Electronic Supplementary Information

A facile, low-cost synthesis of high-performance silicon-based composite anodes with high tap density for lithium-ion batteries

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Table S1. Electrochemical data of the Si-based composite electrodes

Electrode	Theoretical capacity (mA h g^{-1})	1st charge capacity (mA h g^{-1})	1st discharge capacity (mA h g^{-1})	1st Coulombic efficiency (%)	Capacity retention (n^{th}/1st charge capacity) (%)
Si–Al_2O_3@C	1457	1427	1183	83	43.6 (n = 40)
Si–$NiSi_2$–Al_2O_3@C	978	1020	787	77	89.0 (n = 50)

- *Calculation of theoretical specific capacity*

Pure Si has a theoretical capacity of ~ 3579 mA h g^{-1}. The contribution of graphite to the reversible capacity was assumed to be zero due to the loss of its layered structure as shown in the XRD results in Fig. 2a. The contribution of $NiSi_2$ phase to reversible capacity was also assumed to be negligible because the $NiSi_2$ phase is stable over cycling.[1, 2]

Table S2. Variations of each resistance component values of the Si-based composite electrodes upon cycling

Electrode	Component	Resistance (Ω mg)			
		at 1st cycle	at 5th cycle	at 20th cycle	at 40th cycle
Si–Al_2O_3@C	R_s	5.5	6.4	10.1	12.5
	R_{int}	7.5	19.2	127.0	164.9
	R_{ct}	38.6	39.8	151.6	403.9
Si–$NiSi_2$–Al_2O_3@C	R_s	7.1	7.7	6.7	15.5
	R_{int}	6.0	8.8	32.0	54.4
	R_{ct}	43.4	39.9	66.4	135.9

Table S3. Comparison of the tap densities, specific capacities, volumetric capacities, and areal capacities of several Si-based materials. Calculations were made by assuming that the composite electrodes could be prepared with the measured tap density.

Electrode	Tap density ($g\ cm^{-3}$)	Specific capacity ($mA\ h\ g^{-1}$)	Volumetric capacity ($mA\ h\ cm^{-3}$)	Areal capacity ($mA\ h\ cm^{-2}$)
Nano Si[3]	0.16	1200	192	-
Milled Si[3]	0.70	1200	840	0.84
Si-C composite[4]	0.68	1600	1088	0.96
$Si–NiSi_2–Al_2O_3@C$	1.34	720	965	1.2

- *Calculation of the areal capacity*

The areal capacity was calculated by the multiplying the specific capacity by the electrode loading mass (only active material).

