Supplementary information

Combination of solid state NMR and DFT calculation to elucidate the state of sodium in hard carbon electrodes

Ryohei Morita,[a] Kazuma Gotoh,[*ab] Mika Fukunishi,[bc] Kei Kubota,[bc] Shinichi Komaba,[bc] Naoto Nishimura,[d] Takashi Yumura,[d] Kenzo Deguchi,[e] Shinobu Ohki,[e] Tadashi Shimizu[e] and Hiroyuki Ishida[a]

a. *Graduate School of Natural Science & Technology, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan*
b. *Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Nishikyo-ku, Kyoto 615-8245, Japan*
c. *Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan*
d. *Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*
e. *National Institute for Materials Science, Tsukuba, Ibaraki 305-0003, Japan*

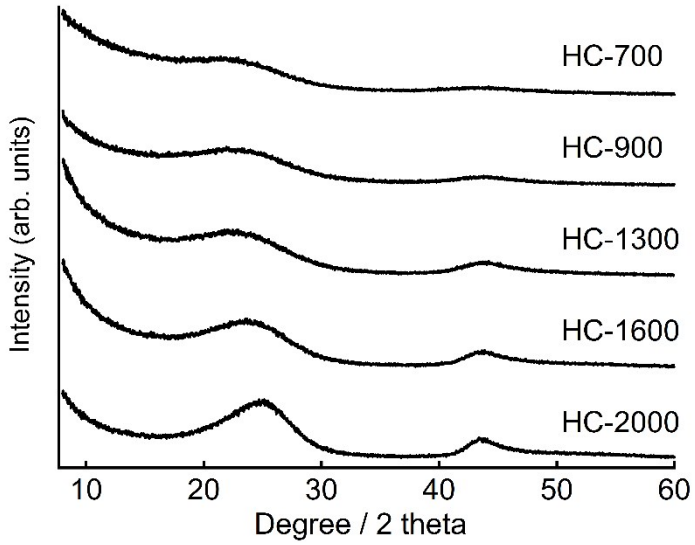

Fig S1. Powder XRD patterns of HC-700, HC-900, HC-1300, HC-1600, and HC-2000.

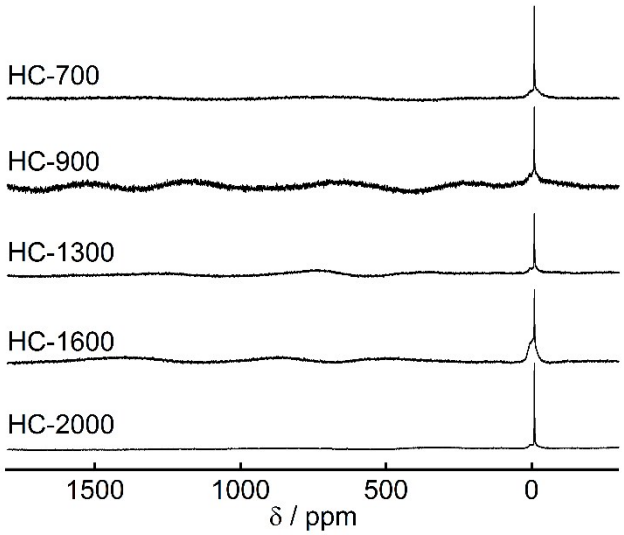

Fig. S2 ^{23}Na MAS NMR spectra (from 1800 to -300 ppm) of sodiated HC-700, HC-900, HC-1300, HC-1600 and HC-2000 samples. No quasi-metallic sodium peak was observed in each spectrum.

