



# Different charge storage mechanisms at some carbon electrodes in redox active electrolyte revealed by electrochemical impedance spectroscopy



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## ABSTRACT

Different charge storage mechanisms at some carbon electrodes in redox active electrolyte are distinguished by electrochemical impedance spectroscopy technique. Significance of monitoring capacitive impedance contribution(s) in distinguishing battery-like and pseudocapacitive charge storage mechanisms is predicted by impedance modelling and verified experimentally. Experimental verification is made by comparison of capacitive impedance contributions in impedance spectra of graphite vs. glassy carbon electrodes. Impedance measurements are made at the same potential values in the supporting H<sub>2</sub>SO<sub>4</sub> electrolyte and H<sub>2</sub>SO<sub>4</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> redox active electrolyte, respectively.

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## 1. Introduction

Presence of a redox couple in a supporting electrolyte has already been found valuable in the field of electrochemical capacitor, EC, and supercapacitor, SC devices [1–4]. Within this context of research, fast redox reaction coupled with high electrode capacitance(s) accomplished mostly by high surface-porous carbon electrodes, has been found advantageous for devices with improved charge storage capacities. Different redox systems have already been tested for such a purpose. Among them, Fe(CN)<sub>6</sub><sup>3-/4-</sup>, I<sup>-</sup>/I<sub>2</sub>, or quinone/hydroquinone, Q/HQ, are found useful, mostly due to proper formal redox potentials, high redox reaction rates, good solubilities and moderate stabilities of compounds [4–6]. It has already been pointed out that utility of an EC/SC electrode in redox active electrolyte is related to the type of involved charge storage mechanism [1,3,7]. Two types of charge storage mechanisms with different electrochemistry lying behind have generally been defined [7,8]. For the battery-like mechanism, the quantity of charge generated by redox reaction is stored by the amount of reactants in the bulk of electrolyte solution. In this case, the EC/SC electrode stores charges through a combined effect of high surface electrode capacitance and faradaic redox reaction. For

the pseudocapacitive charge storage mechanism, however, the amount of charge generated by faradaic redox reaction is manifested as additional enhancement of electrode capacitance [3,7,8]. This phenomenon has already been explained in terms of either surface adsorption of redox species [3] or their retention at the electrode surface region by thin-layer electrochemistry, TLE, usually accomplished with highly porous electrodes [9,10]. Fast redox reaction at surface confined species with restricted mass transport makes the pseudocapacitive charge storage more beneficial for high power applications than the battery-like mechanism [1,3,10]. For evaluation of a charge storage mechanism, electrochemical techniques such as cyclic voltammetry and galvanostatic charging/discharging have usually been applied [3,7,11]. Electrochemical impedance spectroscopy technique [12], however, has been applied more sporadically, providing data focused mainly to the changes of electron transfer resistance values [5,6,13], what is generally insufficient for evaluation of any charge storage mechanism.

Herein the results of measurements, modelling and comparison of impedance spectra of different charge storage mechanisms at graphite and glassy-carbon electrodes in the supporting electrolyte containing potassium ferrocyanide will be presented. K<sub>4</sub>Fe(CN)<sub>6</sub> is the water soluble compound where negatively charged Fe(CN)<sub>6</sub><sup>4-</sup> complex ions generate one electron transfer oxidation/reduction reaction of the Fe(CN)<sub>6</sub><sup>3-/4-</sup> redox couple [14]:



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R-1 reaction is considered either like typical outer-sphere electron transfer reaction, inherently associated with fast electron transfer controlled by mass transport of redox active species toward/from the electrode surface [15–17], or slower reaction with suppressed electron transfer [18–20]. In both cases, the overall kinetics of R-1 can relatively easily be handled to derive the electrical impedance analogue, describing at the same time the battery-like charge storage in impedance terms. Electrical impedance analogue has to be modified for more complex R-1 that involves surface confined redox species corresponding to either TLE [9,10], adsorption of  $\text{Fe}(\text{CN})_6^{3-/4-}$  complex ions [3,11], or even some forms of adsorbed complexes such as ferri-ferrocyanide (Prussian Blue) generated by oxidation-reduction potential cycles [21,22]. In this case, the electrical impedance analogue must take into account the amount of surface confined redox species defining a pseudocapacitance. Thus modified impedance analogue has already been applied for some other systems with surface confined redox active species [23,24], but never in the context of pseudocapacitive charge storage mechanism at carbon electrodes in a redox active electrolyte.