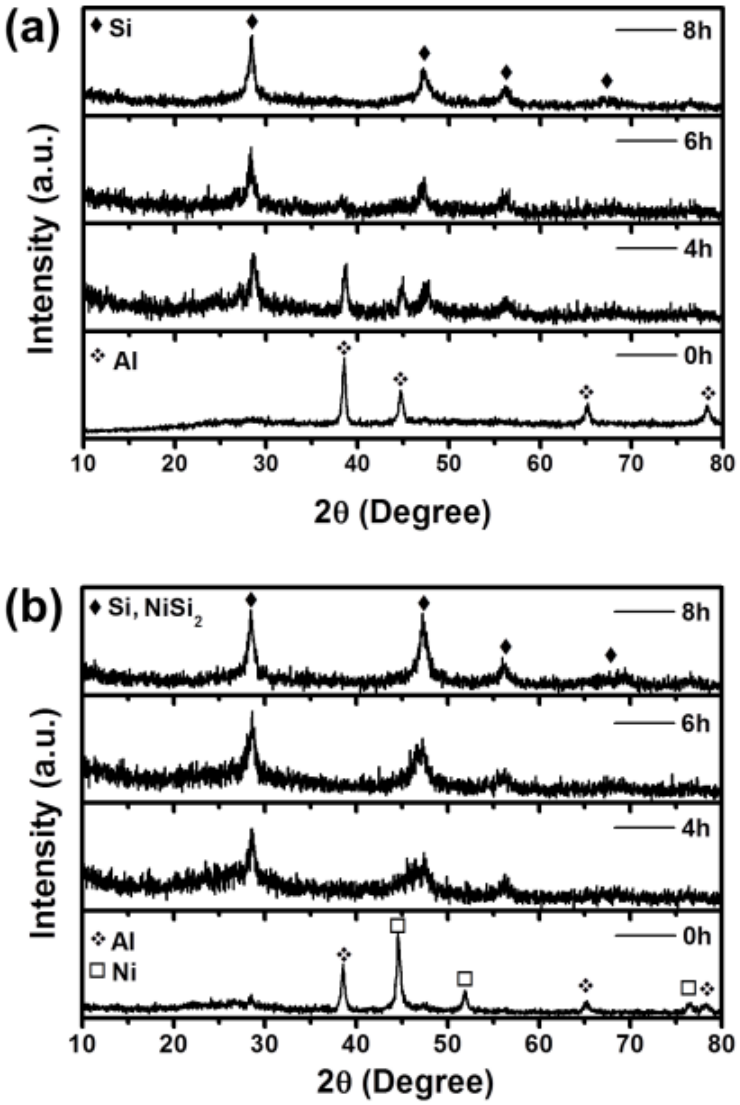

Fig. S1. XRD patterns of the (a) Si–Al_2O_3@C and (b) Si–$NiSi_2$–Al_2O_3@C (sample prepared with x = 0.75 in reaction 2) composites after different milling times.

Several sharp peaks corresponding to metallic Al were observed before milling. While these peaks gradually decreased, the Si peaks began to develop and became sharpened as the milling time increased. Finally, no Al peaks were observed and only Si peaks remained after 8 h.

