

## Supporting information

### Application of Diluted Electrode Method to Sodium-ion Insertion into Hard Carbon Electrode

Yuki FUJII,<sup>a,§</sup> Ryoichi TATARA,<sup>a,§§</sup> Daisuke IGARASHI,<sup>a,§</sup> Tomooki HOSAKA,<sup>a,§§</sup> Rena  
TAKAISHI,<sup>b</sup> Eisuke SHIYAMA,<sup>b</sup> Takashi MATSUYAMA,<sup>b</sup> and Shinichi  
KOMABA<sup>\*,a,§§§</sup>

<sup>a</sup> *Department of Applied Chemistry, Tokyo University of Science, Shinjuku, Tokyo 162-  
8601, Japan*

<sup>b</sup> *NIPPON A&L INC. 3-1-98 Kasugadenaka, Konohanaku, Osaka 554-8558, Japan*

*\* Corresponding Author: [komaba@rs.tus.ac.jp](mailto:komaba@rs.tus.ac.jp)*

$$m_{\text{HC}} = \rho_{\text{HC}} \times V_{\text{HC}}, \quad (\text{S1})$$

$$m_{\text{Ni}} = \rho_{\text{Ni}} \times (95 - V_{\text{HC}}), \quad (\text{S2})$$

$$m_{\text{Binder}} = \rho_{\text{Binder}} \times 5, \quad (\text{S3})$$

$$V_{\text{electrode}} = \pi \times r^2 \times h, \quad (\text{S4})$$

$$\begin{aligned} V_{\text{pore}} &= V_{\text{electrode}} - V_{\text{HC}} - V_{\text{Ni}} - V_{\text{Binder}} \\ &= V_{\text{electrode}} - \frac{m_{\text{HC}}}{\rho_{\text{HC}}} - \frac{m_{\text{Ni}}}{\rho_{\text{Ni}}} - \frac{m_{\text{Binder}}}{\rho_{\text{Binder}}}, \end{aligned} \quad (\text{S5})$$

$$n_{\text{ele}} = c_{\text{ele}} \times V_{\text{pore}}, \quad (\text{S6})$$

$$n_{\text{ins}} = 250 \times \frac{3600}{96485} \times m_{\text{HC}}, \quad (\text{S7})$$

$$Q_{\text{Ni}} = 0.113 + 0.0746e^{-\frac{i}{1.09 \times 10^{-5}}} + 0.128e^{-\frac{i}{4.60 \times 10^{-4}}}, \quad (\text{S8})$$

$$Q_{\text{HC}} = Q_{\text{All}} - Q_{\text{Ni}} \times m_{\text{Ni}}/1000, \quad (\text{S9})$$

$$Q_{\text{HC,Mass}} = 1000 \times \frac{Q_{\text{HC}}}{m_{\text{HC}}}, \quad (\text{S10})$$

where

$m_{\text{HC}}$ : HC mass,

$m_{\text{Ni}}$ : Nickel mass,

$m_{\text{Binder}}$ : Binder mass,

$\rho_{\text{HC}}$ : HC density (1.52 g cm<sup>-3</sup>),

$\rho_{\text{Ni}}$ : Nickel density (8.91 g cm<sup>-3</sup>),

$\rho_{\text{Binder}}$ : Binder density (1.3 g cm<sup>-3</sup>),

$V_{\text{electrode}}$ : Electrode volume,

$V_{\text{pore}}$ : Pore volume of the electrode,

$V_{\text{HC}}$ : Hard carbon volume in electrode,

$V_{\text{Ni}}$ : Nickel volume in electrode,

$V_{\text{Binder}}$ : Binder volume in electrode,

$r$ : Working electrode radius (0.5 cm),

$h$ : Electrode thickness (~45 μm),

$c_{\text{ele}}$ : Electrolyte concentration (1 mol dm<sup>-3</sup>),

$n_{\text{ele}}$ : Moles of Na<sup>+</sup> in electrolyte inside electrode pores,

