Electronic Supporting information (ESI) for Ge nanocrystals tightly and uniformly distributed in carbon matrix through nitrogen and oxygen bridging bonds for fast-charging high-energy-density lithium-ion batteries†

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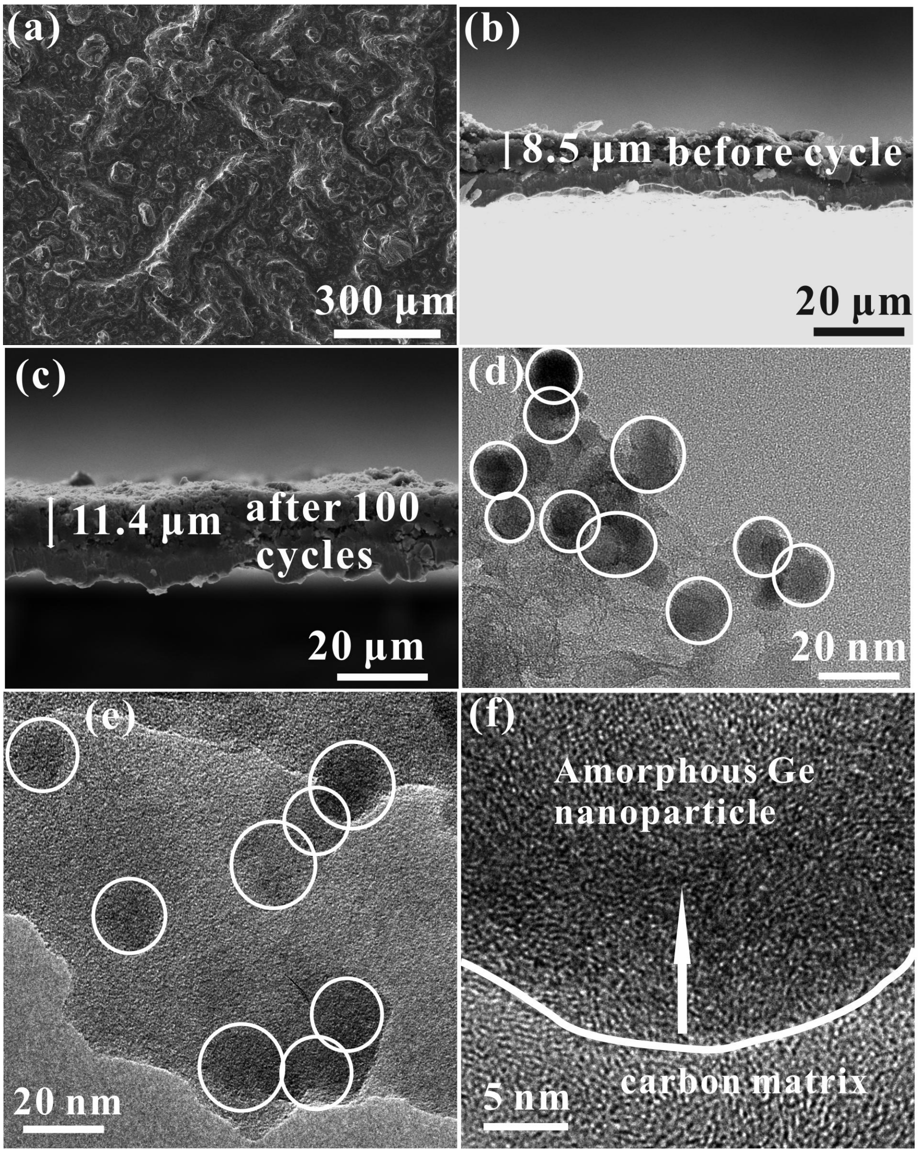

Fig. S1. (a) Top-view SEM image after 100 cycles, (b,c) Cross-sectional SEM images before cycling (b) and after 100 cycling (c), and (d-f) HRTEM images after 100 cycles.

Table S1 Lithium ion storage performances of Ge-based composites reported. The charge capacity mean those obtained in the final cycle. C_C-charge capacity (mAh g^{-1}), C_R-capacity retention (%), M_L-mass loading (mg cm^{-2}), J-current density (C or A g^{-1}, 1 C=1.6 A g^{-1}), N_C-cycle number, NA-not available.

