Supplementary Information

“Thermally Controlled Dual Stabilization Mechanisms of Modified Kenaf-Derived Lignin-Based Aqueous Binders for Silicon Electrodes Used in Lithium-ion Batteries”

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Experimental methods with supporting data

Fabrication of kenaf-derived lignin copolymerized with polyacrylamide (KL-PAM)

Kenaf lignin (KL) was supplied by Herat Plaza Co., Ltd. (Fukushima, Japan) in a dried state after washing with water. KL is a soda lignin–based lignin obtained from kenaf using a conventional soda pulping process with an aqueous sodium hydroxide solution. The obtained KL was pulverized for 30 minutes using a crusher (Ishikawa Factory Co., Ltd., Japan) to obtain KL powder. The KL powder was mixed with 8 mol/L potassium hydroxide (FUJIFILM Wako Pure Chemical Corporation, Japan) and purified water, and stirred. Polyacrylamide (PAM) (Himolock E-200, HYMO Co., Ltd., Japan) was then added at a weight ratio of KL:PAM = 10:1, followed by further stirring until a uniform KL–PAM composite was obtained. The pH of KL-PAM was measured using a pH meter (LAQUA twin, HORIBA Ltd., Japan), and the measured value was 13.7.

Thermal analysis

Thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses were performed using a thermal analyzer (Thermo plus EVO2, Rigaku Co., Ltd., Japan). Prior to the measurements, the furnace chamber was purged with nitrogen at a flow rate of 250 mL min^{-1} for 30 min to establish an inert atmosphere. Alumina was used as the reference material, and the sample mass was fixed at 10 mg. Thermal analysis was conducted under a nitrogen atmosphere (250 mL min^{-1}) by heating the samples from room temperature to 1000 °C at a rate of 5 °C min^{-1}, holding at 1000 °C for 30 min. KL-PAM was dried at 50 °C for 24 h and then pulverized prior to analysis, whereas PAM was used in liquid.

The thermal analysis results of PAM is shown in Fig. 1S.

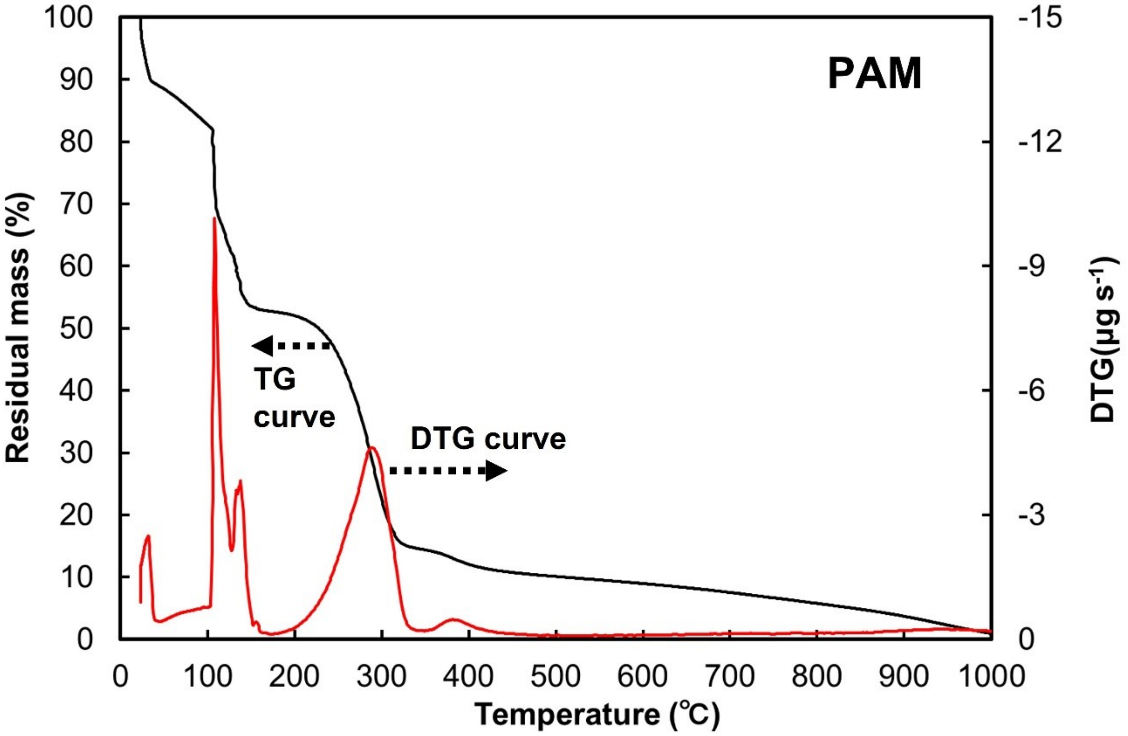

Fig. S1 TG and DTG curves of PAM obtained from thermal analysis.

