

Activation Energy of Ion Diffusion in an Electrode Material: Theoretical Calculation and Experimental Estimation with LiCoVO_4 as an Example

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Supplementary Materials

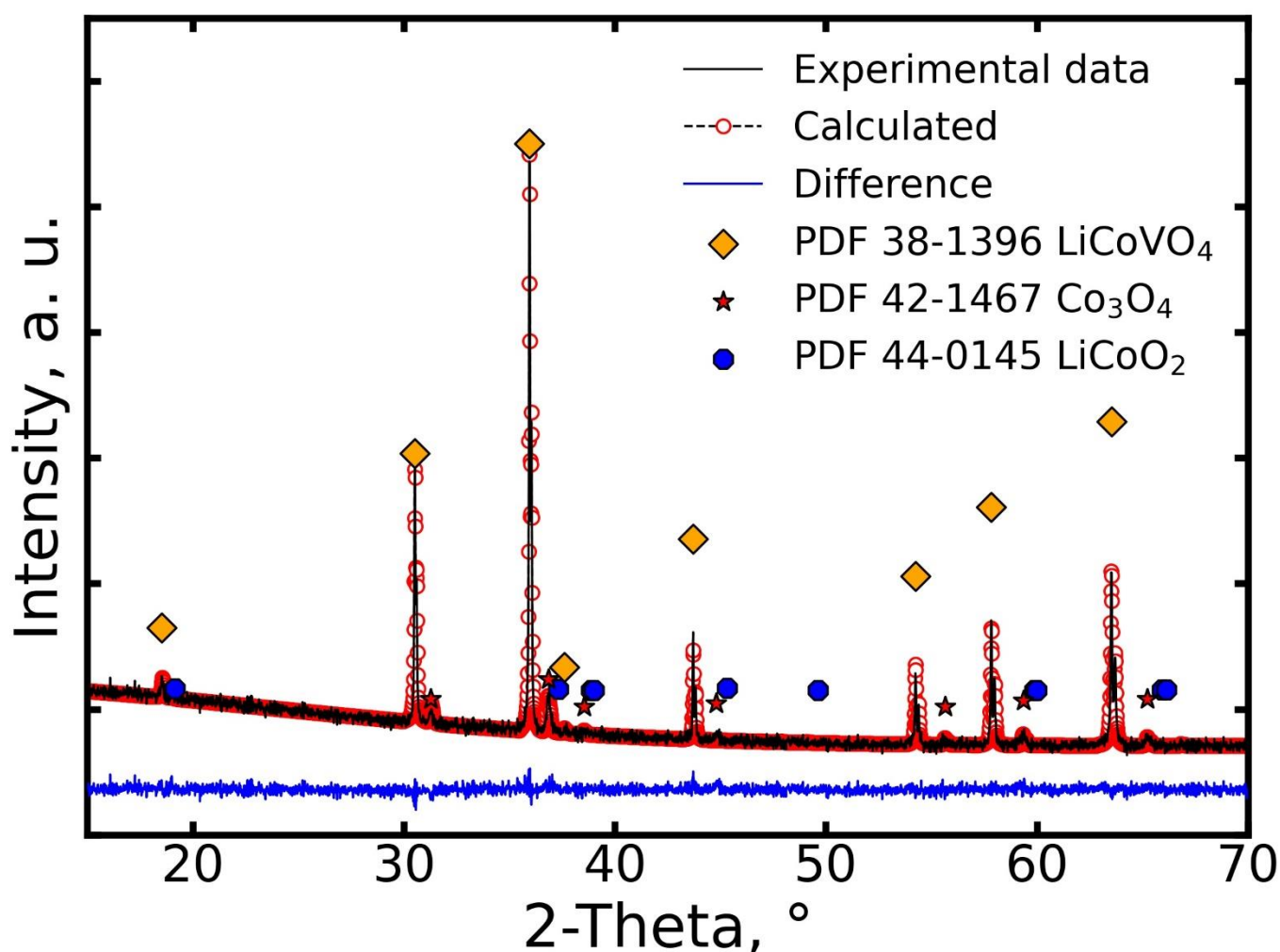


Figure S1. X-ray powder diffraction pattern of a LiCoVO_4 sample and illustration of the analysis result by the Rietveld technique *.