Samples	C_C	C_R	M_L	J	N_C	References
Ge/C	1607.8	108.3	1.1	0.1 C	100	**This work**
Ge/C	1082.3	98.8	1.1	2 C	1000	**This work**
Ge/C	875.5	94.4	1.1	5 C	3000	**This work**
Ge/C	745.3	NA	1.1	10 C	NA	**This work**
Ge/C	491.7	NA	1.1	20 C	NA	**This work**
Ge/C	1562.3	99.9	2.0	0.1 C	100	**This work**
Ge/C	1189.1	99.1	3.0	0.1 C	100	**This work**
Ge/C	1009.4	97.6	4.0	0.1 C	100	**This work**
3DOP Ge@N-C	1250	51.2	1	0.1 A g^{-1}	50	Adv. Funct. Mater. 2020, 2000373.
3DOP Ge@N-C	1140.2	98.7	1	1 A g^{-1}	200	Adv. Funct. Mater. 2020, 2000373.
3DOP Ge@N-C	1000	NA	1	5 A g^{-1}	1200	Adv. Funct. Mater. 2020, 2000373.
3DOP Ge@N-C	508.2	NA	1	40 A g^{-1}	NA	Adv. Funct. Mater. 2020, 2000373.
Ge@3D-grahpite tube	1668	NA	2	0.5 C	1	ACS Nano 13 (2019) 7536-7544.
Ge@3D-grahpite tube	1316	NA	2	0.5 C	1000	ACS Nano 13 (2019) 7536-7544.
Ge@3D-grahpite tube	752	NA	2	40 C	NA	ACS Nano 13 (2019) 7536-7544.
GeO_2(s)/Ge(c)	1333.5	88.9	0.44-0.62	0.1 A g^{-1}	30	Adv. Funct. Mater. 29 (2019) 1807946.
GeO_2(s)/Ge(c)	665.3	55.4	0.44-0.62	0.5 A g^{-1}	100	Adv. Funct. Mater. 29 (2019) 1807946.
GeO_2(s)/Ge(c)	1024.4	NA	0.44-0.62	0.4 A g^{-1}	NA	Adv. Funct. Mater. 29 (2019) 1807946.
GeO_2(s)/Ge(c)	1162.1	NA	0.44-0.62	0.1 A g^{-1}	NA	Adv. Funct. Mater. 29 (2019) 1807946.
Core shell Ge@NC	806	80.6	0.8-2	5 C	400	Chem. Eng. J. 360 (2019) 1301-1309.
Core shell Ge@NC	917	78	0.8-2	1 C	1000	Chem. Eng. J. 360 (2019) 1301-1309.
Core shell Ge@NC	360	NA	0.8-2	20 C	NA	Chem. Eng. J. 360 (2019) 1301-1309.
C/Ge/GeO_2	791	54	2-3	0.05 A g^{-1}	50	Adv. Funct. Mater. 28 (2018) 1800938.
C/Ge/GeO_2	700	NA	2-3	0.05 A g^{-1}	NA	Adv. Funct. Mater. 28 (2018) 1800938.
C/Ge/GeO_2	110	NA	2-3	0.5 A g^{-1}	NA	Adv. Funct. Mater. 28 (2018) 1800938.
Peapod-like Ge/CNx	1080	90	NA	0.5 C	1200	J. Mater. Chem. A 4 (2016) 7585-7590.
Peapod-like Ge/CNx	874	NA	NA	8 C	NA	J. Mater. Chem. A 4 (2016) 7585-7590.
Peapod-like Ge/CNx	1000	78	NA	0.05 C	50	J. Mater. Chem. A 4 (2016) 7585-7590.
Ge/NC (PF)	684	84.4	0.5-0.7	0.2 A g^{-1}	200	ACS Appl. Mater. Interfaces 8 (2016) 27788−27794
Ge/NC (PF)	400	NA	0.5-0.7	5 A g^{-1}	NA	ACS Appl. Mater. Interfaces 8 (2016) 27788−27794
Ge/NC (PF)	732	95	0.5-0.7	0.1 A g^{-1}	100	ACS Appl. Mater. Interfaces 8 (2016) 27788−27794
Ge@C box	497	NA	NA	30 C	NA	Adv. Energy Mater. 6 (2016) 1501666.
Ge@C box	1065.2	NA	NA	0.5 C	500	Adv. Energy Mater. 6 (2016) 1501666.
C-GeNWs-CNFs	1520	NA	NA	0.1 C	100	Small 11 (2015) 2762-2767.

