

Governing Parameter of Peak Currents in Square-wave Voltammetry Finally Identified

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Abstract

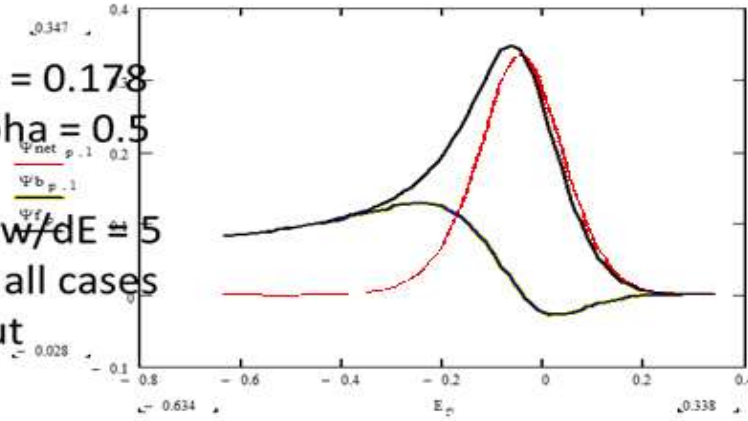
In square-wave voltammetry (SWV), the dependence of peak current on multiple experimental and kinetic parameters has long hindered the formulation of a Randles–Ševčík–type relationship. In this work, we demonstrate that the magnitude of peak currents can be governed by a single dimensionless parameter, defined as

$$JKG = \text{constant} \times [dE \cdot F / (RT)] \cdot (E_{sw}/dE)^{1/2} \cdot [K/(1+K)].$$

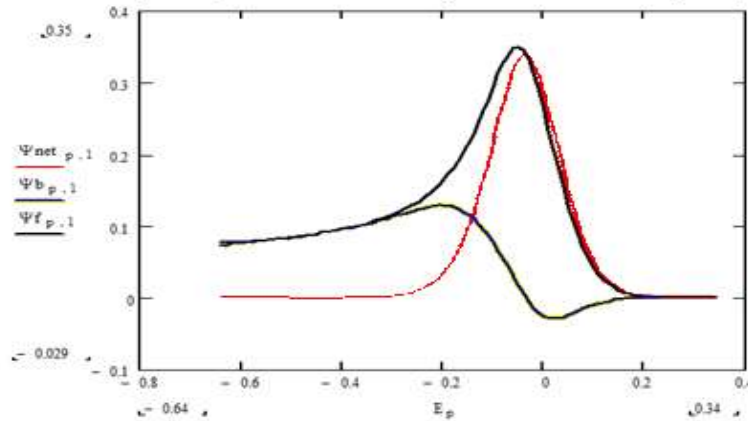
This parameter integrates the effects of potential step, square-wave amplitude, temperature, and kinetic dimensionless parameter K (defined as $K = k_s (Df)^{-0.5}$) into a unified descriptor JKG (from the initials of Janeva-Kokoskarova-Gulaboski). Simulations and theoretical analysis show that, when JKG is held constant, peak currents remain invariant across wide kinetic regimes and large ranges of temperatures, if the ratio E_{sw}/dE is kept constant. The proposed formulation provides a fundamental basis for simplified interpretation of SWV responses and establishes a pathway toward a generalized theoretical framework, in which also the effect of electron transfer coefficient α (now hidden in the “constant”) will be taken into account.

$K_{ET} = 0.178$
 $\alpha = 0.5$

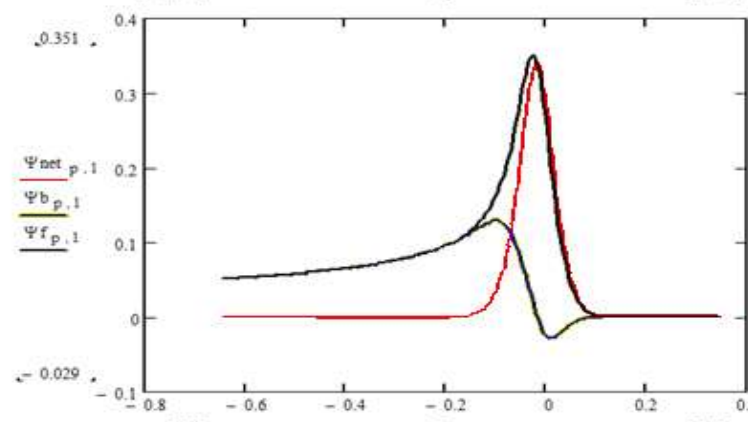
$E_{sw}/dE \approx 5$
 in all cases
 But



