Simple derivation of equations 5, and 6 in the paper: V.A. Sethuraman, V. Srinivasan, J. Newman, "Analysis of Electrochemical Lithiation and Delithiation Kinetics in Silicon", Journal of The Electrochemical Society, Volume 160, Issue 2, Pages A394-A403, 2013. DOI: 10.1149/2.008303jes

For the reaction $xLi + Si + xe^- \rightleftharpoons Li_xSi$, (1)
occurring under galvanostatic conditions, the applied current can be written as,

$$I_{app} = I_{DL} + I_{Main} + I_{side\,rxn} \qquad (2)$$

where I_{DL} is current due to charging the double-layer, I_{main} is current due to the main reaction (lithiation and delithiation), and $I_{side\,rxn}$ is current due to the reduction of the electrolyte components (parasitic reaction)

Under open-circuit conditions, eqn (2) can be written as,

$$-I_{DL} = I_{Main} + I_{side\,rxn} \qquad (3)$$

Expanding,

$$-C_{dl}\frac{dV}{dt} = i_0\left\{\exp\left[\frac{\alpha_a F}{RT}(V-U)\right] - \exp\left[-\frac{\alpha_c F}{RT}(V-U)\right]\right\} + i_{0,side\,rxn}\left\{\exp\left[-\frac{\alpha_{side\,rxn}F}{RT}(V-U_{side,rxn})\right]\right\} \qquad (4)$$

This is Eqn [4] in the paper

For the lithiation reaction [forward reaction in (1)], assuming Tafel kinetics, and without the side reaction,

$$-C_{dl}\frac{dV}{dt} = -i_0\exp\left[-\frac{\alpha_c F}{RT}(V-U)\right] \qquad (5)$$

Analytic solution for (5):

$$\frac{dV}{dt} = \frac{i_0}{C_{dl}}\exp\left[-\frac{\alpha_c F}{RT}(V-U)\right]$$

$$\exp\left[\frac{\alpha_c F}{RT}(V-U)\right]dV = \frac{i_0}{C_{dl}}\cdot dt \qquad (6)$$

Integrating (6), we get

$$\frac{RT}{\alpha_c F}\cdot\exp\left[\frac{\alpha_c F}{RT}(V-U)\right] = \frac{i_0}{C_{dl}}t + C \qquad (7)$$

Using the initial condition, when $t=0$, $V=V_0$, we get

$$C = \frac{RT}{\alpha_c F}\exp\left[\frac{\alpha_c\cdot F}{RT}(V_0-U)\right] \qquad (8)$$

Substituting (8) in (7), and re-arranging,

$$\exp\left[\frac{\alpha_c F}{RT}(V-U)\right] = \frac{\alpha_c F}{RT}\frac{i_0}{C_{dl}}\cdot t + \exp\left[\frac{\alpha_c F}{RT}(V_0-U)\right]$$

This is eqn [5] in the paper

$$V = U + \frac{RT}{\alpha_c F}\ln\left\{\frac{\alpha_c F}{RT}\frac{i_0}{C_{dl}}\cdot t + \exp\left[\frac{\alpha_c F}{RT}(V_0-U)\right]\right\} \qquad (9)$$

Let $\beta = \exp\left[\frac{\alpha_c F}{RT}(V_0 - U)\right]$

and (9) becomes, $$V = U + \frac{RT}{\alpha_c F} \ln\left[\frac{\alpha_c}{RT} \frac{i_0}{C_{dl}} . t + \beta\right] \qquad (10)$$

Differentiating (10),

$\frac{d}{dx}\left[a \ln(bx+c)\right] = \frac{ab}{(bx+c)}$

$$dv = \frac{\frac{RT}{\alpha_c F} \cdot \frac{\alpha_c F}{RT} \cdot \frac{i_0}{C_{dl}}}{\left(\frac{\alpha_c F}{RT} \frac{i_0}{C_{dl}} . t + \beta\right)} dt = \frac{i_0 RT}{\alpha_c F i_0 t + \beta RT C_{dl}} dt$$

$\frac{d}{dt} \ln t = \frac{1}{t} \Rightarrow dt = t . d\ln t$

$$= \frac{1}{\frac{\alpha_c F}{RT} . t + \frac{\beta C_{dl}}{i_0}} . dt = \frac{1}{\frac{\alpha_c F}{RT} + \frac{\beta C_{dl}}{i_0 t}} . d\ln t$$

$$\frac{dv}{d\ln t} = \left[\frac{1}{\frac{\alpha_c F}{RT} + \frac{\beta C_{dl}}{i_0 t}}\right] \qquad (11)$$

At long times, (11) reduces to

$$\frac{dv}{d\ln t} = \frac{RT}{\alpha_c F} \qquad (12)$$

This is eqn[6] in the paper

Symbols:

C_{dl} – Double-layer Capacitance, F/cm^2
V – Cell potential, V
t – time, s
i_0 – exchange current density for lithiation/delithiation, A/cm^2
α_a – apparent transfer coefficient, anodic
α_c – apparent transfer coefficient, cathodic
F – Faraday's Constant, 96485 C/mole equiv
R – Gas constant, 8.314 J/mol/K
T – Temperature, K
U – Equilibrium potential, V