Preparation of the Anode

The active material consisted of micro-sized Si 80 wt%, a conductive additive (Denka black, Li-43, Denka Co., Ltd.) 5 wt%, and a binder 15 wt% of either KL–PAM or polyvinylidene fluoride (PVDF) (Kureha Corporation, Japan). For the KL–PAM binder, purified water was used as the solvent, whereas N-methyl-2-pyrrolidone (NMP; Kishida Chemical Co., Ltd., Japan) was used as the solvent for PVDF, and the components were mixed to prepare a slurry. For the KL–PAM–CMC electrode, water was used as the solvent and carboxymethyl cellulose (CMC) (Cellogen BSH-6, DKS Co., Ltd., Japan) was used to prepare the slurry (the composition ratio is described in the main text). Each prepared slurry was coated onto a copper foil current collector (18-μm thick) with a Baker-type applicator (Hosen Co., Ltd., Japan), followed by drying overnight at 100 °C in air using a forced-convection oven. After drying, the electrode sheets were pressed at 10 MPa using an ultra-high-pressure hydraulic press and subsequently punched into circular disks with a diameter of 15 mm using a hand punch. Thermal treatments up to 200 °C were carried out using a glass tube oven (GT-200, Shibata Scientific Technology Ltd., Japan) filled with argon gas, in which the samples were held at the target temperature for more than 3 h. Thermal treatments at 400 °C and above were performed using a ceramic electric tubular furnace (ARF-40K, Asahi Rika Seisakusho Co., Ltd. Japan) under a nitrogen atmosphere (300 mL min^{-1}), with a heating rate of 5 °C min^{-1} to the target temperature, followed by a holding time of 1 h. Table S1 shows the information on the electrodes and electrode slurries used.

Table S1 Information on the electrodes and electrode slurries.

	Electrode of active material thickness (μm)	Mass of electrode active material (mg)	Areal loading of the electrode ($mg\,cm^{-2}$)	Solid content of electrode slurry (wt%)
KL-PAM-2	20	1.52	0.09	20.3
KL-PAM-4	26	1.76	0.10	
KL-PAM-6	26	1.44	0.08	
KL-PAM-8	35	3.28	0.19	
KL-PAM-CMC-6	42	3.68	0.21	15.9
PVDF	22	2.64	0.15	41.6

x in KL-PAM-x or KL-PAM-CMC-x indicates first digit of the applied heat-treatment temperature of 200, 400, 600 or 800°C.

Electrode surface morphology and chemical composition analysis

Electrodes surface morphology was observed using field-emission scanning electron microscopy (FE-SEM) (JSM-6500F, JEOL Ltd., Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed using an XPS system (PHI 5000 VersaProbe III, ULVAC-PHI, Inc., Japan) equipped with an Al Kα X-ray source to analyze the surface composition and chemical bonding states of the electrodes. Elemental compositions were determined from survey spectra (1100–0 eV, pass energy of 280 eV; Fig. S2) based on the peak of O 1s, K 2p, C 1s, and Si 2p. Narrow scan spectra of C 1s, O 1s, K 2p, and Si 2p were acquired at the pass energy of 55 eV to analyze the corresponding chemical bonding states.

The SEM images of the electrode surfaces are shown in Fig. S3. Fig. S3(a) and (b) present enlarged SEM images of the KL-PAM-6 and KL-PAM-8 electrodes shown in Fig. 2(a), respectively. Fig. S3(c) and (d) show the SEM images of the KL-PAM-CMC-6 and PVDF electrodes, respectively. The narrow scan spectra of O1s, K2p, and Si2p of the KL-PAM electrodes are shown in Fig. S4.