* We varied the parameters such as the coefficients of a polynomial for the background, the zero offset of the goniometer, the scale factor and unit cell parameters for LiCoVO_4 and Co_3O_4 phases, the half-width parameters in accordance with the Pseudo-Voigt function, the coordinates of oxygen atoms for the main phase. We used the FullProf Suite. The main result can be viewed in the List S1.

List S1. Main results of XRD analysis by the Rietveld technique

We did not vary the marked (*) values or parameters. But we specify them because the result may depend on them.

Phase LiCoVO₄

Atomic coordinates and occupancies

Atom	x = y = z	Biso(*)	Occ.(*)
Li	0.500(*)	0.5	1
Co1	0.500(*)	0.5	0.7
Co2	0.125(*)	0.5	0.3
V1	0.500(*)	0.5	0.3
V2	0.125(*)	0.5	0.7
O	0.2460 ± 0.0005	0.5	4

Cell parameter: $a = (8.2772 \pm 0.0001) \text{ \AA}$

Phase Co₃O₄

Cell parameter: $a = (8.0868 \pm 0.0005) \text{ \AA}$

Reliability-factors

R_p : 1.22 R_{wp} : 1.55 R_{exp} : 1.64 χ^2 : 0.89

Weight fractions

LiCoVO₄ (87 ± 1)%

Co₃O₄ (13 ± 1)%

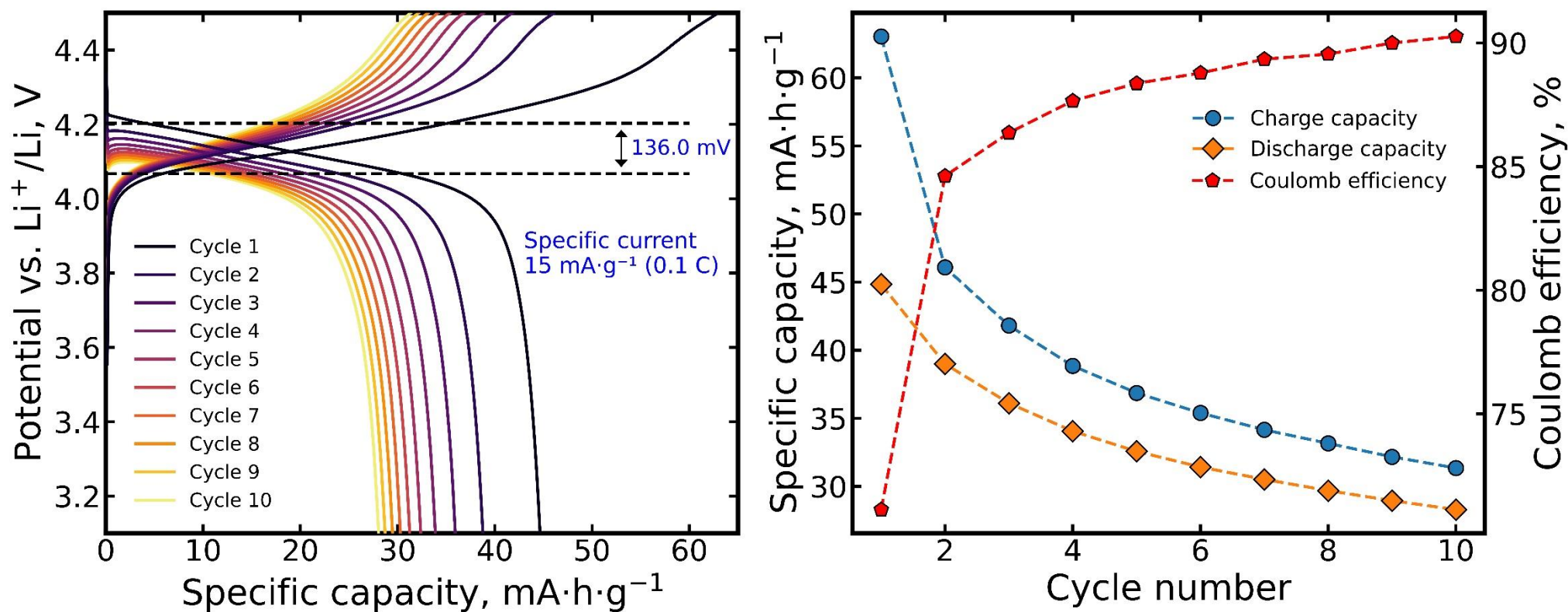


Figure S2. The curves of galvanostatic charge and discharge of the electrode based on LiCoVO_4 , and the change in electrode capacitance and Coulomb efficiency during cycling at temperature of 30°C . The data from [9].