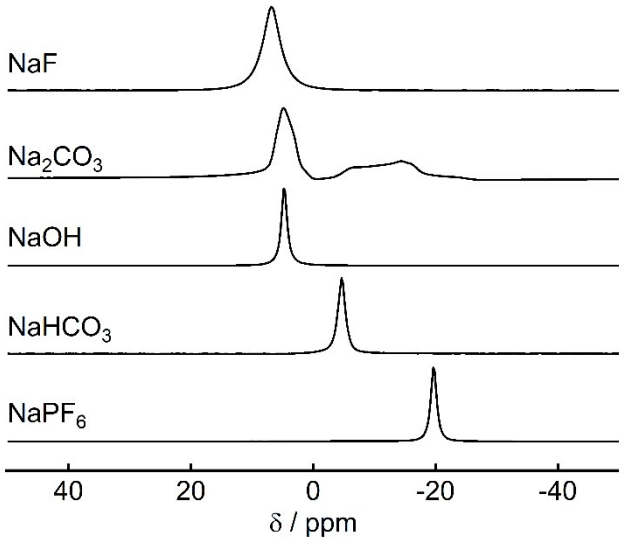

Fig. S3 ^{23}Na MAS NMR spectra of some inorganic sodium compounds.

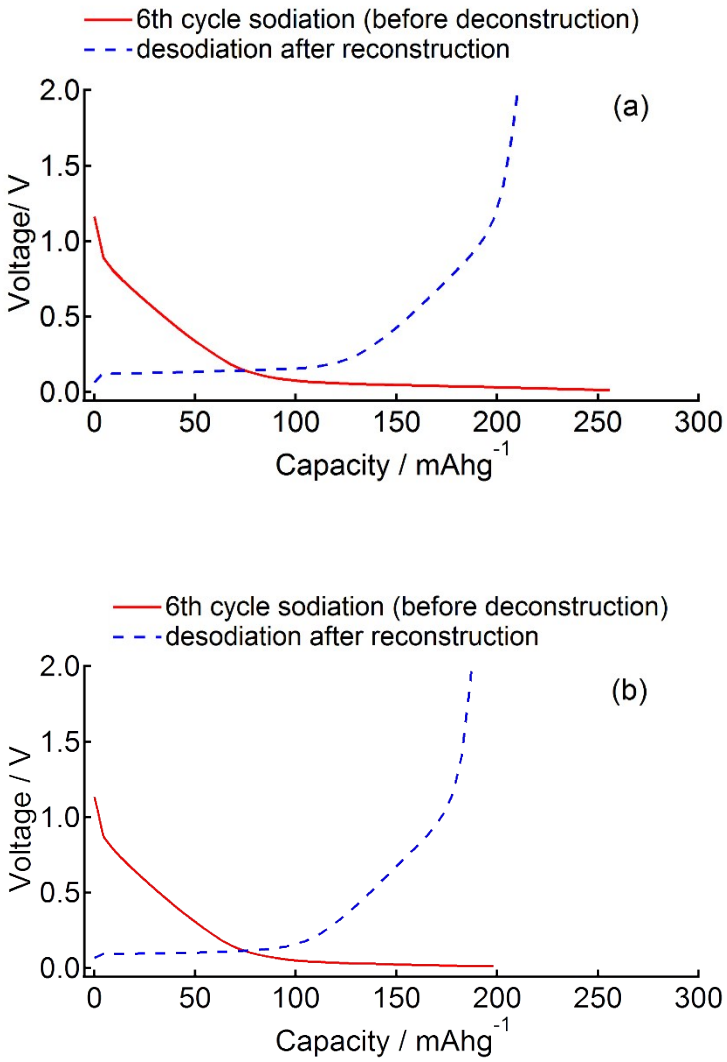

Fig. S4 Charge/discharge curves of two reassembled HC-1300 cells.