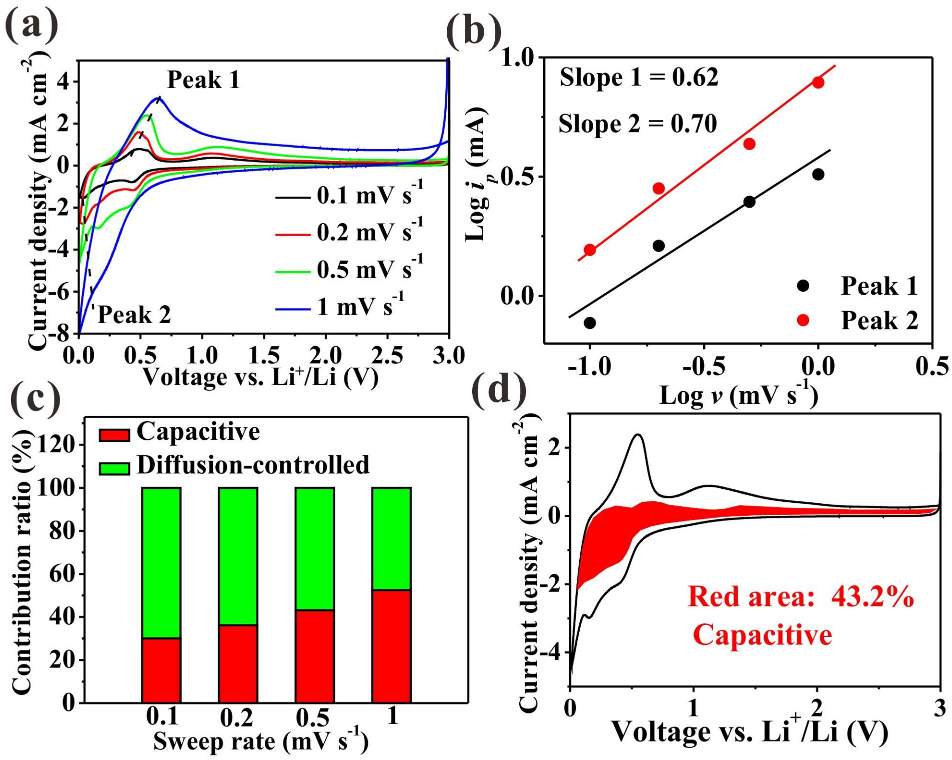

Fig. S2 (a) CV curves at different *v*, (b) Line relationship of Log(*i*) vs Log(*v*) at peaks 1-4 marked in (a), (c) Contribution percentages of pseudocapacitance at different *v,* and (d) The detailed pseudocapacitive contribution at 0.5 mV s^{-1}.

The relationship of scanning rate (*v*) and peak current (i_p) in the CV curves accords with the equation (1) [J. Mater. Chem. A 8 (2020) 3822-3833; J. Power Sources 465 (2020) 228206.]:

$$\mathrm{Log}(i_p) = a\log(v) + \log(b) \qquad (1)$$

Where *a* and *b* are empirical value. The 0.5 and 1 of *a*-value correspond to diffusion-controlled and pseudocapacitive behavior, respectively, which are obtained as slope from plots of Log(*i*) versus Log(*v*) at peaks 1-2 (Fig. S2a). The *a*-value ranges from 0.5 to 1 (Fig. S2b), implying that the high capacity of Ge/C nanocomposite is contributed from both diffusion- and pseudocapacitive-controlled behaviors. The relationship of total capacity at a given *v* and voltage (V) complies with following equation (2) :

$$i\,(\mathrm{V}) = k_1 v^{1/2} + k_2 v \qquad (2)$$

Where $k_1v^{1/2}$ and k_2v correspond to the diffusion- and pseudocapacitive-controlled behaviors, respectively. It is observed that the contribution percentages of pseudocapacitance increases from 30.1% to 52.5% with the increase of *v* from 0.1 to 1 mV s^{-1} (Fig. S2c), indicating that the behavior of pseudocapacitance plays a significant role in the total capacity, especially at high *v*. Fig. S2d shows the detailed pseudocapacitive contribution (the red area) at 0.5 mV s^{-1}.

