Germanium coating boosts lithium uptake in Si nanotube battery anodes

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Synthesis of active materials and fabrication of the half coin cell

Both Si nanotubes (Si NT) and Si/Ge double layered nanotubes (Si/Ge DLNT) array were synthesized on 15 μm thick stainless steel substrate (Nilaco, Tokyo, Japan). The detailed synthesis condition and procedure for SiNT and Si/Ge DLNT growth are described in our previous reports.[1, 2] The precise masses of the active materials were estimated using a microbalance (Sartorius SE2, resolution 1 μg, Sartorius, Germany). A half coin cell (2032R-type) was assembled using Si NT and Si/Ge DLNT as working electrodes, a pure lithium metal foil as a counter electrode and 1.3 M $LiPF_6$ in ethylene carbonate/diethylene carbonate (EC/DEC, 3:7 vol %, PANAX StarLyte, S. Korea) as an electrolyte and a polypropylene (PP) separator.

Calculation of the voltage decay during the discharge experiment.

We here present the calculation of the voltage decay and capacity of the system modeled by the simplified electrical circuit of Fig. 6(a) of the main text. Given the purpose of this study and the experimental behavior of R_{ct}, R_a and C_μ in Figs. 4 and 5 of the main text and, we assume R_{ct} and C_μ to be voltage independent, while R_a depend exponentially on bias as:

$$R_a(V) = R_{ct} + aV \tag{1}$$

When switching on the current source, the capacitor is charged and the total bias at $t=0$ is given by:

$$V(t=0) = V_0 \tag{2}$$

After the switch, $t>0$, the constant current, $I_0>0$, flows in the circuit, the capacitor is being discharged and the total bias is:

$$V_{tot}(t) = V_0 - V(t) \tag{3}$$

$V(t)$ is linked to the impedance of the system, $Z(t)$, at any time by:

$$V(t) = Z(t) * I_0 u(t) \tag{4}$$

,where $u(t)$ is the well-known Heaviside distribution.

Equation (4) can be solved in the Laplace domain:

$$V=\left(R_a(V)+\frac{1}{sC_a}\right)\frac{I_0}{s} \tag{5}$$

Eqs. (1) and (5) lead to:

$$V(s)=\frac{R_{ct}I_0}{s-aI_0}-\frac{1}{aC_a}\frac{aI_0}{s(s-aI_0)} \tag{6}$$

Hence, applying the inverse Laplace transform and inserting the latter into Eq. (3), one gets:

$$V_{tot}(t)=V_0-\left[\left(R_{ct}I_0+\frac{1}{aC_a}\right)e^{aI_0t}-\frac{1}{aC_a}\right]u(t) \tag{7}$$

From Eq. (7) we can now generate the voltage decay as a function of time or charge ($Q=I_0t$). In particular, we can also obtain the time t_0 necessary for the voltage to vanish:

$$t_0=\frac{1}{aI_0}\ln\left[\frac{V_0+\frac{1}{aC_a}}{R_{ct}I_0+\frac{1}{aC_a}}\right] \tag{8}$$

The time t_0 allows one to calculate the capacity of the system, expressed in percent:

$$Capacity=\frac{t_0I_0}{t_{0,\min}I_{0,\min}}\times 100 \tag{9}$$

Where, $t_{0,\min}$ is the time corresponding to the slowest discharge, for an extraction current $I_{0,\min}$.

Finally, we can derive the rate C that corresponds to the current necessary for the total voltage to vanish in one hour (3600 s). C is therefore obtained through Eq. (7):

$$0=V_0-\left[\left(R_{ct}C+\frac{1}{aC_a}\right)e^{3600aC}-\frac{1}{aC_a}\right] \tag{10}$$

,which leads to transcendental equation:

$$Ye^Y=3600\frac{a}{R_{ct}}\left[\left(V_0+\frac{1}{aC_a}\right)e^{\frac{3600}{R_{ct}C_a}}\right] \tag{11}$$

, with $Y = 3600\frac{a}{R_{ct}}\left(R_{ct}C + \frac{1}{aC_a}\right)$.

The solution to Eq. (11) can be found numerically or using the Lambert W function:

$$Y = W\left[3600\frac{a}{R_{ct}}\left[\left(V_0 + \frac{1}{aC_a}\right)e^{\frac{3600}{R_{ct}C_a}}\right]\right] \quad (12)$$

Consequently,

$$C = \frac{1}{3600.a}W\left[3600\frac{a}{R_{ct}}\left[\left(V_0 + \frac{1}{aC_a}\right)e^{\frac{3600}{R_{ct}C_a}}\right]\right] - \frac{1}{aC_aR_{ct}} \quad (13)$$

For theses simulations, the alloying resistance was assumed to vary linearly with voltage as: $R_a(V) = R_{ct} + aV$. The values of the parameters were: $C_a = 2\,\mathrm{F}$, $a = 1\,\mathrm{A^{-1}}$. The mass was fixed to 1 mg.

References

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