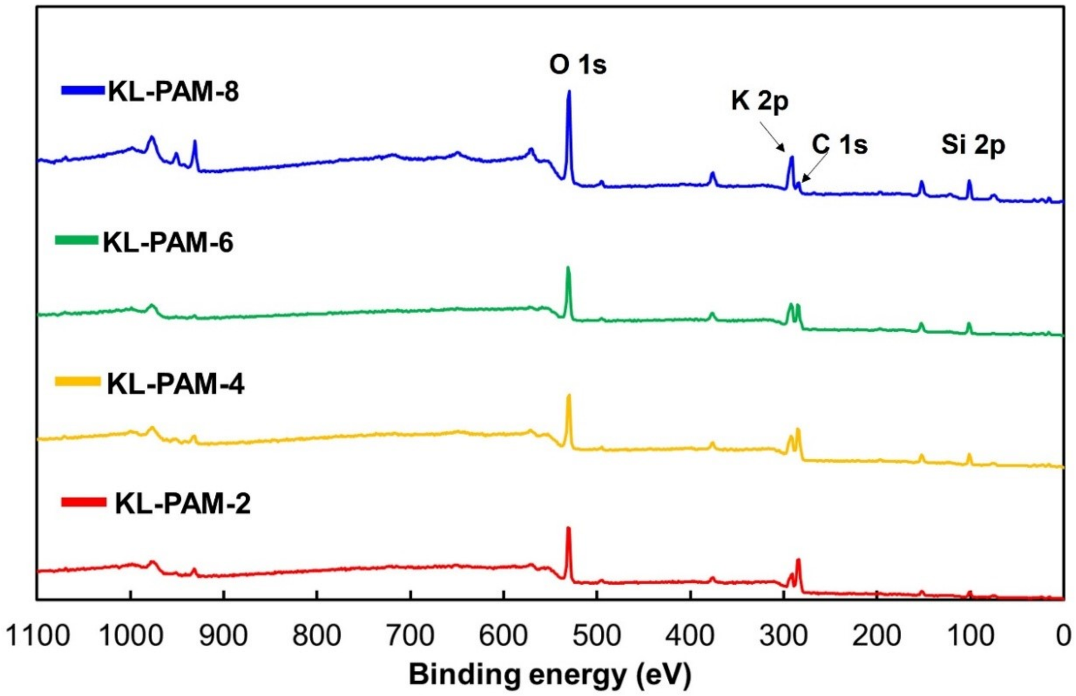

Fig. S2 XPS survey spectra of each electrode.

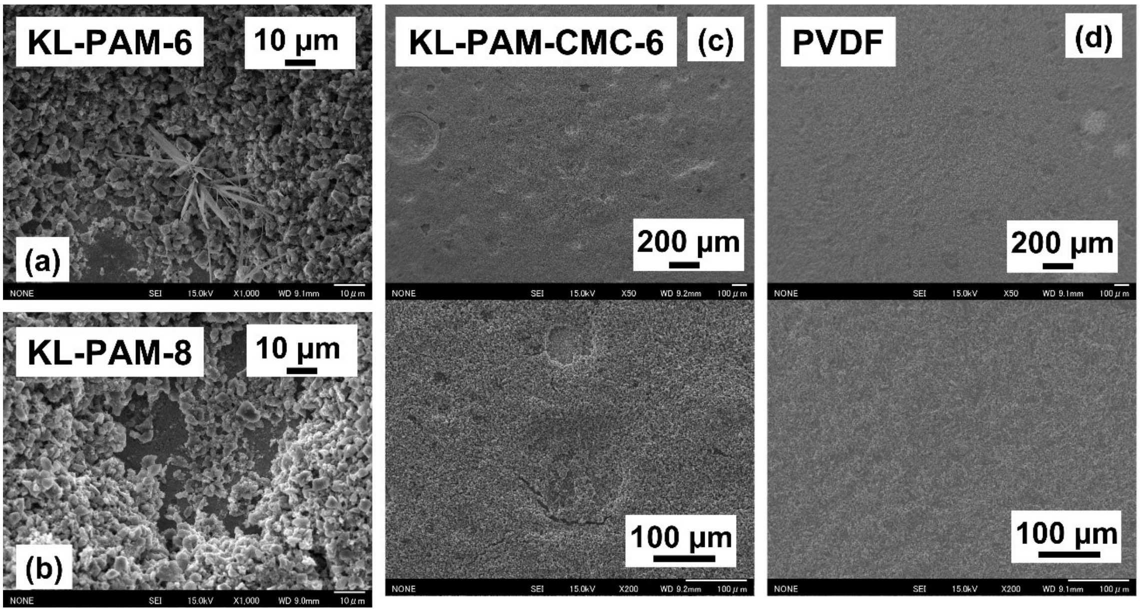

Fig. S3 SEM images of the electrode surfaces. (a), (b) Enlarged SEM images of the KL-PAM-6 and -8. (c) KL-PAM-CMC-6. (d) PVDF. The numbers of 6 and 8 indicate the applied heat-treatment temperatures of 600 and 800°C, respectively.