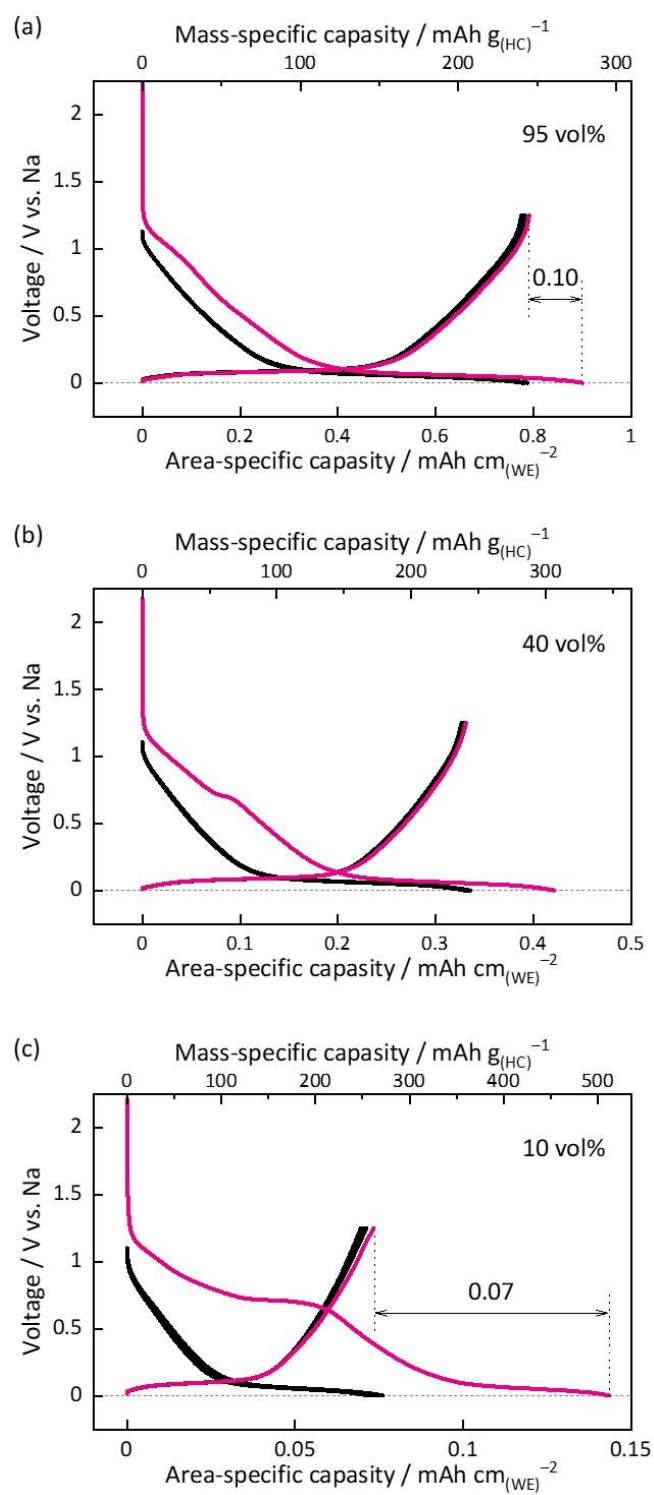
$n_{\text{ins}}$ : Moles of Na<sup>+</sup> corresponding to a 250 mAh g<sup>-1</sup> charge in the HC electrodes,

$Q_{\text{All}}$ : Charge capacity [mAh],

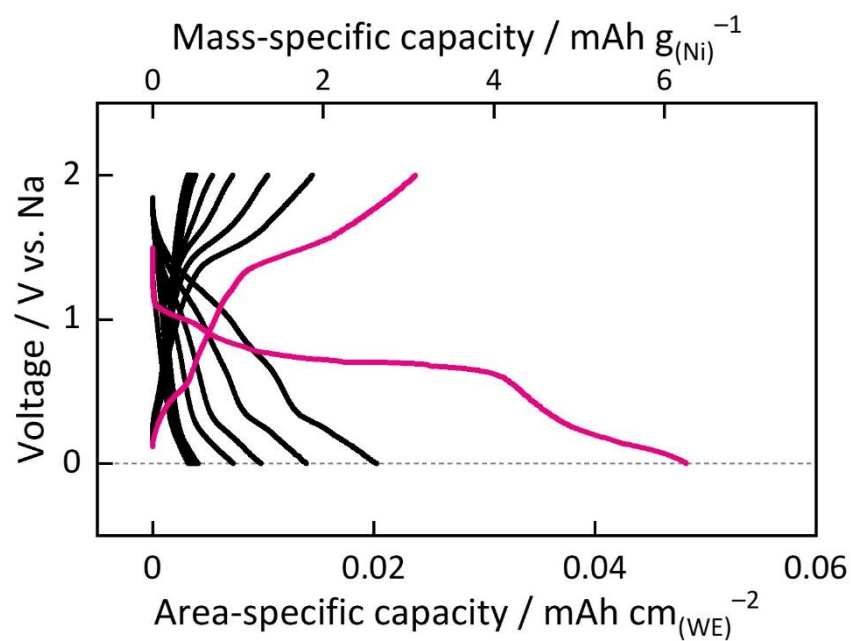
$Q_{\text{HC}}$ : Corresponding HC capacity in  $Q_{\text{All}}$  [mAh],