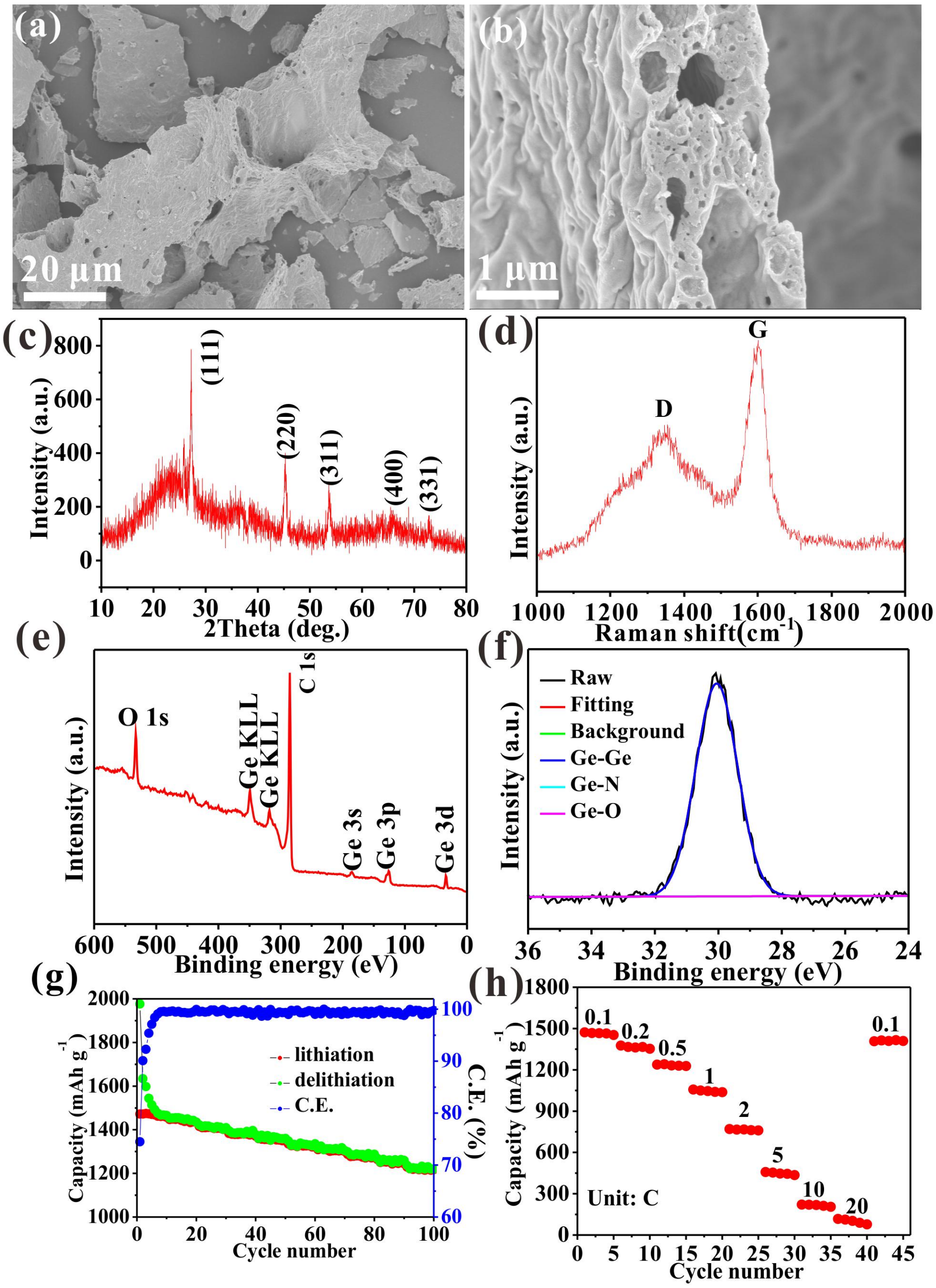

Fig. S3 (a,b) SEM images, (c) XRD pattern, (d) Raman spectrum, (e) XPS survey peak, (f) Ge 3d, (g) cycling performance, and (h) rate performance of sample obtained by pyrolysis of BS at 650 ^{o}C for 2 h.