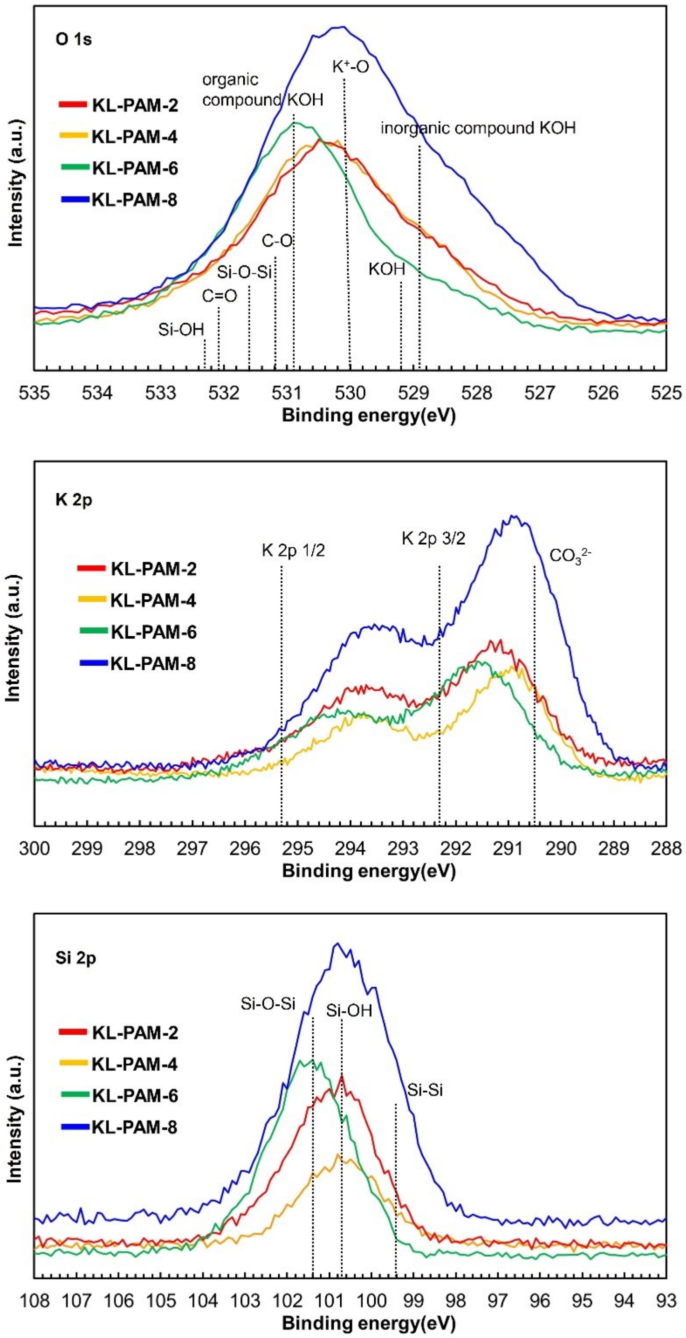

Fig. S4 Narrow scan spectra of O1s, K2p, and Si2p of the KL-PAM electrodes. x in KL-PAM-x indicates first digit of the applied heat-treatment temperature of 200, 400, 600 or 800°C.

Half-cell assembly and electrochemical characterization

Half-cells were assembled using a two-electrode flat cell (HS flat cell, Hosen Co., Ltd., Japan). Lithium metal foil was used, a porous polypropylene membrane was employed as the separator, and 1 mL of electrolyte consisting of 1 M $LiPF_6$ dissolved in an ethylene carbonate/diethyl carbonate (EC/DEC 50 vol%/50 vol%) mixture was injected into each cell. All cell assembly procedures were carried out inside an argon-filled glove box. Galvanostatic rate and cycle tests were conducted using a battery charge–discharge tester (HJ1005SD8, Hokuto Denko Co., Japan). All electrochemical measurements were performed at room temperature (25 °C) within a voltage window of 0–1 V. For the rate test, the current density was sequentially changed to 0.1, 1, 5, 10, and 0.1 mA cm^{-2}, and four charge–discharge cycles were performed at each current density. The cycle test was performed by galvanostatic cycling at the current density of 1 mA cm^{-2} for 100 cycles.