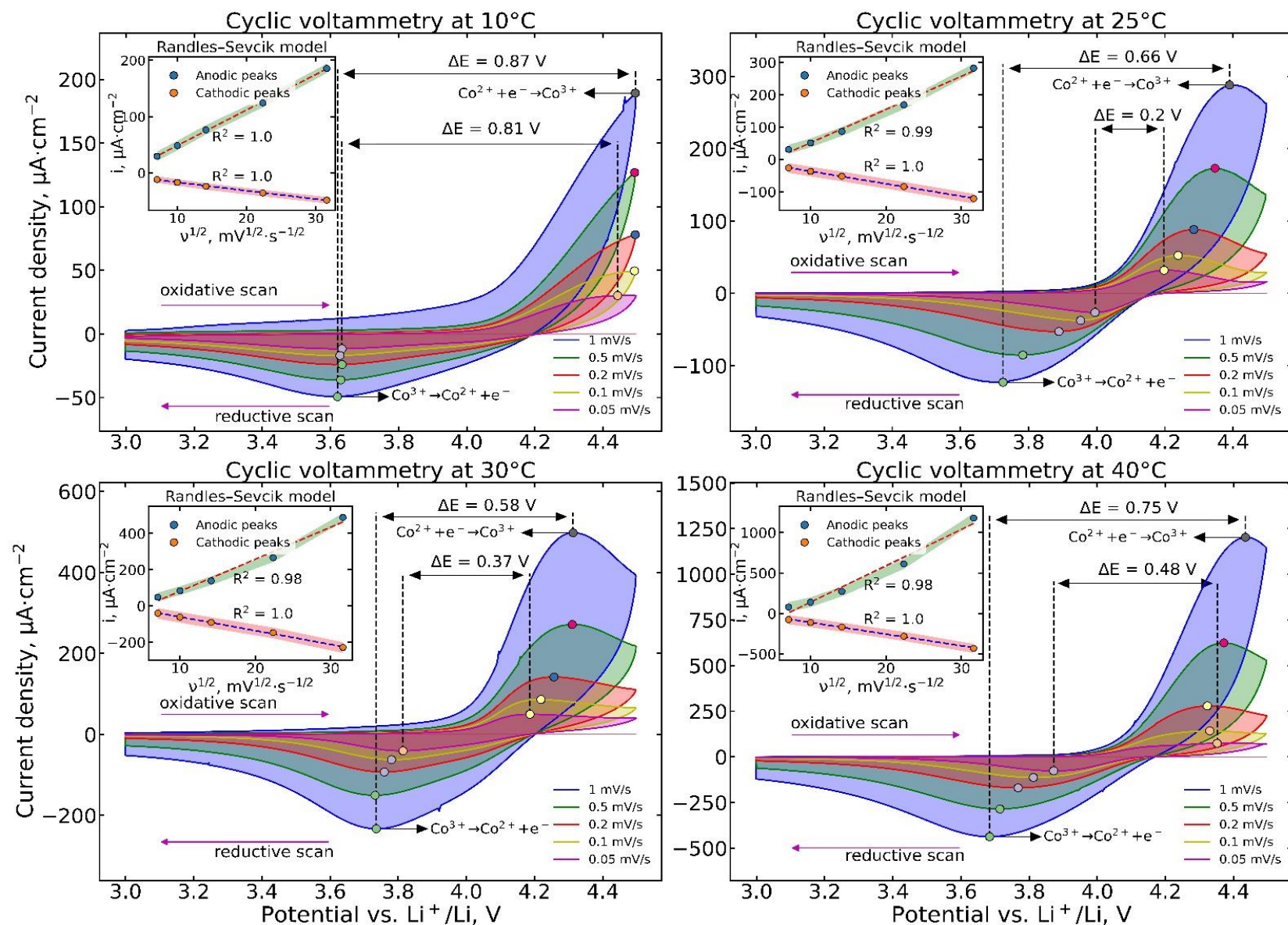


Figure S3. Cyclic voltammograms of LiCoVO_4 taken at temperatures of 10, 25, 30 and 40°C in the potential range from 3.0 to 4.5 V. The polarization rate increased from 0.05 to 1 $\text{mV}\cdot\text{s}^{-1}$. Inserts show the dependence of the peak current density on the potential sweep rate in linearized coordinates.