Figs. S3a,b show that the Ge/C composite without N and O atoms has similar morphology with Ge/C composite with N and O atoms. Fig. S3c shows typical XRD diffraction peaks of Ge crystals. Fig. S3d shows that the composite contains free carbon. Figs. S3e and f show that Ge-N and Ge-O bonds are absent. The Ge/C composite without N and O delivers a first capacity of 1472.4 mAh g^{-1} with a low capacity retention of 82.7% after 100 cycles at 0.1 C (Fig. S3g). The Ge/C composite without N and O delivers a capacity of 1452.9, 1353.1, 1228.3, 1038.6, 760.1, 436.6, 205.3, and 78.3 mAh g^{-1} at 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 C, respectively (Fig. S3h).

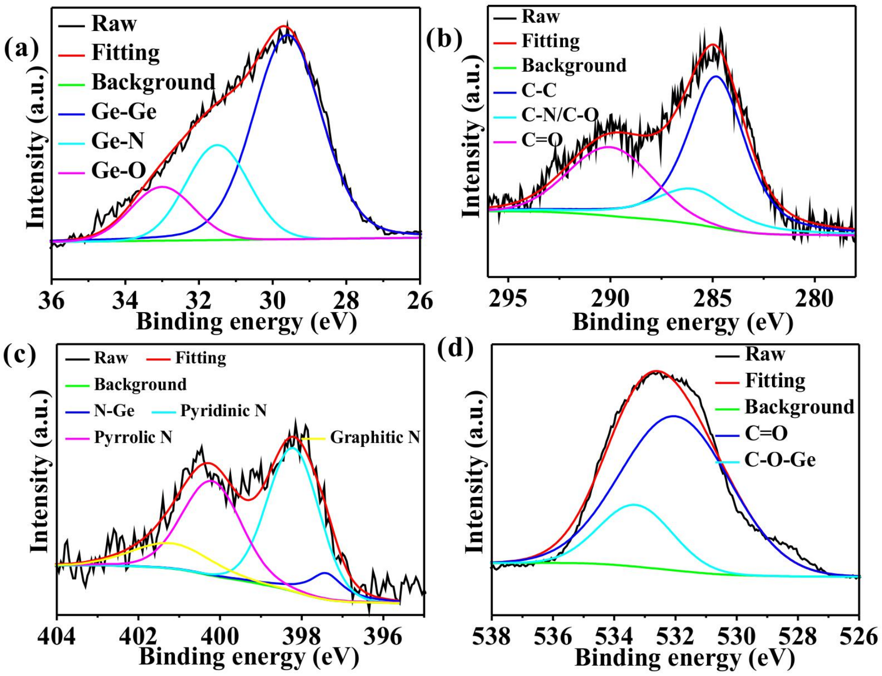

Fig. S4 XPS spectra of Ge 3d (a), C 1s (b), N 1s (c), and O 1s (d) after 100 cycles. Before testing, the electrode was subjected to Ar etching for 2 h.

From Fig. S4, the Ge-N-C and Ge-O-C bonds are still retained in the Ge/C nanocomposites after 100 cycles, suggesting that the N and O atoms tightly bridge the Ge nanocrystals and carbon matrix during cycling.