The relationship between the electrode potential and the specific capacity for the first cycle and the last cycle at each current density, as obtained from the KL-PAM-CMC-6 and PVDF rate tests are shown in Fig. S5. The specific capacities for Li-ion insertion and extraction and Coulombic efficiency during rate tests of half-cells using each electrode are shown in Fig. S6. The insertion and extraction specific capacities and coulombic efficiency during cycle testing of KL-PAM-4 and KL-PAM-CMC-6 are shown in Fig. S7.

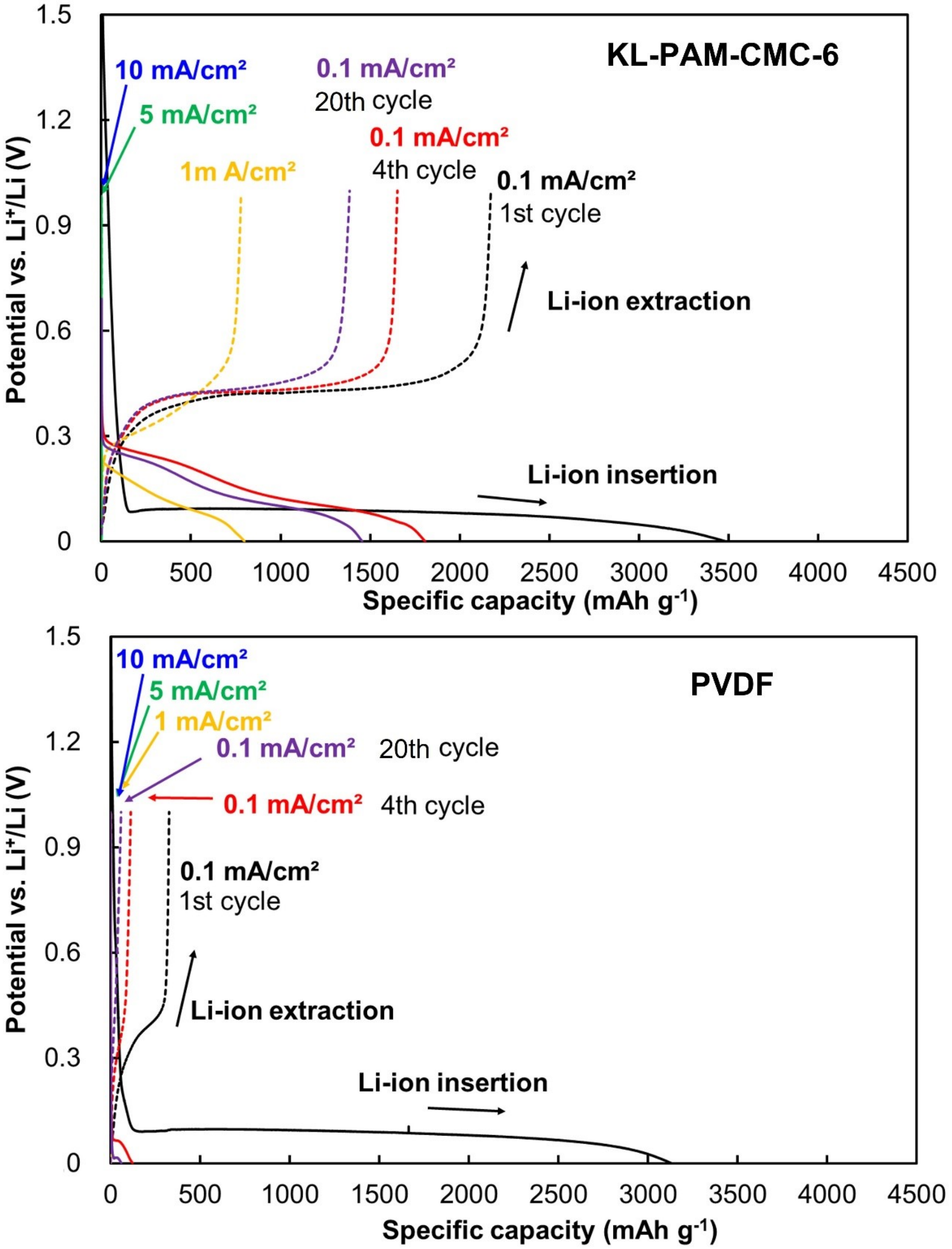

Fig. S5. Relationship between the potential and specific capacity of KL-PAM-CMC-6 and PVDF at the rate tests.