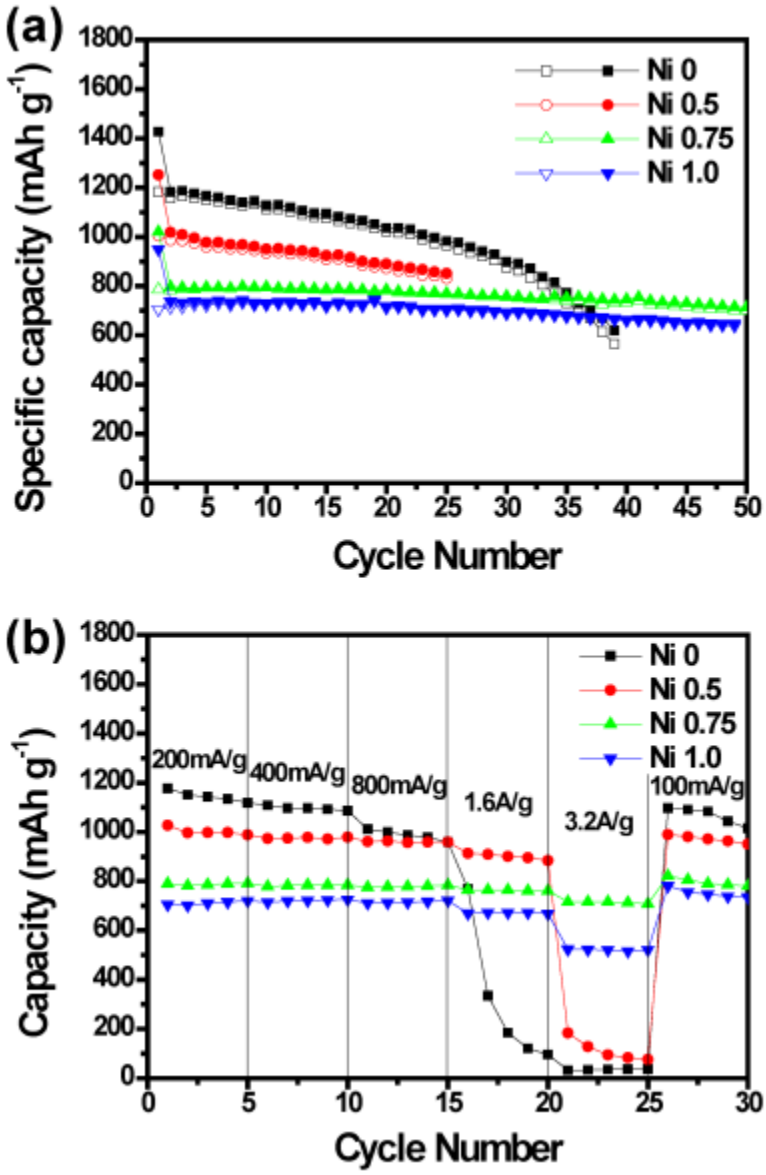

Fig. S2. (a) Cycle performance of the Si–Al_2O_3@C and Si–$NiSi_2$–Al_2O_3@C composites at a current density of 100 mA g^{-1} within a voltage range of 0.0 – 2.0V (vs. Li / Li^+). (b) Rate performance of the Si–Al_2O_3@C and Si–$NiSi_2$–Al_2O_3@C composites at various current densities. The discharge current density was fixed at 100 mA g^{-1}.

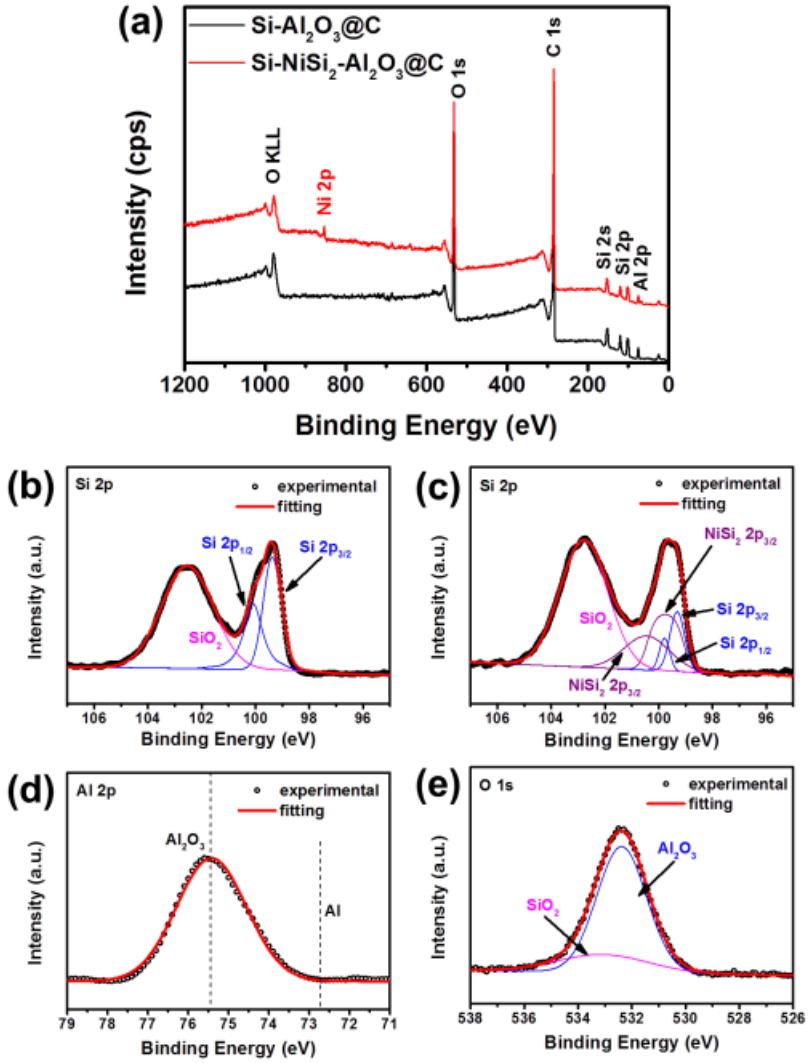

Fig. S3. (a) XPS survey spectra of the Si–Al_2O_3@C and Si–$NiSi_2$–Al_2O_3@C composites. XPS peak fitting results of (b) Si 2p spectrum in the Si–Al_2O_3@C composite and (c) Si 2p, (d) Al 2p, and (e) O 1s spectra in the Si–$NiSi_2$–Al_2O_3@C composite.

