

Fig. S1. The kinetics of C₆H₁₁OH (1), C₆H₁₀(O) (2) and C₆H₁₁OOH (3) accumulation upon C₆H₁₂ oxidation by H₂O₂, MeCN, 40 °C.

Reaction conditions: (a), (b), (d): [C₆H₁₂]₀ = [H₂O₂]₀ = 1.8 M; (c): [C₆H₁₂]₀ = 0.36 M, [H₂O₂]₀ = 1.8 M. (a), (b), (c): [VO(acac)₂]₀ = 0.06 × 10⁻³ M; (d): [VO(acac)₂]₀ = 0.6 × 10⁻³ M; (a), (d): [H₂C₂O₄]₀ = 50 × 10⁻³ M; (b), (c): [H₂C₂O₄]₀ = 5 × 10⁻³ M.

Fig. S2. The relationships between VO(acac)₂/OxalH molar ratios and the resulted solutions pH.

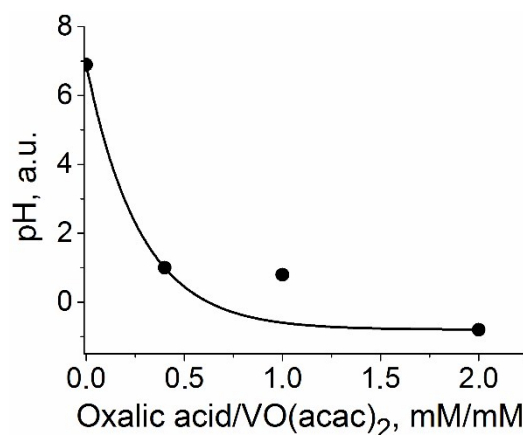


Fig. S3. Relationships between ORP of VO(acac)₂-based system and pH in dependence of H₂O₂ added.

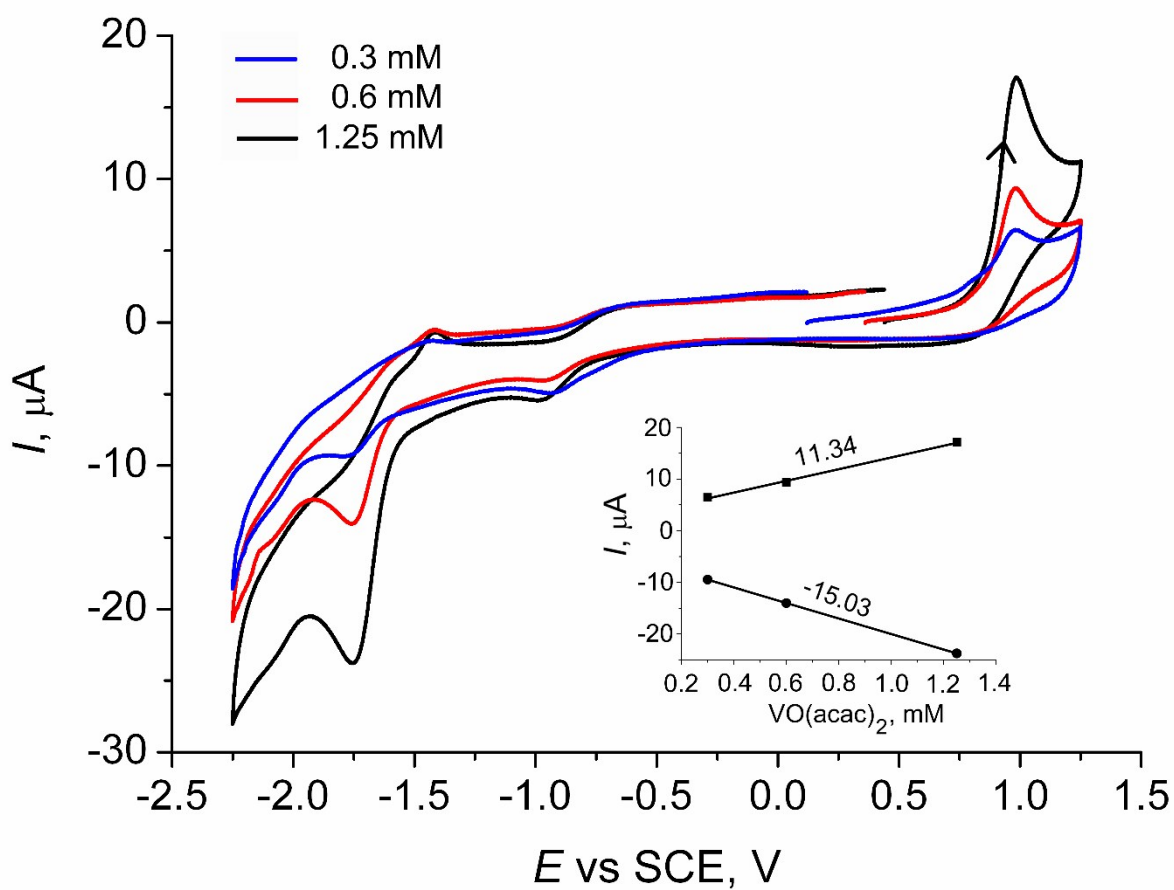
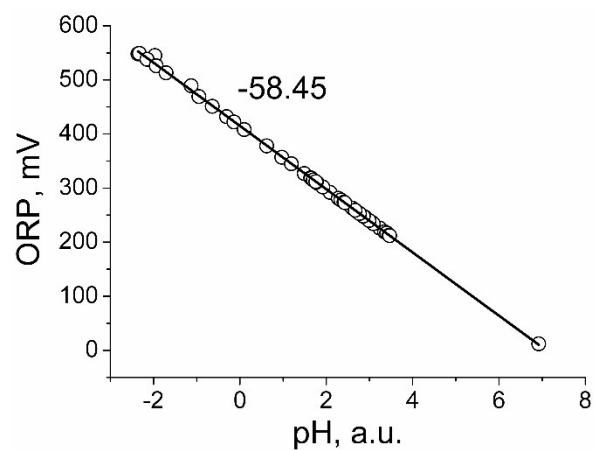