$E_{sw} = 60 \text{ mV}$
 $dE = 12 \text{ mV}$
 $T = 361.5 \text{ K}$



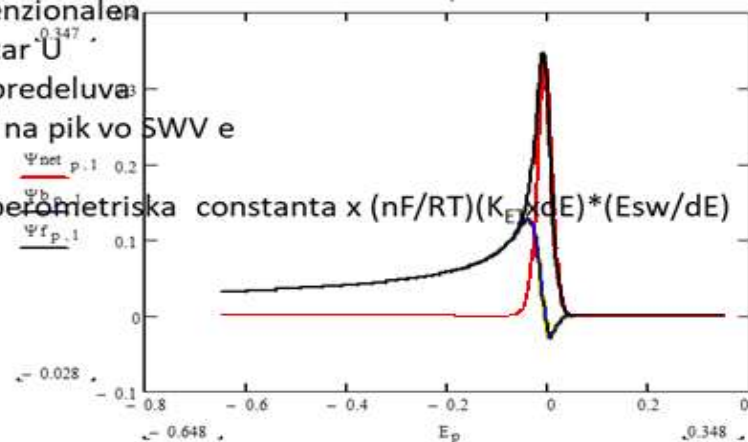
$E_{sw} = 50 \text{ mV}$
 $dE = 10 \text{ mV}$
 $T = 301.15 \text{ K}$



$E_{sw} = 25 \text{ mV}$
 $dE = 5 \text{ mV}$
 $T = 150.75 \text{ K}$

Bezdimenzionalen
 Parametar U
 Sto ja opredeluje
 Strujata na pik vo SWV e

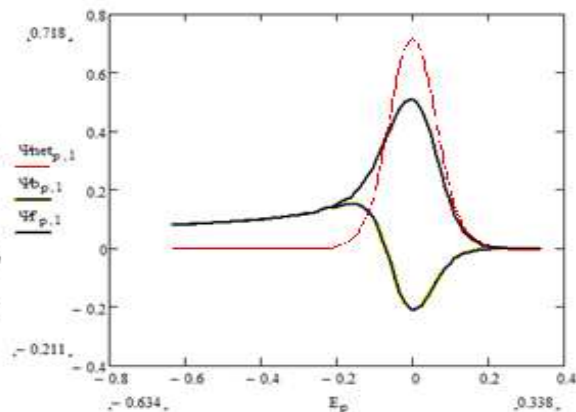
$U = \text{Amperometriska konstanta} \times (nF/RT)(K_{ET}dE) * (E_{sw}/dE)$



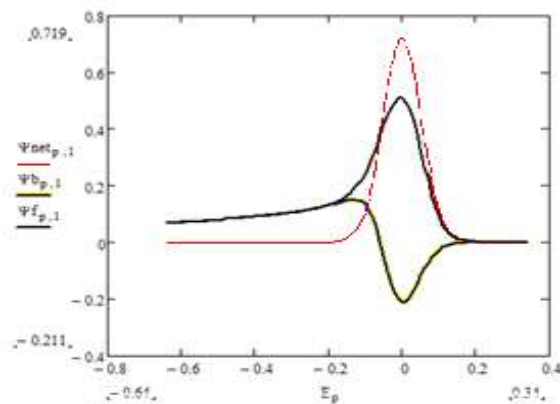
$E_{sw} = 10 \text{ mV}$
 $dE = 2 \text{ mV}$
 $T = 60.25$

$K_{ET} = 10$
 $\alpha = 0.5$

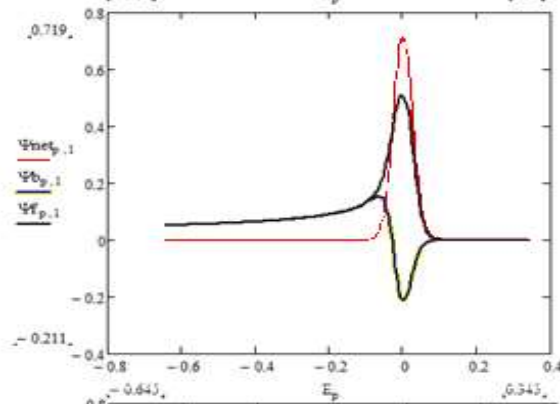
$E_{sw}/dE = 5$
in all cases
But...



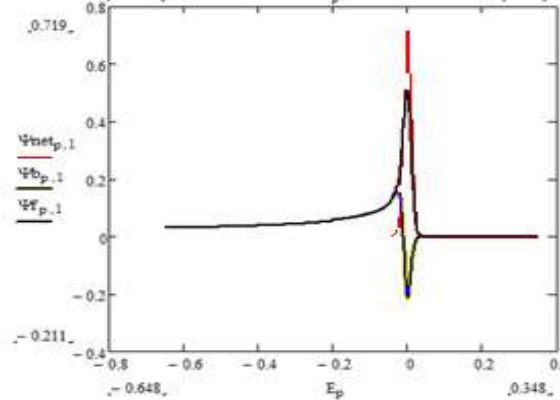
$E_{sw} = 60 \text{ mV}$
 $dE = 12 \text{ mV}$
 $T = 361.5 \text{ K}$



