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Quasireversible maximum under conditions of novel electrochemical techniques

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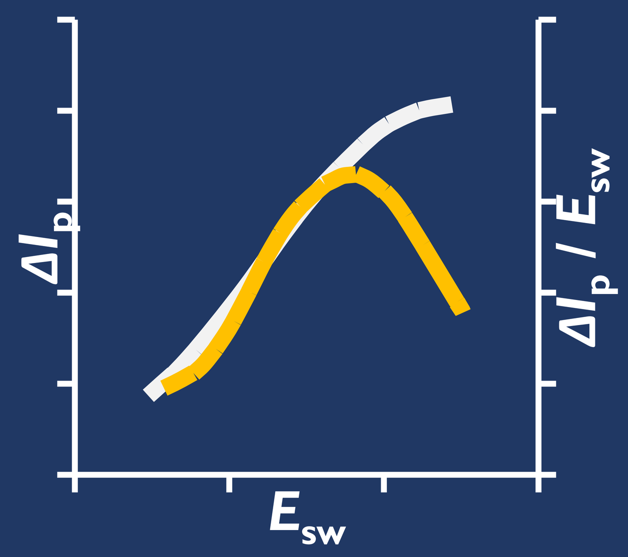
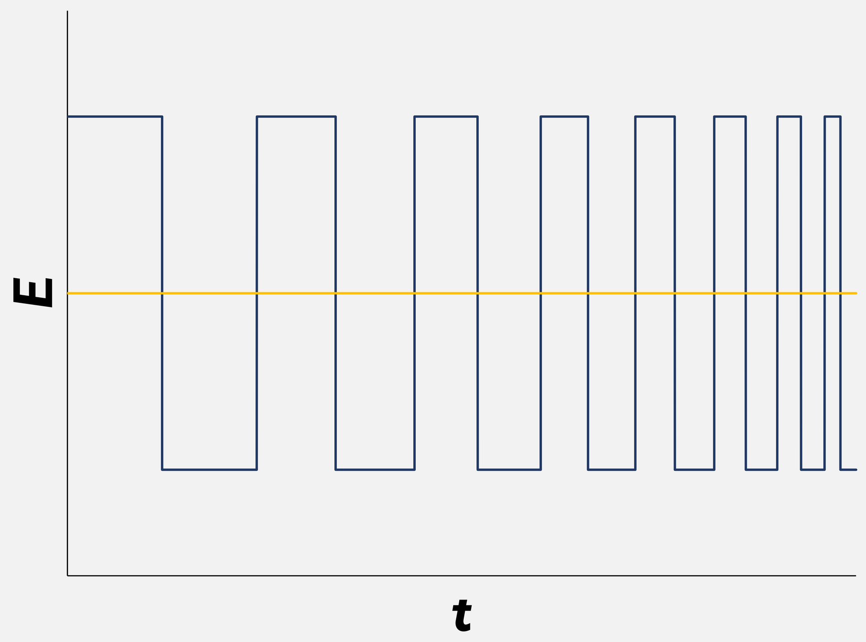
Introduction

Square-wave voltammetry (SWV) is ranked as pulse voltammetric techniques, which is widely applied for studying mechanisms and kinetics of electrode processes. Despite its many advantages, it is considered as relatively complex technique. Due to the complexity of the results, it causes difficulties in data interpretation. Our research on simplifying electrokinetic studies results in three electrochemical techniques. These techniques are based on the measurement of the characteristic, parabolic dependence of the current as a function of the applied frequency or amplitude in a form of so-called quasireversible maximum based either on amplitude or frequency[1,2]. The position of the quasireversible maximum provides important data on electrode reaction kinetics because it enables estimation of the standard rate constant.