To eliminate sample charging effects, we manually shifted the XPS spectrum based on C 1s peak position (284.5 eV). The position of the C 1s peak was measured at 284.5 and 284.35 eV, respectively, in the Si–Al_2O_3@C and Si–$NiSi_2$–Al_2O_3@C composites.

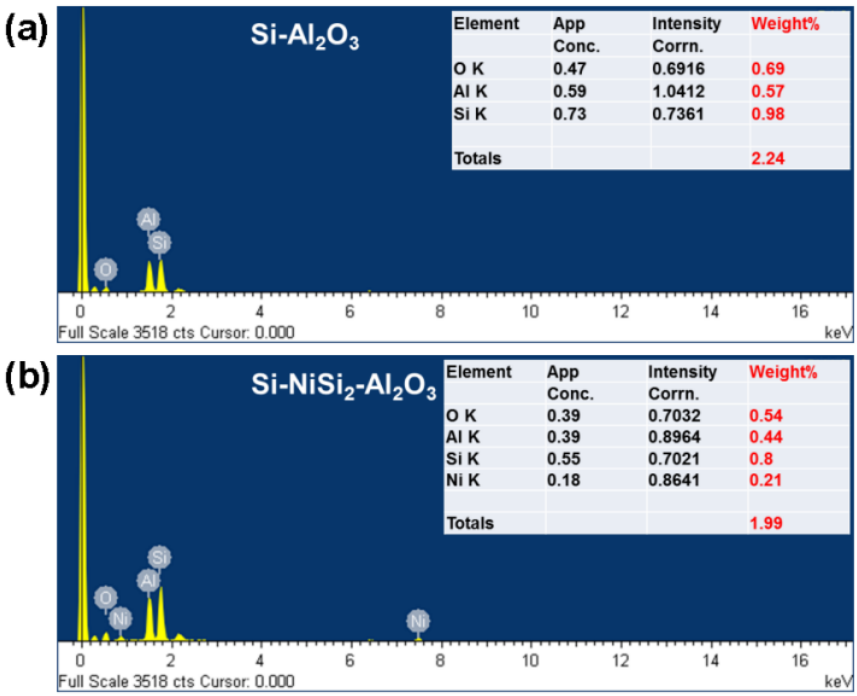

Fig. S4. SEM/EDS results of the (a) Si–Al_2O_3 and (b) Si–$NiSi_2$–Al_2O_3 composites.

- *Estimation of the amounts of Si, $NiSi_2$, Al_2O_3, and C in the composites*

Fe contaminant is negligible even after the mechanical milling for 8 h. Due to the use of carbon tape, SEM/EDS measurement was conducted before milling with 10 wt. % of graphite. The amount of carbon is fixed at 10 wt. %.

1. The Si–Al_2O_3@C composite

(1) Based on the chemical reaction below, the quantities in the Table below were obtained:

$$6\ SiO + 4\ Al \rightarrow 6\ Si + 2\ Al_2O_3$$

	MW(g/mol)	mole	Mass (g)	Weight %
Si	28.085	3	126.3825	40.7
Al_2O_3	101.961	2	203.922	49.3
C				10.0

Weight % ratio (Si : Al_2O_3 : C) = 1 : 1.21 : 0.246

(2) Based on the SEM/EDS analysis (Fig. S4a, total wt. % is 2.24), the quantities in the Table below were obtained:

Method	Total Si (wt. %)	Si in $NiSi_2$ (wt. %)	Only Si (wt. %)	Al + O (wt. %)	Si : Al_2O_3 ratio	Si : $NiSi_2$ ratio	Si : C ratio
EDS	0.98	-	0.98	1.26	1 : 1.286	-	1 : 0.254

Weight % ratio (Si : Al_2O_3 : $NiSi_2$: C) = 1 : 1.286 : 0.254

The amounts of Si, Al_2O_3, and C in the final composite were quite similar to those calculated based on the amounts of precursors used for the synthesis.