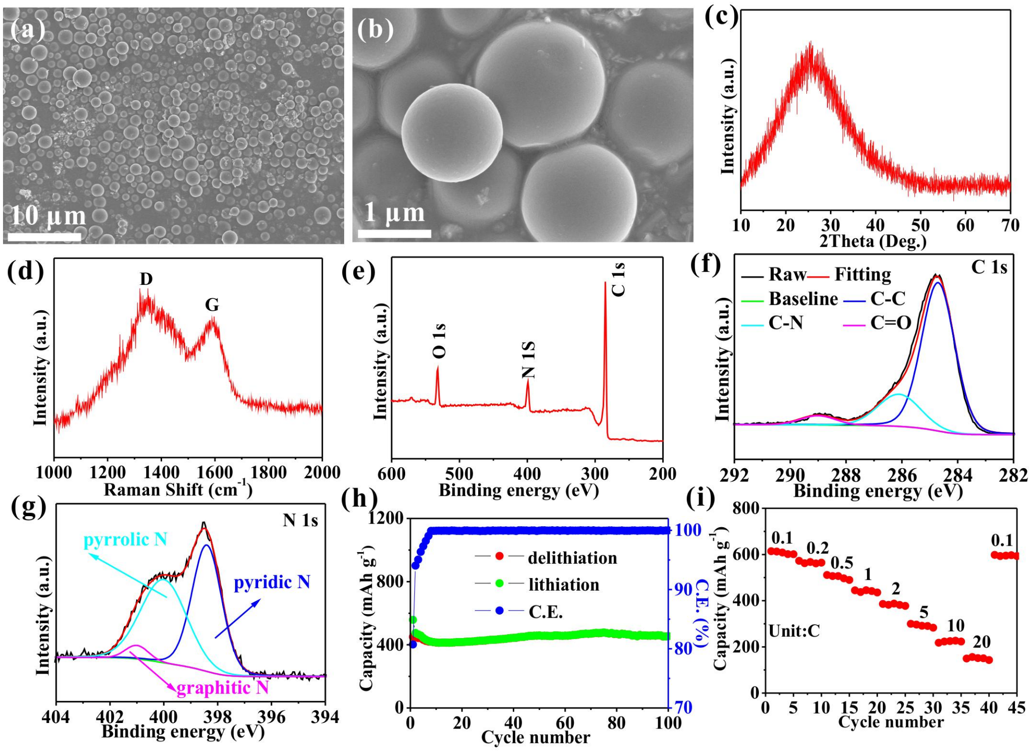

Fig. S5 (a,b) SEM images, (c) XRD pattern, (d) Raman spectrum, (e) XPS survey peak, (f) C 1s, (g) N 1s, (h) cycling performance at 1 C, and (i) rate performance of sample obtained by pyrolysis of DMF at 650 °C for 2 h.

Figs. S5a,b show that the carbon matrix has spherical morphology with smooth surface. The formation mechanism of spherical morphology has been discussed in detail in our previous reports [Diam. Relat. Mater., 2018, 87, 10-17.]. However, in the case of the substrate material, the decomposition products of DMF do not form spheres alone, but are coated on the surface of the substrate material, which has similar result with our previous report [J. Mater. Chem. A, 2019, 7, 4804-4812.]. Fig. S5c only shows a broad XRD diffraction peak, suggesting that the carbon matrix is amorphous. Fig. S5d shows typical D and G peaks of carbon materials. Figs. S5e-g show that the carbon matrix only contains C, N, and O atoms and is N,O-codoped. The carbon matrix delivers a first capacity of 450.4 mAh g^{-1} with a high capacity retention of 101.1% after 100 cycles at 1 C (1 C=0.6 A g^{-1}) (Fig. S5h). The carbon matrix delivers a capacity of 614.2, 572.6, 511.2, 444.9, 386.1, 299.8, 218.2, and 149.8 mAh g^{-1} at 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 C, respectively (Fig. S5i).

Table S2 R_s, R_f, and R_{ct} of the Ge/C with N and O atoms electrodes during cycles.

Cycle number	R_s (Ω)	R_f (Ω)	R_{ct} (Ω)
uncycled	0.94	0	86.1
After 1st cycle	1.04	6.72	68.4
After 10th cycles	1.21	6.77	63.7
After 100th cycles	1.32	6.81	45.3

Calculation of gravimetric/volumetric energy density

The gravimetric (Wh kg^{-1})/volumetric (Wh l^{-1}) energy density can be determined from equations (1)/(2), respectively .

$$\text{Gravimetric energy density (Wh kg}^{-1}\text{)} = \left(\frac{Cc \times V}{S\left(m_{cathode} + m_{anode}\right)} \right) \tag{1}$$

$$\text{Volumetric energy density (Wh kg}^{-1}\text{)} = \left(\frac{Cc \times V}{S\left(t_{cathode} + t_{anode}\right)} \right) \tag{2}$$

Where $C_{cathode}$-cathode capacity (165.3 mAh g^{-1}); V-nominal voltage (3.1 V); $S_{electrode}$-electrode area (0.95 cm^2); $m_{cathode}/m_{anode}$-active mass of cathode/anode; $t_{cathode}/t_{anode}$-thickness of cathode (79.8 µm)/anode (16.9 µm) materials.