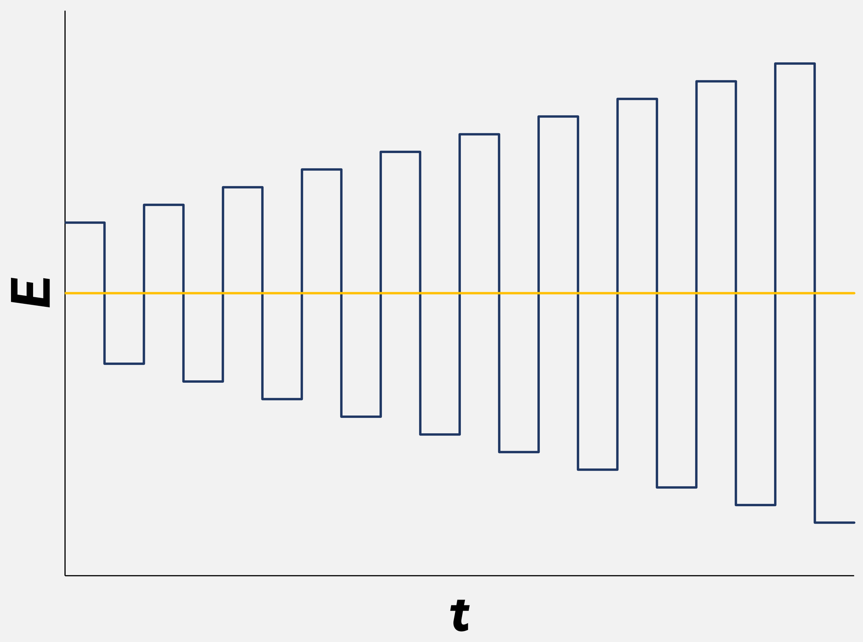


Methods

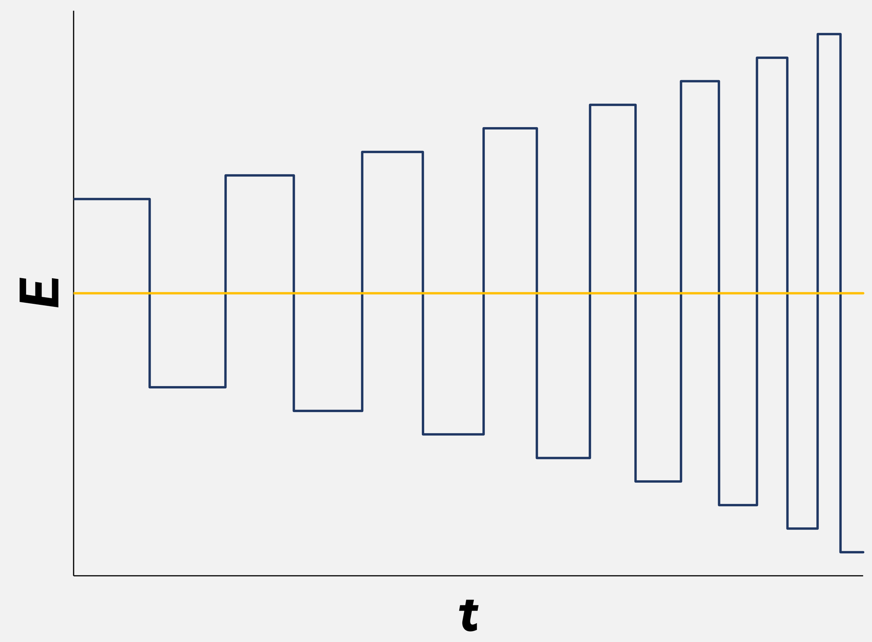
In order to simplify electrokinetic and mechanistic studies, the potential modulation applied to the working electrode under square wave conditions was modified. The underlying staircase potential, which is typical for SWV, is replaced with constant mid-potential[3]. Any subsequent changes involve the modification of the basic parameters i.e. amplitude and frequency. The resulting emergence of three novel electrochemical techniques enable receive of information on the rate of reaction in an alternative, simple and fast procedures.



The potential modulation of technique called f-EFS consists of SW forward and reverse potential pulses imposed on a constant mid-potential. The duration of potential cycles progressively decreases (i.e. the frequency increases during the experiment).