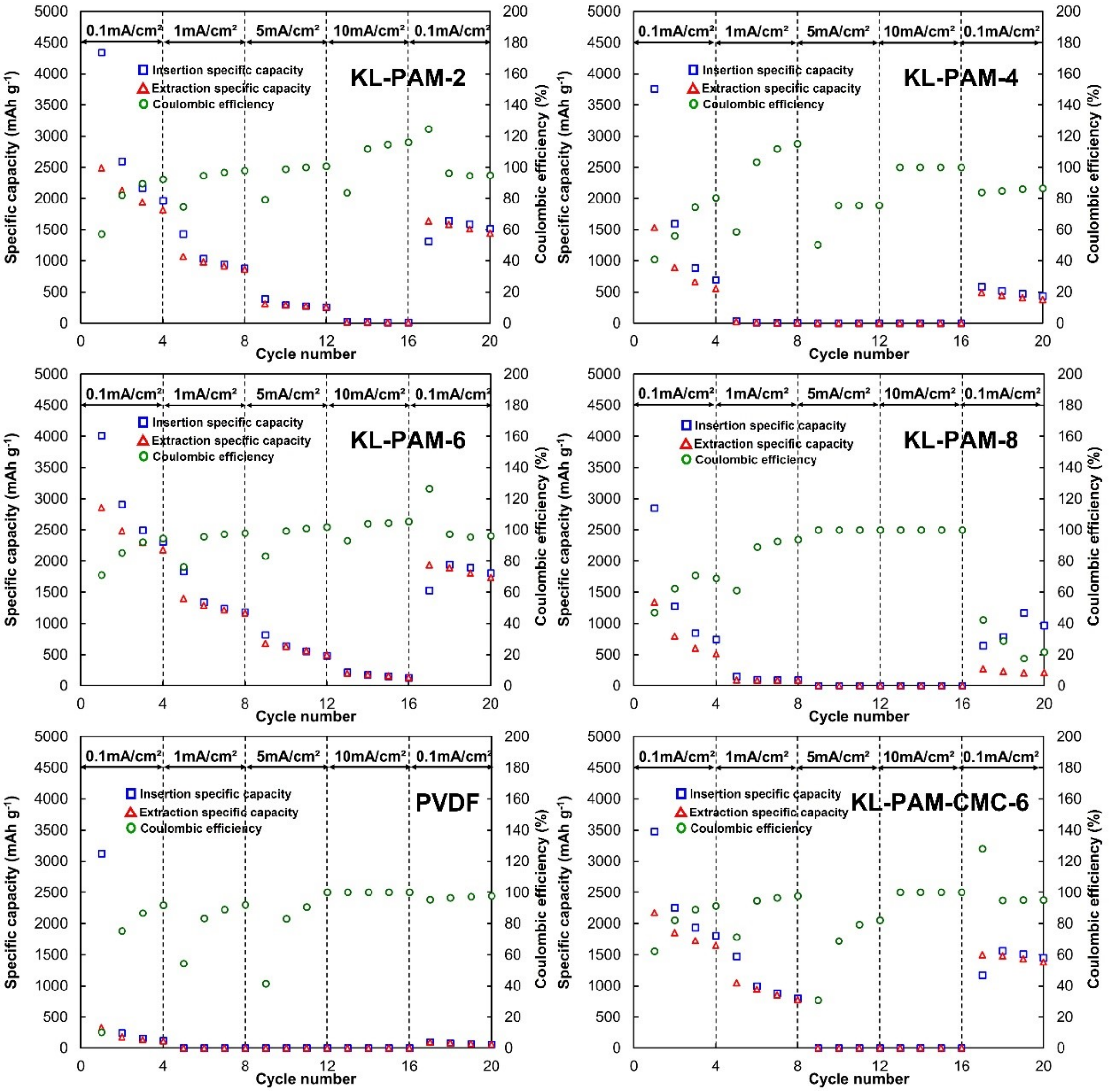

Fig. S6 Specific capacities for Li-ion insertion and extraction and Coulombic efficiency during rate tests of half-cells using each electrode. x in KL-PAM-x or KL-PAM-CMC-x indicates first digit of the applied heat-treatment temperature of 200, 400, 600 or 800°C.

