

## Determining charge transfer kinetic constants for fast reversible systems on porous electrodes using Electrochemical Impedance Spectroscopy

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Among the possible electrolytes suggested as substitutes for vanadium-based ones in redox flow batteries, aqueous organic based electrolytes have recently attracted high interest. These electrolytes are organic compounds presenting relatively high solubility in water. Molecules such as Indigo Carmine, Viologen and TEMPO, can then provide very fast charge-transfer reaction kinetics in neutral or mildly acidic or basic aqueous electrolytes. The resulting electrolytes may have less environmental concerns and possibly lower production cost than vanadium electrolytes, while showing higher reversibility and energy density. Although the charge transfer kinetics of these molecules on simple electrodes such as glassy carbon can be readily acquired by classical methods, other methods are desired for studying them on carbon felt electrodes which are commonly used in industrial applications. Electrochemical Impedance Spectroscopy is considered to be an appropriate analytical measurement. However, it faces two challenges for deriving reliable kinetic data for two reasons: First, the complicated porous structure of the carbon felt electrode requires an adapted analytical model that differs from planer electrodes. Second, the very fast kinetics of the electrolyte ( $k_0 \sim 10^{-2} \text{ cm}\cdot\text{s}^{-1}$  on glassy carbon) result in very low impedance values. Here we present our work on the kinetic study of organic aqueous electrolytes developed in HIGREEW project by EIS, on glassy carbon as a first approach, and then on different commercial carbon felts. Apparent kinetic constant (normalized to the geometric surface area of the porous electrode) is derived by fitting the impedance spectra using equivalent circuit models as a first approach. Prospects of using more complex physical models from the literature are discussed.

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### References :

- [1] Carretero-Gonzalez, J. et al, "Highly water-soluble three-redox state organic dyes as bifunctional analytes", *Energy Environ. Sci.*, vol(9) (2016), 3521
- [2] Beh, E.S. et al, "Neutral pH Aqueous Organic–Organometallic Redox Flow Battery with Extremely High Capacity Retention", *ACS Energy Lett.*, vol(2) (2017), 639