$Q_{\text{Ni}}$ : Corresponding double-layer capacitance derived from Ni in  $Q_{\text{All}}$  [mAh g<sub>(Ni)</sub><sup>-1</sup>],

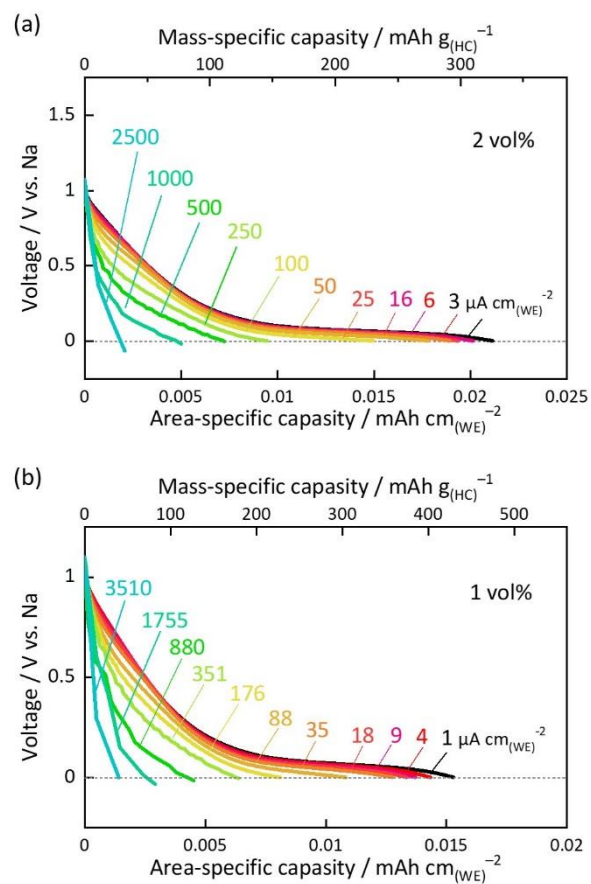
$Q_{\text{HC,Mass}}$ : HC mass-specific capacity [mAh g<sub>(HC)</sub><sup>-1</sup>].



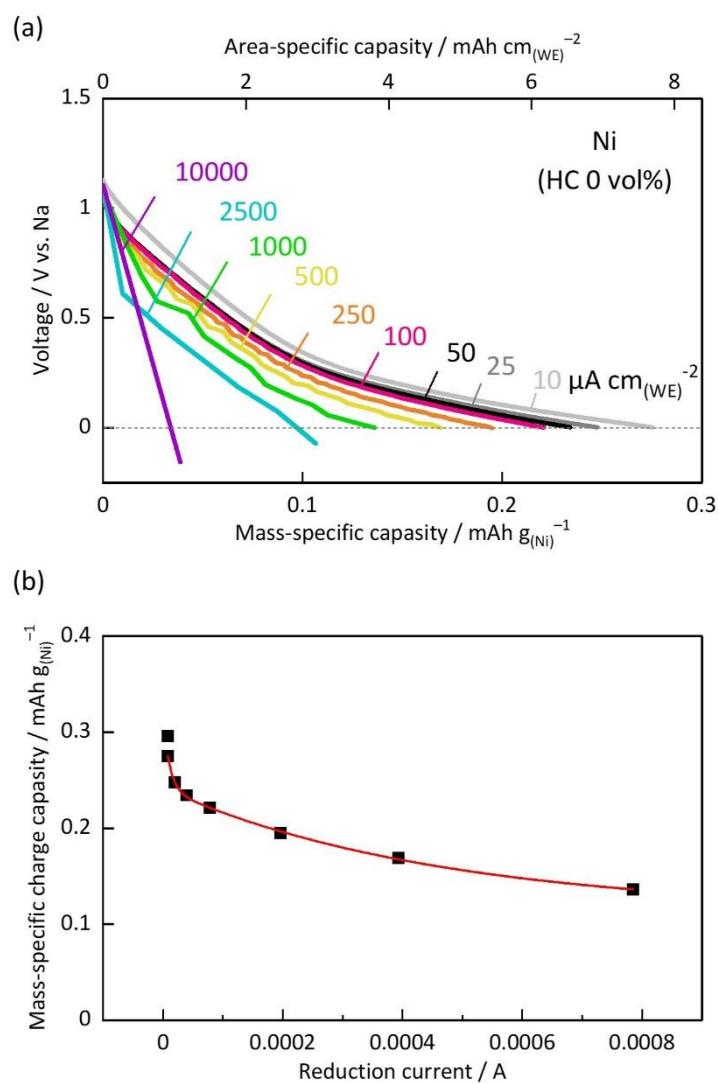
**Figure S1.** Charge–discharge curves in the 1<sup>st</sup>–6<sup>th</sup> cycles obtained for (a) 95, (b) 40, and (c) 10 vol% diluted HC electrodes. The red lines represent the curves for the 1<sup>st</sup> cycle.