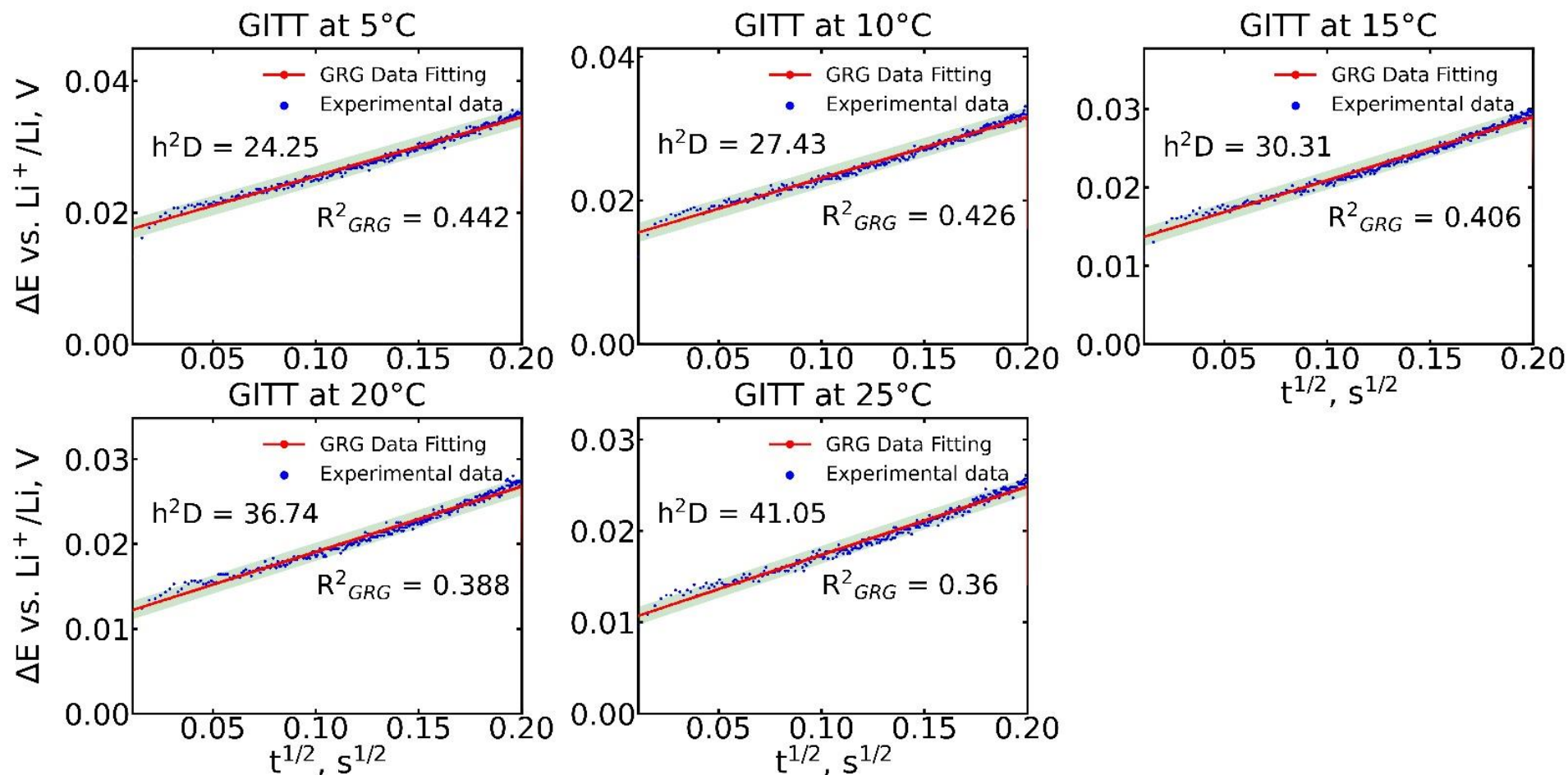


Figure S4. Fitting a linear regression of the potential transient to the square root of time during the current pulse; Blue markers - experimental data; red markers are the results of simulation based on equation 5. The magnitude of the pulsed current is 500 μA . The duration of the pulse and relaxation is 40 ms. Temperature range from 5 to 25°C in steps of 5°C.