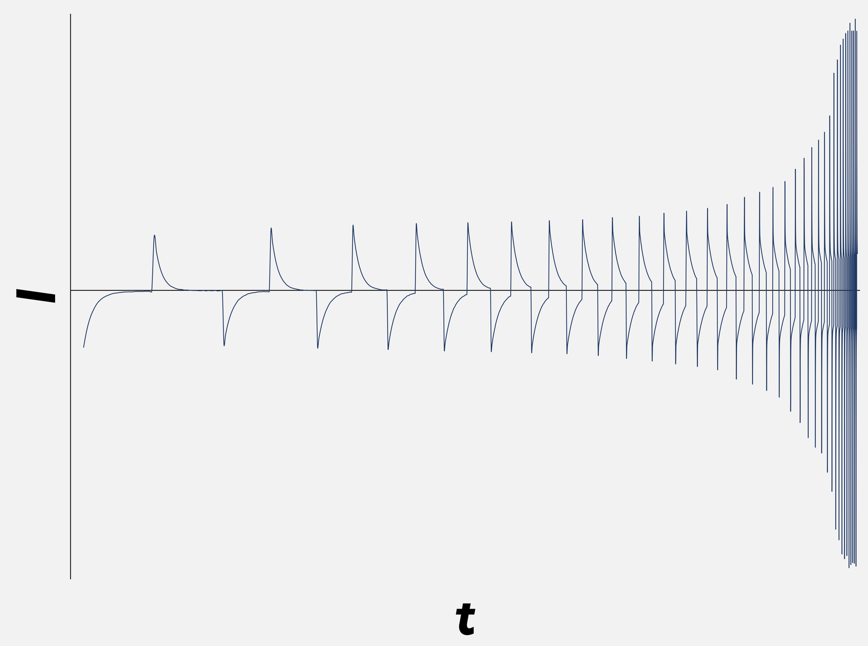
The potential modulation of E_{sw}-EFS consists of SW forward and reverse potential pulses of constant frequency imposed on a constant mid-potential. The duration of potential cycles is constant but the height of the pulses (i.e. amplitude) progressively increases.

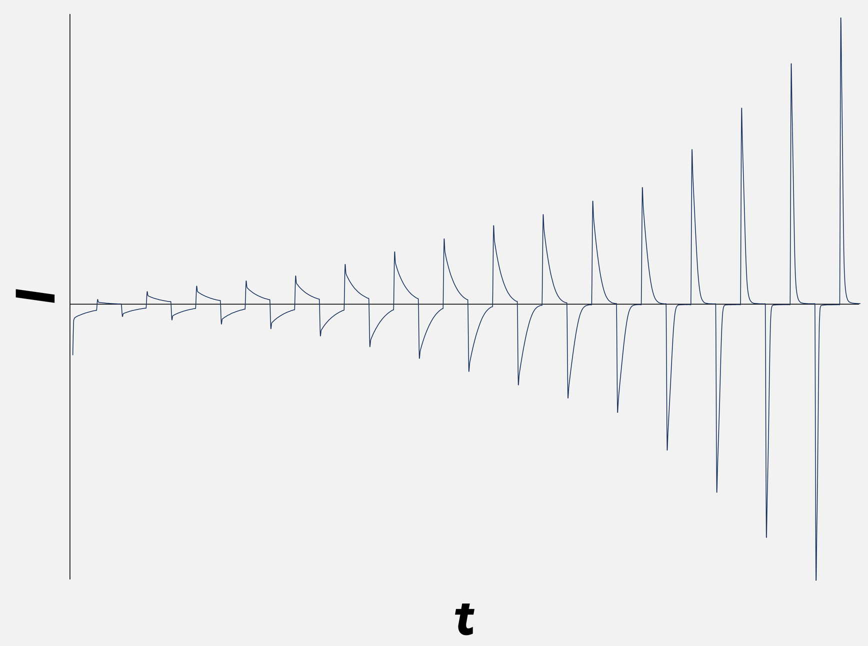


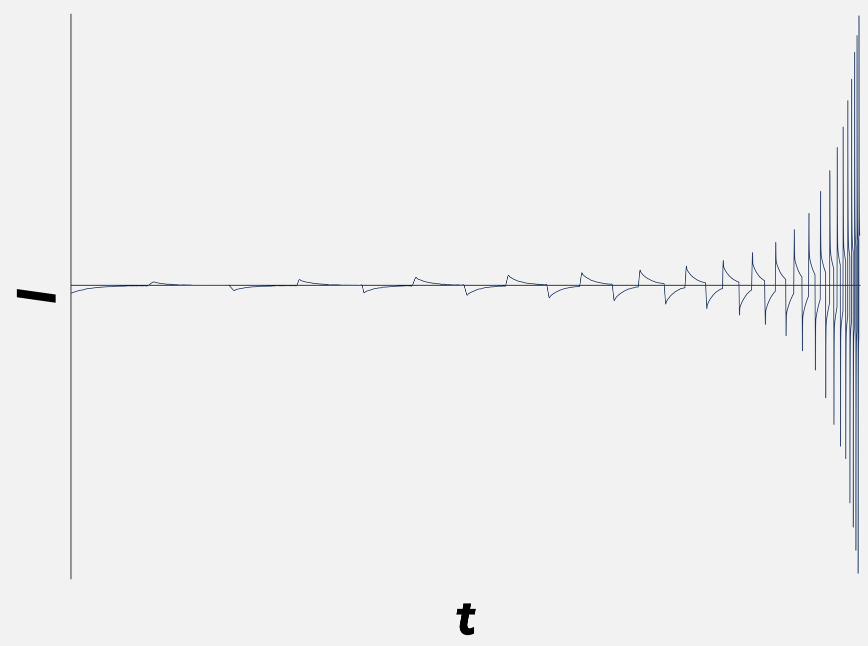
The technique called multi-EFS was created by combination of f-EFS and E_{sw}-EFS. The duration of potential cycles progressively decreases. At the same time, the amplitude of pulses for the following cycles gradually increases.