**Figure S2.** Charge–discharge curves in the 1<sup>st</sup>–30<sup>th</sup> cycles obtained for 0 vol% diluted HC electrodes (i.e., nickel-only electrode). The red lines represent the curves for the 1<sup>st</sup> cycle.



**Figure S3** Charge–discharge curves obtained at various current densities with (a) 2 vol% and (b) 1 vol% diluted HC electrodes. The color variation indicates the difference in current densities. The HC electrodes were discharged at 1.25 V at a constant current density of 10  $\mu\text{A cm}_{(\text{WE})}^{-2}$  prior to each charging process.



**Figure S4.** (a) Charge–discharge curves obtained at various current densities with 0 vol% diluted HC electrodes (nickel-only electrodes). The color variation indicates the difference in current densities. (b) Relationship between reduction current and mass-specific charge capacities. The red line shows the fitting line obtained using OriginPro software to derive Equation S8.

Table S1. Capacity obtained from 95 vol% HC electrode

Area-specific density $\mu\text{A cm}_{(\text{WE})}^{-2}$	current Mass-specific density $\text{mA g}_{(\text{HC})}^{-1}$	$Q_{\text{All}}$ (without $Q_{\text{Ni}}$ ) $\text{mAh g}_{(\text{HC})}^{-1}$	$Q_{\text{HC}}$ $\text{mAh g}_{(\text{HC})}^{-1}$
50	15	240	240
100	31	227	227
250	77	159	159
501	155	105	105
1000	309	90	90
2497	772	68	68
5006	1548	50	50
9995	3091	24	24

Table S2. Capacity obtained from 40 vol% diluted HC electrode

Area-specific density $\mu\text{A cm}_{(\text{WE})}^{-2}$	current Mass-specific density $\text{mA g}_{(\text{HC})}^{-1}$	$Q_{\text{All}}$ $\text{mAh g}_{(\text{HC})}^{-1}$	$Q_{\text{HC}}$ $\text{mAh g}_{(\text{HC})}^{-1}$
50	36	240	239
100	73	234	232
250	182	207	206
501	364	133	132
1000	727	84	83
2497	1816	63	62
5006	3641	47	46
9996	7269	11	10

Table S3. Capacity obtained from 10 vol% diluted HC electrode

Area-specific density $\mu\text{A cm}_{(\text{WE})}^{-2}$	current Mass-specific density $\text{mA g}_{(\text{HC})}^{-1}$	$Q_{\text{All}}$ $\text{mAh g}_{(\text{HC})}^{-1}$	$Q_{\text{HC}}$ $\text{mAh g}_{(\text{HC})}^{-1}$
10	36	269	255
25	89	259	247
50	179	252	240
100	357	235	224
250	892	160	150
501	1788	100	92
1000	3570	74	68
2497	8914	38	33
5004	17864	15	9
9649	34445	17	11

Table S4. Capacity obtained from 2 vol% diluted HC electrode

Area-specific density $\mu\text{A cm}_{(\text{WE})}^{-2}$	current Mass-specific density $\text{mA g}_{(\text{HC})}^{-1}$	$Q_{\text{All}}$ $\text{mAh g}_{(\text{HC})}^{-1}$	$Q_{\text{HC}}$ $\text{mAh g}_{(\text{HC})}^{-1}$
2	25	344	261
3	49	326	244
6	100	310	232
16	249	298	227
25	384	292	224
50	771	274	211
100	1540	230	170
250	3843	146	92
501	7710	111	66
1000	15400	77	40



Table S5. Capacity obtained from 1 vol% diluted HC electrode

Area-specific current density $\mu\text{A cm}_{(\text{WE})}^{-2}$	Mass-specific current density $\text{mA g}_{(\text{HC})}^{-1}$	$Q_{\text{All}}$ $\text{mAh g}_{(\text{HC})}^{-1}$	$Q_{\text{HC}}$ $\text{mAh g}_{(\text{HC})}^{-1}$
2	50	429	263
4	100	402	240
9	247	385	233
18	493	375	234
35	986	358	228
88	2469	304	182
176	4925	228	115
351	9857	179	80
880	24689	127	50
1755	49214	82	17