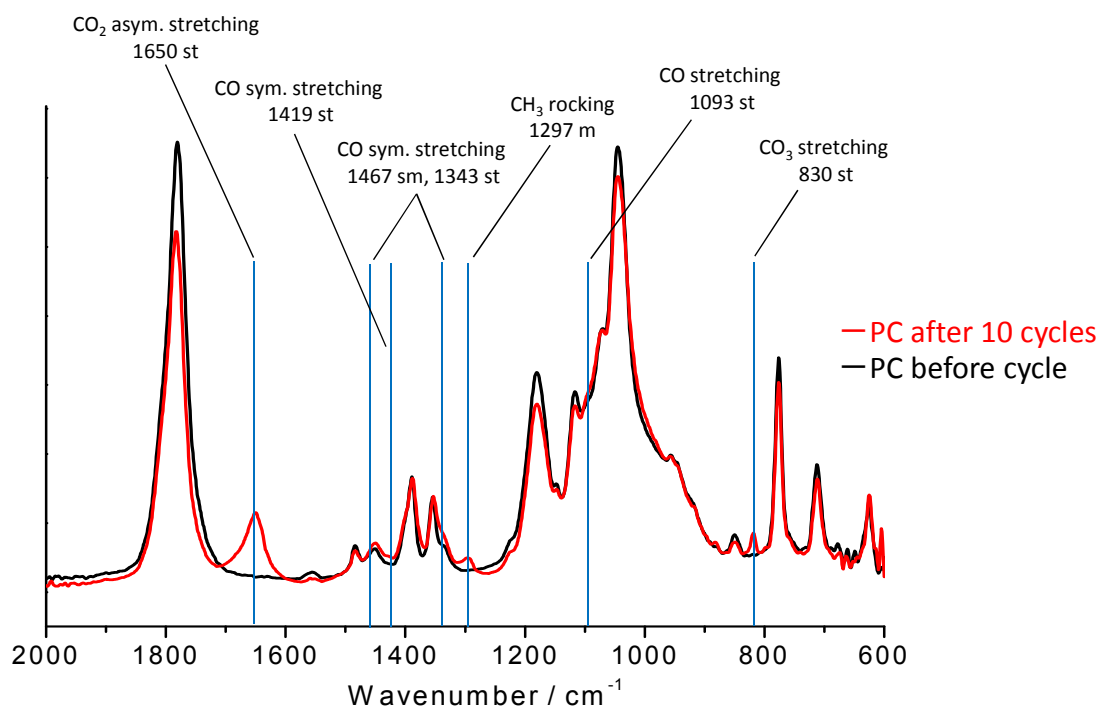


Figure S11 Comparison of FT-IR spectra of the electrolyte solutions held in glass-separators (black) before and (red) after 10 cycle tests in coin-type cells of Na//hard-carbon cell with 1 mol dm⁻³ NaClO₄ in PC. Additional peaks due to decomposition product are indexed as sodium propyl carbonate according to the literatures.

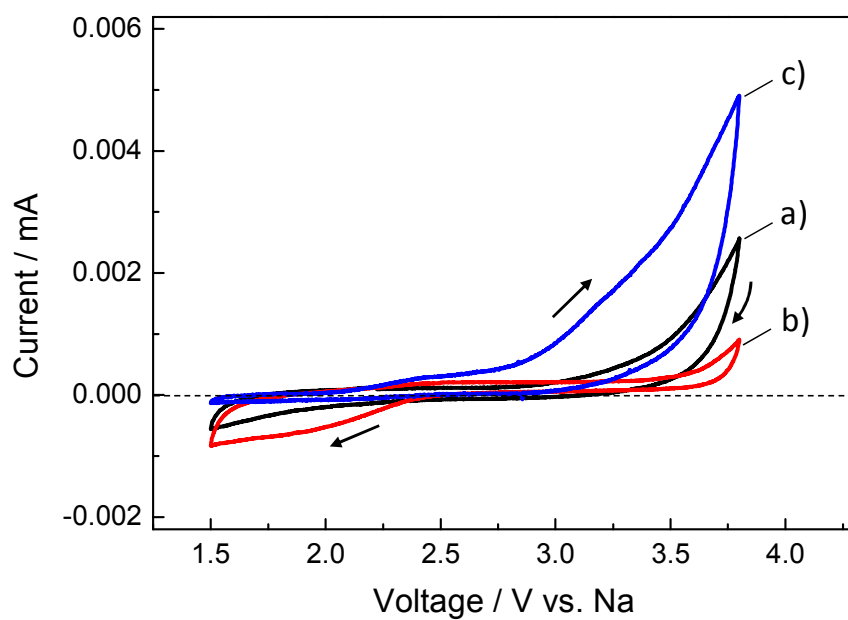


Figure S12. Cyclic voltammograms at the third cycle for Al foil electrodes (10 mm in diameter) at 0.2 mV s^{-1} in $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ in a) PC, b) PC:FEC (98:2 in volume), and c) the PC used in hard-carbon//Na cell after 10 galvanostatic cycles in coin-type Na cells.