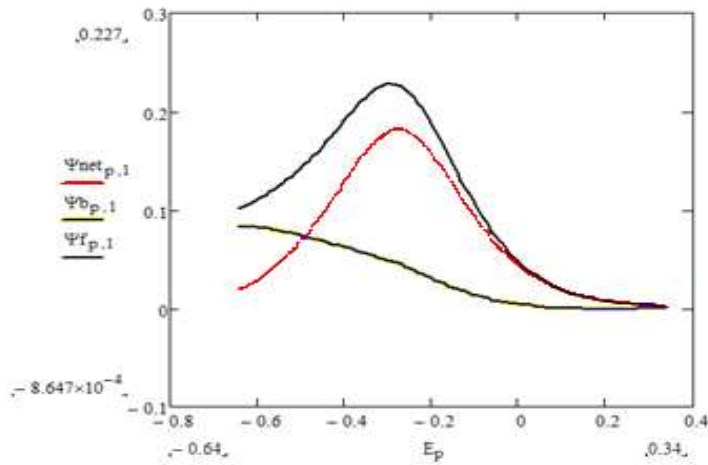
$E_{sw} = 50 \text{ mV}$
 $dE = 10 \text{ mV}$
 $T = 301.15 \text{ K}$



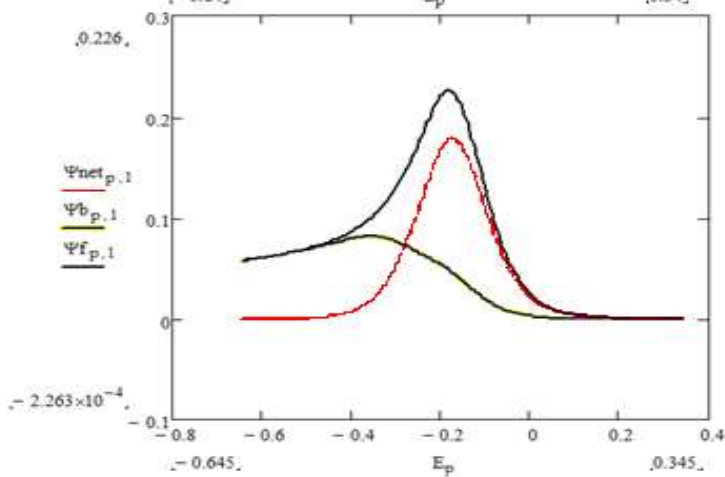
$E_{sw} = 25 \text{ mV}$
 $dE = 5 \text{ mV}$
 $T = 150.75 \text{ K}$



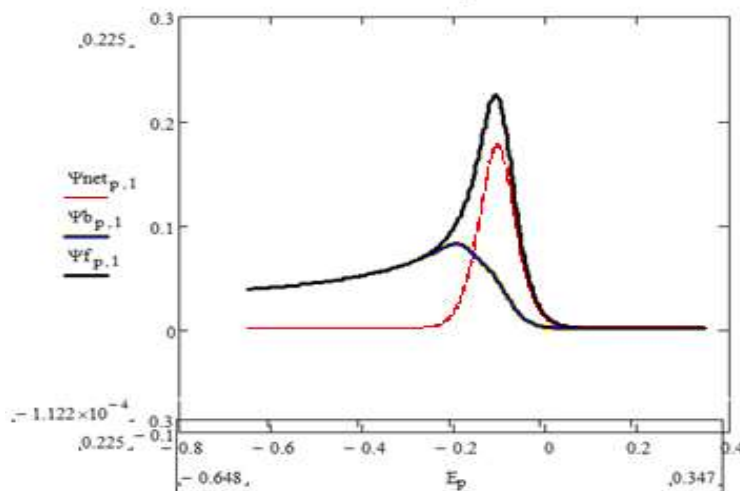
$E_{sw} = 10 \text{ mV}$
 $dE = 2 \text{ mV}$
 $T = 60.25 \text{ K}$



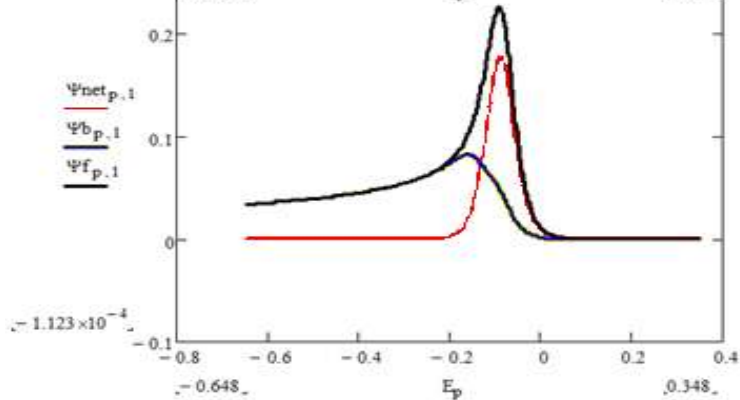
$E_{sw} = 100 \text{ mV}$
 $dE = 10 \text{ mV}$
 $T = 598.65$
 $K_{ET} = 0.02$



$E_{sw} = 50 \text{ mV}$
 $dE = 5 \text{ mV}$
 $T = 298.15$
 $K_{ET} = 0.01$



$E_{sw} = 25 \text{ mV}$
 $dE = 2.5 \text{ mV}$
 $T = 149.65$
 $K_{ET} = 0.005$



$E_{sw} = 20 \text{ mV}$
 $dE = 2 \text{ mV}$
 $T = 119.65$
 $K_{ET} = 0.004$

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