2. The Si–$NiSi_2$–Al_2O_3@C composite

(1) Based on the chemical reaction (x = 0.75) below, the quantities in the Table below are obtained: $6\ SiO + 0.75\ Ni + 4\ Al \rightarrow 4.5\ Si + 0.75\ NiSi_2 + 2\ Al_2O_3$ (x = 0.75)

	MW(g/mol)	mole	Mass (g)	Weight %
Si	28.085	4.5	126.3825	27.3
Al_2O_3	101.961	2	203.922	44.1
$NiSi_2$	114.863	0.75	86.14725	18.6
C				10.0

Weight % ratio (Si : Al_2O_3 : $NiSi_2$: C) = 1 : 1.61 : 0.68 : 0.366

(2) Based on the SEM/EDS measurement (Fig. S4b, total wt. % is 1.99), the quantities in the Table below are obtained:

Method	Total Si (wt. %)	Si in $NiSi_2$ (wt. %)	Only Si (wt. %)	Al + O (wt. %)	Si : Al_2O_3 ratio	Si : $NiSi_2$ ratio	Si : C ratio
EDS	0.8	0.2	0.6	0.98	1 : 1.633	1 : 0.683	1 : 0.368

Weight % ratio (Si : Al_2O_3 : $NiSi_2$: C) = 1 : 1.633 : 0.683 : 0.368

The amounts of Si, $NiSi_2$, Al_2O_3, and C in the final composite were quite similar to that calculated based on the amounts of precursors used for the synthesis.