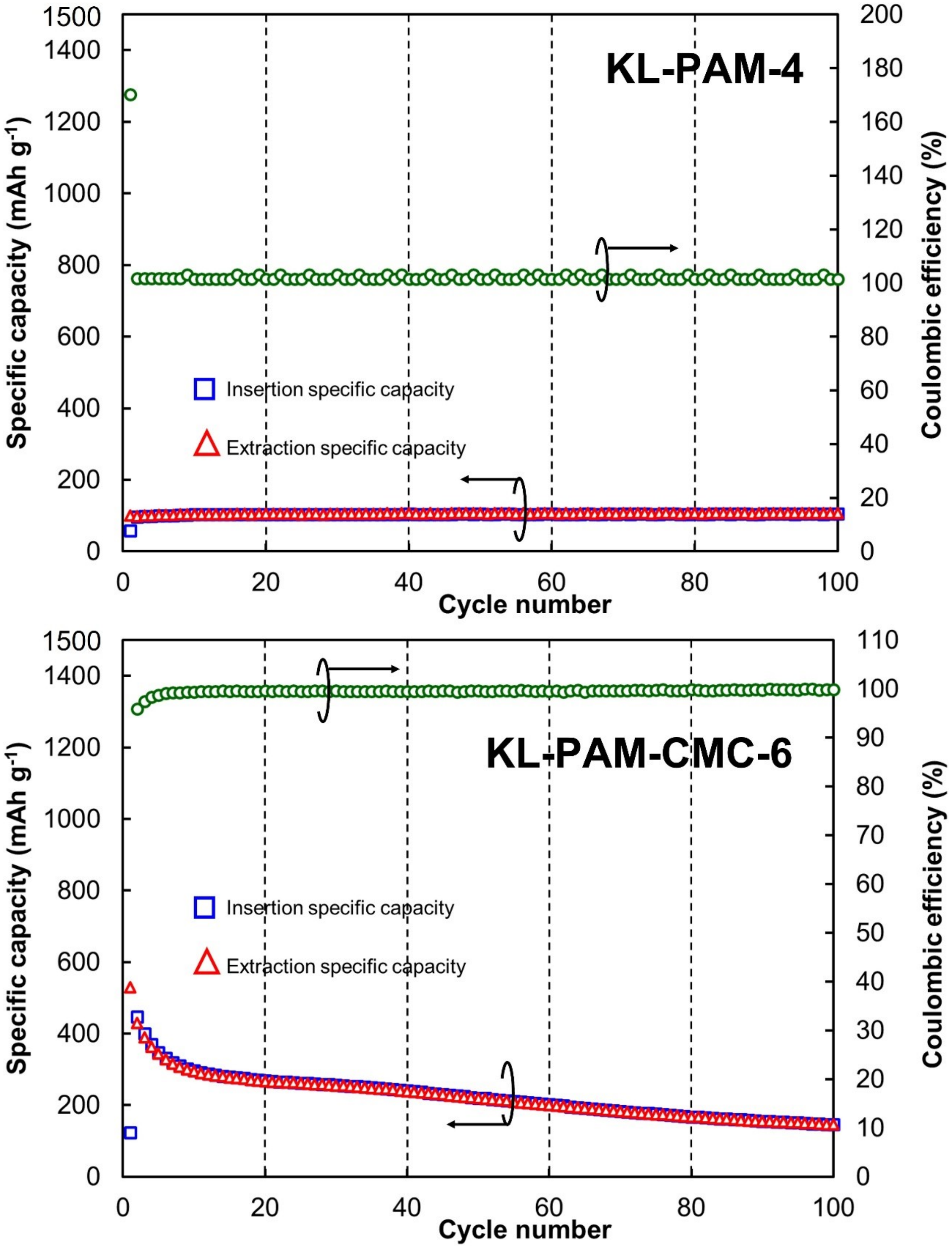

Fig. S7 Insertion and extraction specific capacities and coulombic efficiency during cycle testing of KL-PAM-4 and KL-PAM-CMC-6.