Fig. S4. CV of $\text{VO}(\text{acac})_2$ solutions (anodic scans) taken for various $\text{VO}(\text{acac})_2$ content (initial concentration of $\text{VO}(\text{acac})_2$ in mM is indicated by the respective color), MeCN, 20 °C.
Inset: the height of 0.98 V (squares) and -1.75 V (circles) peaks in dependence of $\text{VO}(\text{acac})_2$ concentration.

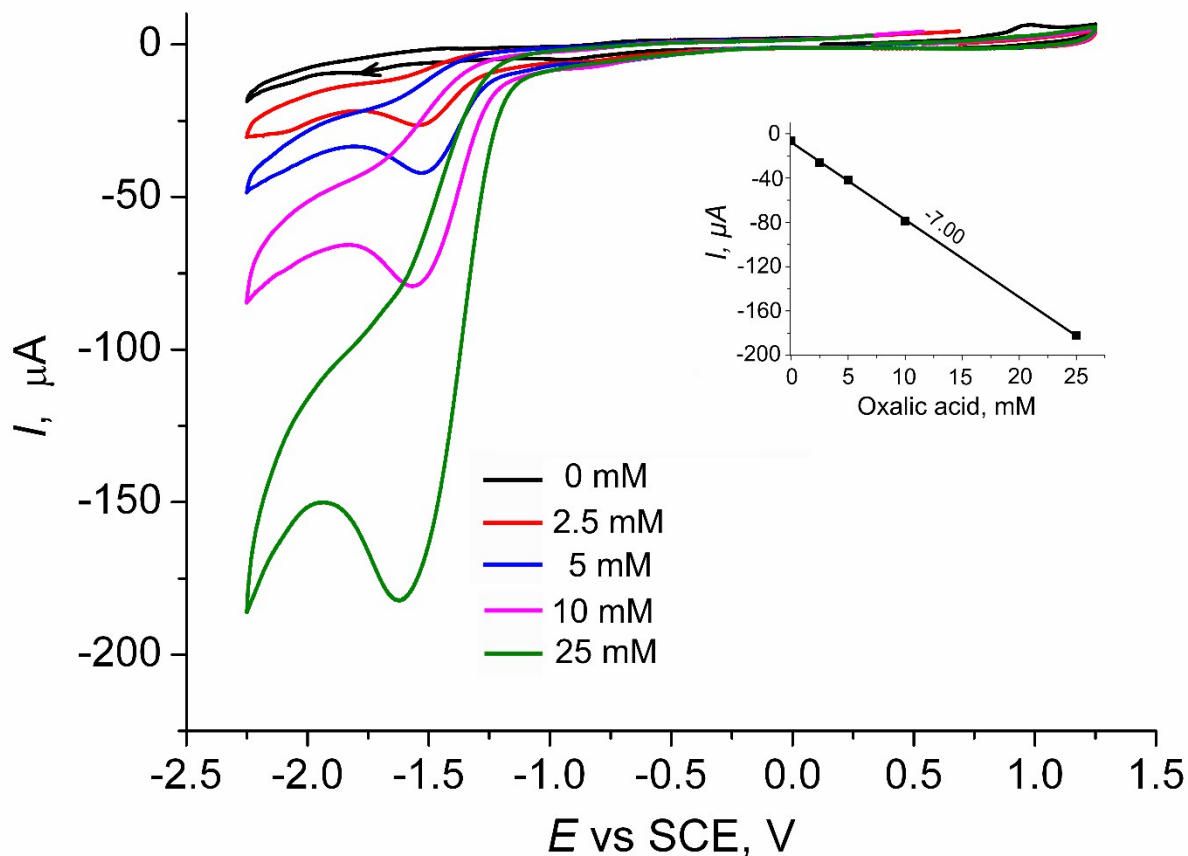


Fig. S5. CV of $\text{VO}(\text{acac})_2 + \text{OxalH}$ solutions (anodic scans) taken in dependence of $\text{H}_2\text{C}_2\text{O}_4$ content (concentration of $\text{VO}(\text{acac})_2$ was equal 1.25 mM; initial concentration of OxalH in mM is indicated by the respective color), MeCN, 20 °C.
Inset: the height of -1.55 V peak alteration in dependence of OxalH concentration.

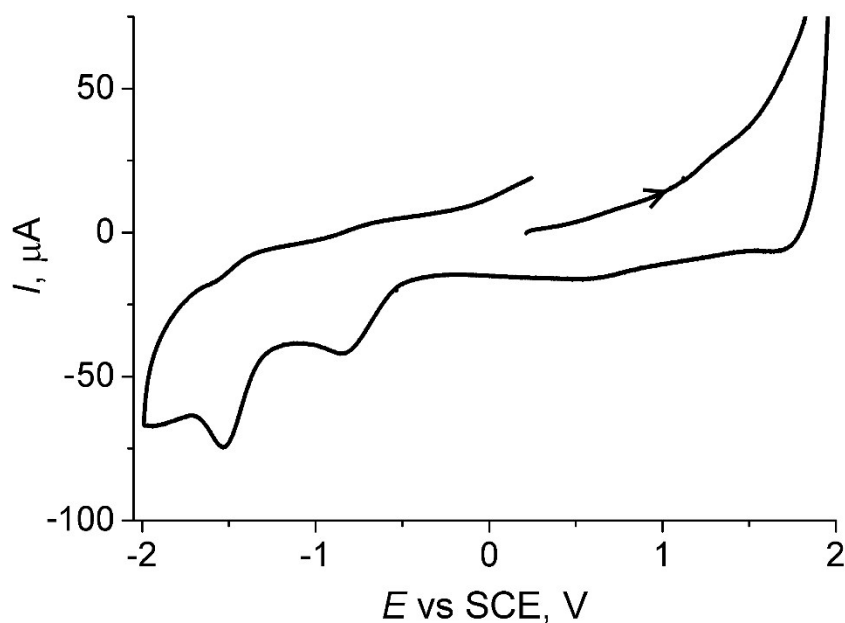


Fig. S6. CV of 2mM OxalH solutions, MeCN, 20 °C (anodic scans).



Scheme S1. The principal electrical scheme for measuring low-frequency complex dielectric spectra: dispersive power capacitor (B, n) and parallel ($R_V C_V$) circuit.

Parallel $R_V C_V$ circuit characterizes the bulk impedance of solution under study: electrical resistance and dielectric polarization.

Dispersive capacitor is characterized by fractional power law dispersion with small exponent $n-1$ according to the expression

$$C^*(\omega) = C_1(\omega) - jC_2(\omega) = B\{\sin(\omega t) - j\cos(\omega t)\}\omega^{n-1}$$

and represents dielectric response of double electrical layers formed near both solution-metal interfaces of filled up cell. Full impedance of this electrical equivalent electrical circuit could be written in the form:

$$\bar{Z}(\omega) = Z_1(\omega) - jZ_2(\omega) = \frac{1}{B\{\cos(\omega t) + j\sin(\omega t)\}\omega^n} + \frac{R_V}{1 + j\omega R_V C_V}$$

Thereby complex capacity of the circuit can be expressed as:

$$C^*(\omega) = C_1(\omega) - jC_2(\omega) = \left\{ \frac{1}{B\{\sin(\omega t) - j\cos(\omega t)\}\omega^{n-1}} + \frac{j\omega R_V}{1 + j\omega R_V C_V} \right\}^{-1}$$