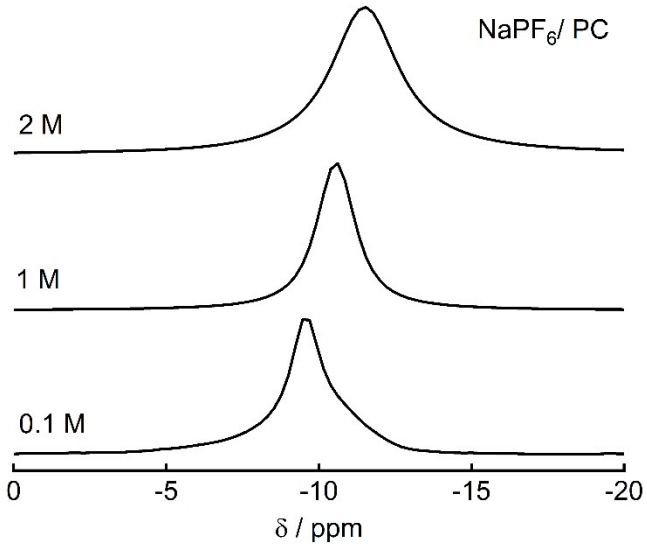

Fig. S5 ^{23}Na NMR spectra of $NaPF_6$ / PC solution taken by a solid NMR probe. Each solution was prepared using $NaPF_6$ powder (Stella Chemifa) and PC (Kishida Chemical).