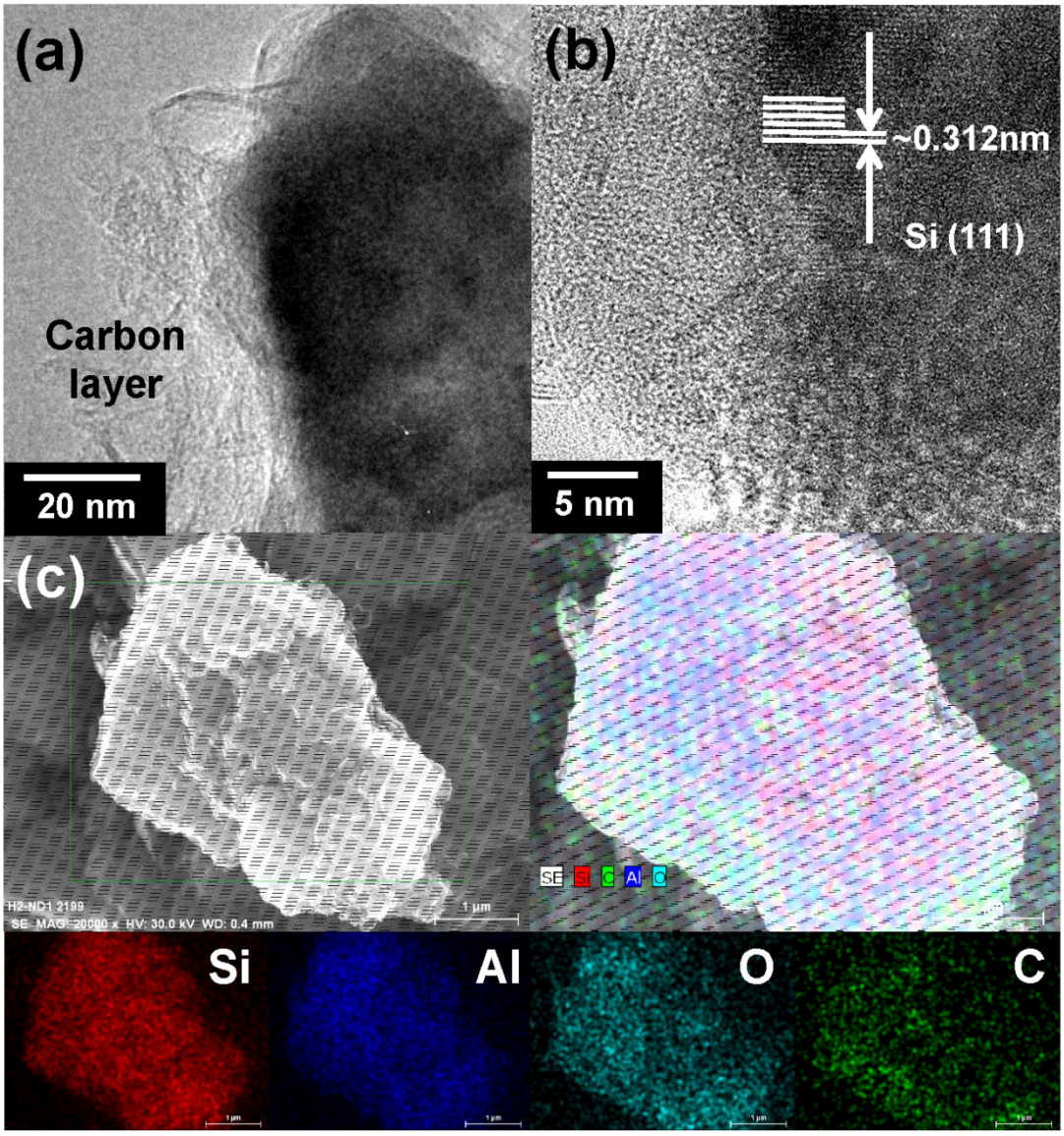

Fig. S5. (a) TEM, (b) HRTEM, and (c) STEM images of the Si–Al_2O_3@C composite. In the STEM, the corresponding EDS mapping images of each element are also shown with different colors.

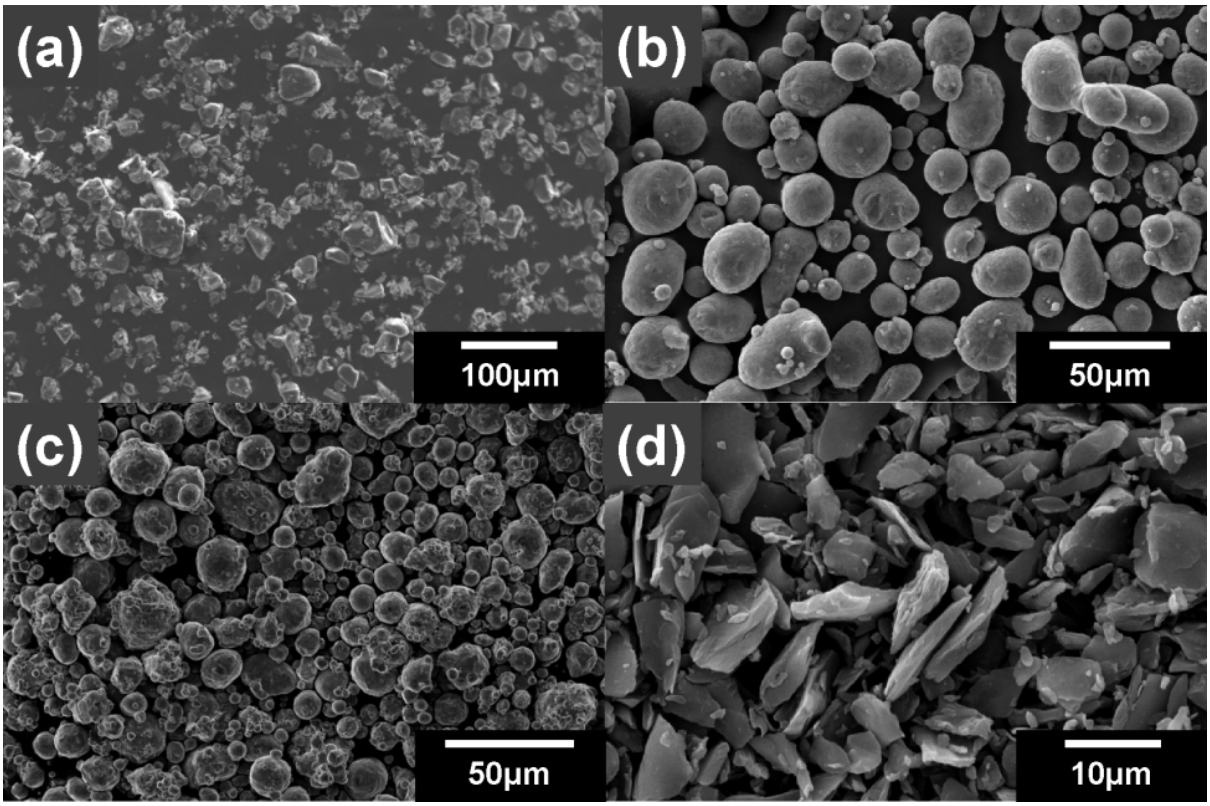

Fig. S6. SEM images of the starting materials used for the synthesis of the Si-based composites: (a) SiO, (b) Al, (c) Ni, and (d) graphite.