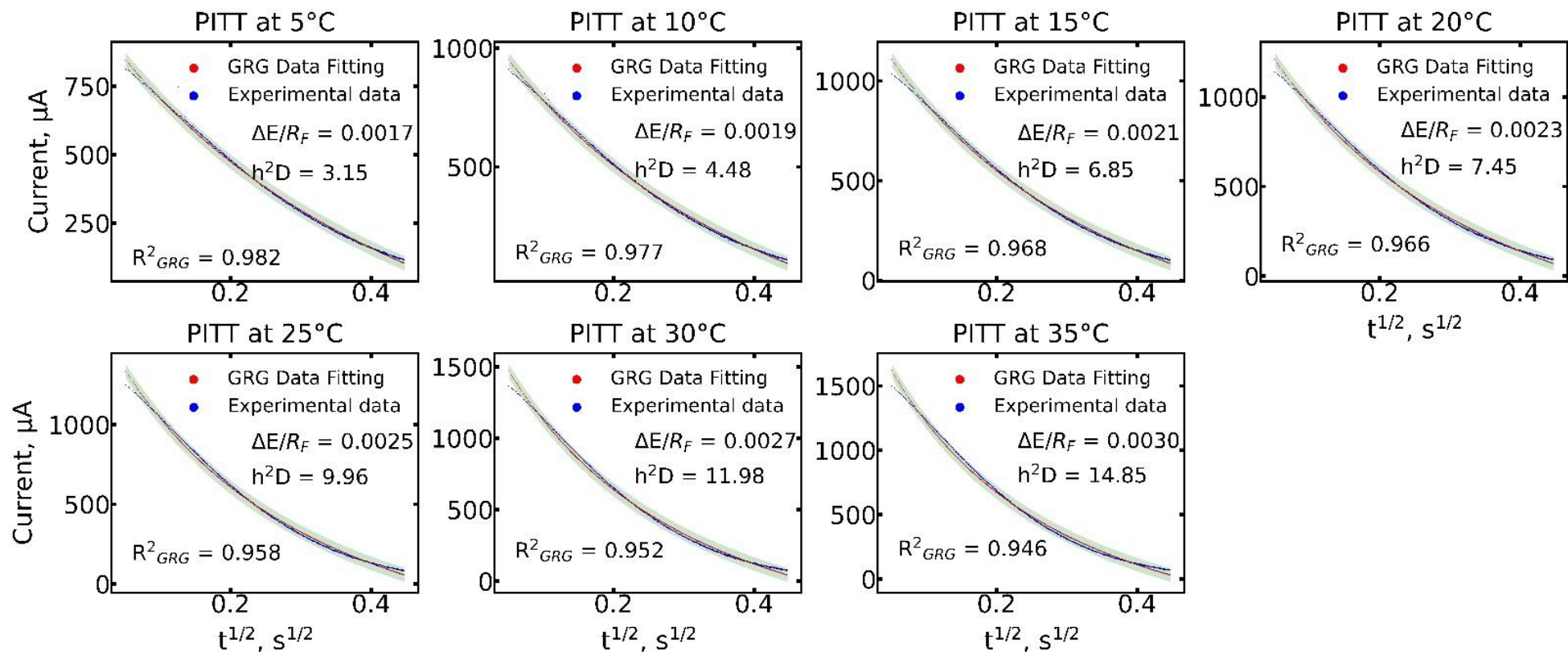


Figure S5. Current transients during potentiostatic impulse. Blue markers - experimental data; red markers are the results of simulation based on equation 6. The value of the potential pulse is 40 mV. The pulse duration is 200 ms. Temperature range from 5 to 35°C in steps of 5°C.