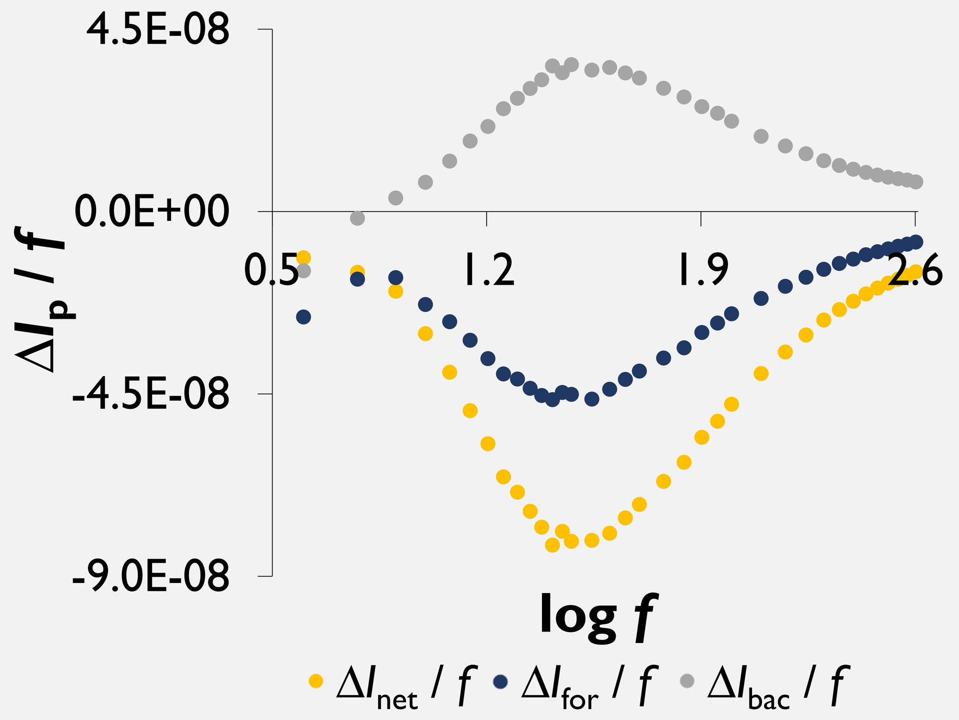
Results

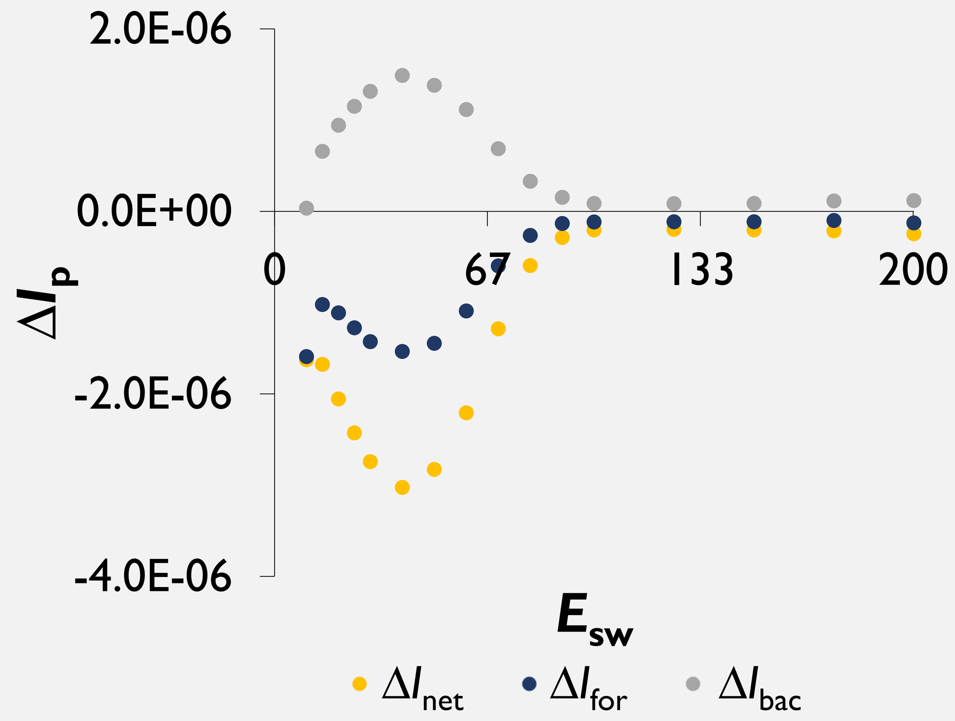
Assessment of quasireversible maximum possible record under conditions of f-EFS, E_{sw}-EFS and multi-EFS was carried out i.a. for azobenzene in Britton-Robinson buffer pH = 4 on a hanging mercury drop electrode. The courses of all dependencies have a characteristic form of a quasi-reversible maximum.

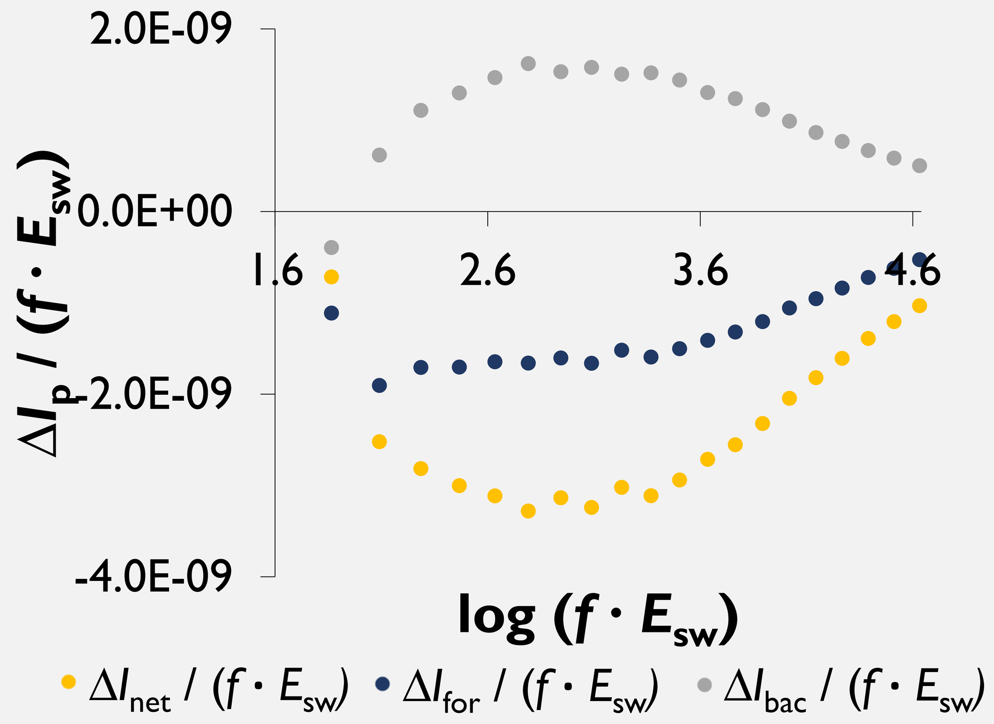












Conclusions

The record of a quasireversible maximum for azobenzene is possible under conditions all three novel electrochemical techniques. These techniques could be applied as useful tool for studying the kinetics of electrode reactions. They can be useful, above all, in studying the kinetics of adsorbed systems on the electrode surface. The plan of futher research is focused on the assessment of the possibility of record a quasireversible maximum for more complex electrode mechanisms, as well as on the development and application of proposed techniques for analytical purposes, e.g. in electrochemical sensors.

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References

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