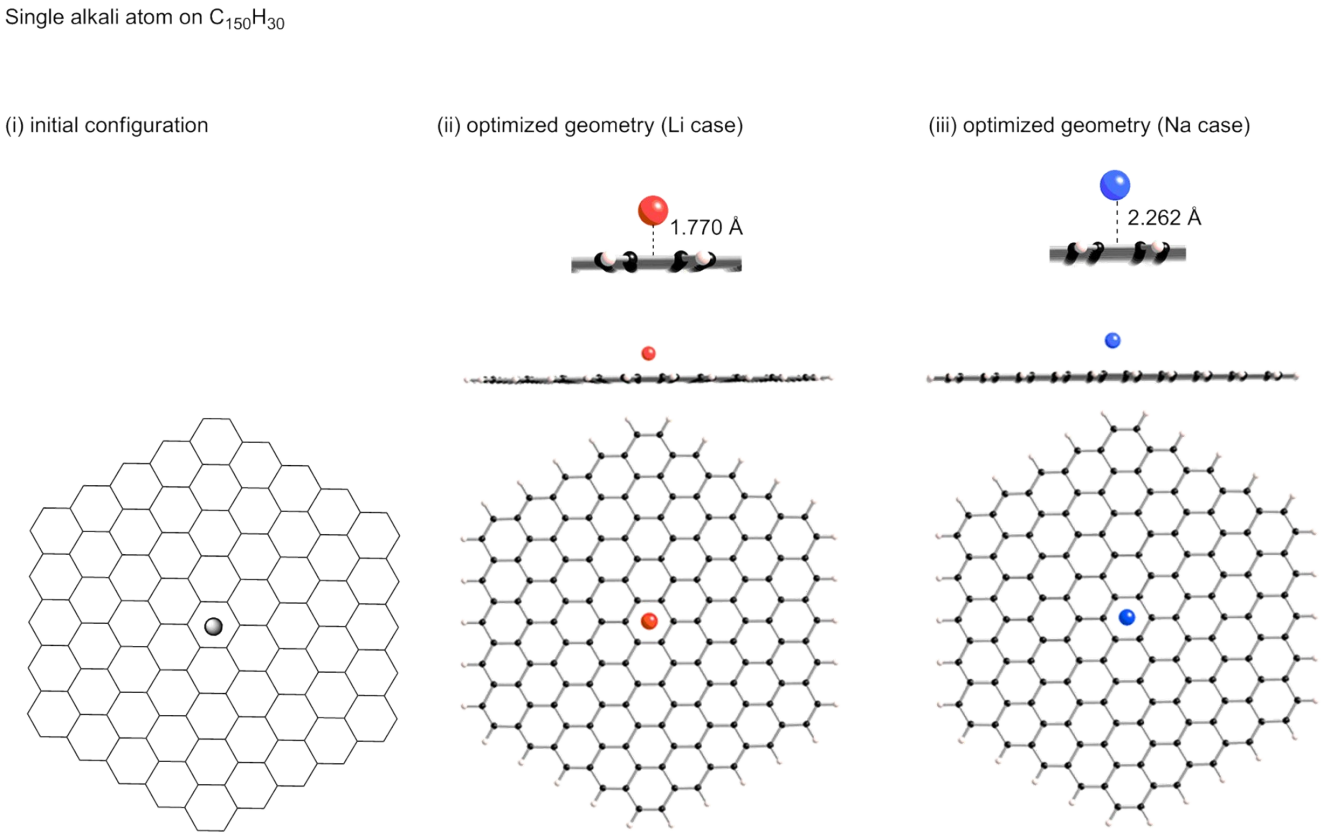

Fig. S6 DFT optimizations of an alkali atom (Li or Na) set at the centre of $C_{150}H_{30}$. The single Li (Na) atom is placed separating from the centre by 1.77 (2.26) Å

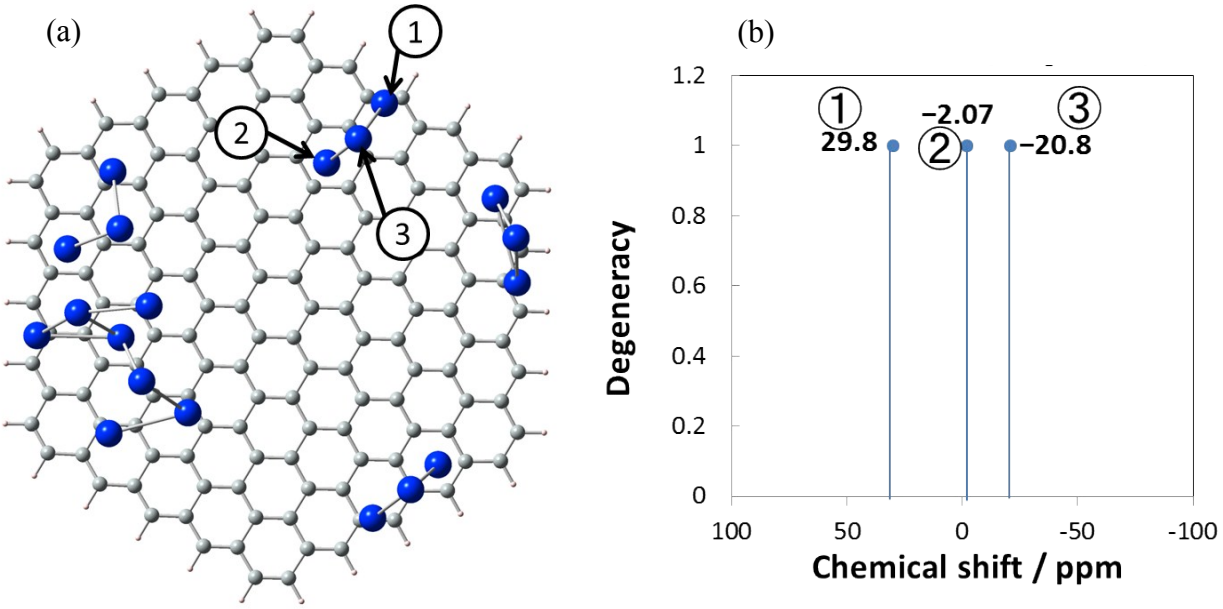

Fig. S7 Chemical shift estimation of one of the Na_3 triangle clusters on a carbon plane using B3LYP/6-31G** function; (a) calculated Na_3 triangle, (b) the estimated chemical shifts values of ①, ②, and ③ atoms. To perform the NMR calculations based on gauge-independent atomic orbital (GIAO) method, we constructed a structure for a Na_3 cluster on $C_{150}H_{30}$ by removing 16 Na atoms (without labels in (a)) from the optimized structure for 19-Na atoms on $C_{150}H_{30}$ ((iii) in Fig. 11).