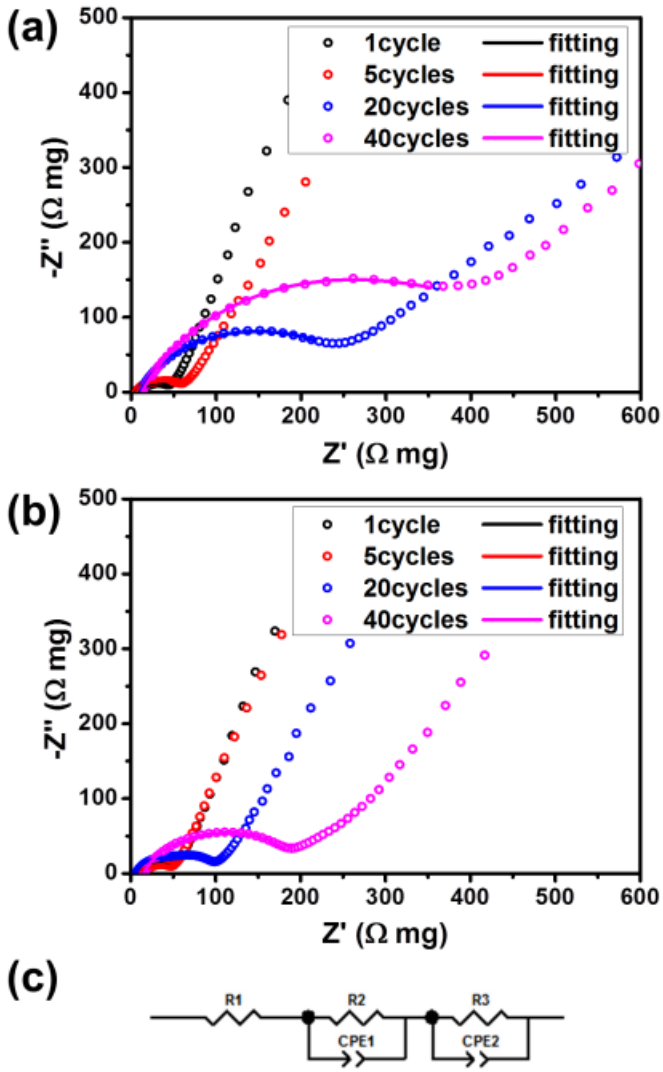

Fig. S7. Impedance spectra and curve fitting results for the (a) Si–Al_2O_3@C and (b) Si–$NiSi_2$–Al_2O_3@C composites. (c) Simplified equivalent circuit used for the curve fitting.

In order to increase the accuracy of the measurement of the interfacial and charge-transfer resistances, curve fittings were conducted without considering the low frequency region (Warburg term).

- Components of the simplified equivalent circuit are below:

R1: Electrolyte resistance

R2: Interfacial resistance, CPE1: Constant phase element of interface

R3: Charge transfer resistance, CPE2: Constant phase element of charge transfer reaction

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2. T. Kim, S. Park and S. M. Oh, *Electrochem. Commun.*, 2006, **8**, 1461-1467.
3. M. Gauthier, D. Mazouzi, D. Reyter, B. Lestriez, P. Moreau, D. Guyomard and L. Roue, *Energy Environ. Sci.*, 2013, **6**, 2145-2155.
4. J. X. Song, S. R. Chen, M. J. Zhou, T. Xu, D. P. Lv, M. L. Gordin, T. J. Long, M. Melnyk and D. H. Wang, *J. Mater. Chem. A*, 2014, **2**, 1257-1262.