## 2. Experimental

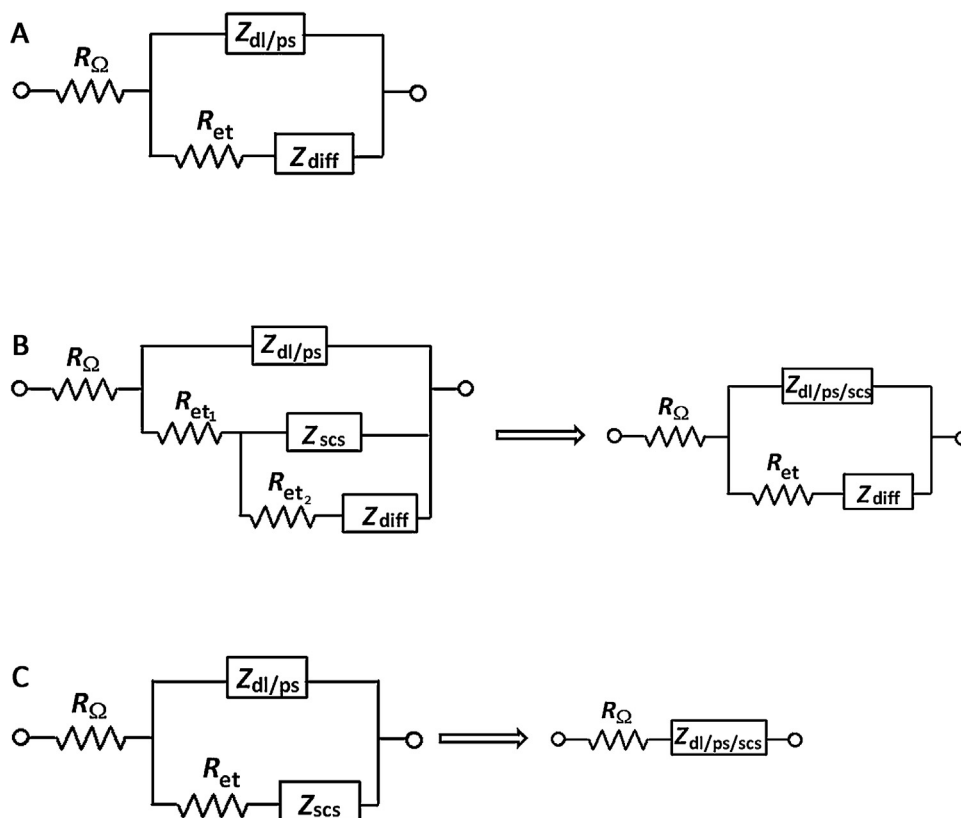
All experiments were performed in the conventional three-electrode cell (diameter of 6 cm and volume of 250 cm<sup>3</sup>). Glassy carbon, GC, standard electrode (EG&G, USA) and graphite, G, rod (Goodfellow, UK) embedded into glass tube (diameter of 0.6 cm) working electrodes were put vertically into the cell, exposing 0.03 cm<sup>2</sup> and 0.07 cm<sup>2</sup> of respective geometrical surfaces to electrolyte. High surface area (~20 cm<sup>2</sup>) platinum spiral in separate compartment and saturated calomel electrode, SCE, (Radiometer, Denmark) equipped with Haber-Luggin capillary and

a Pt wire pseudo-reference electrode [25] were used as the counter and reference electrode, respectively. All potentials,  $E$ , are reported with respect to the SCE.

Electrochemical experiments were carried in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich Inc.) (pH = 0.55) as the supporting electrolyte. Balanced quantities of K<sub>4</sub>Fe(CN)<sub>6</sub> × 3H<sub>2</sub>O (Sigma-Aldrich Inc.) were added directly into supporting electrolyte to give the final concentration of 5 × 10<sup>-3</sup> mol dm<sup>-3</sup>. Always freshly prepared redox active electrolyte solutions of low K<sub>4</sub>Fe(CN)<sub>6</sub>/H<sub>2</sub>SO<sub>4</sub> ratio were used in an order to suppress formation of Fe<sub>3</sub><sup>III</sup>[Fe<sup>III</sup>(CN)<sub>6</sub>]<sub>3</sub> and/or free Fe<sup>3+</sup> ions, necessary for generation of Prussian Blue, Fe<sub>4</sub><sup>III</sup>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sub>3</sub>, and similar hexacyanoferrate complexes [21,22]. High-purity water with resistivity of 18 × 10<sup>6</sup> Ω cm was used for all solution preparations.

Working electrode surfaces were hand-polished, sonicated in ultrapure water and slightly electrochemically pre-conditioned in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. Ten potential cycles between -0.30 and 1.60 V were applied at the scan rate of 10 mV s<sup>-1</sup>, finishing always by the reduction step at -0.20 V [26,27]. All experiments were performed in non-stirred electrolyte solutions, at ambient temperature of (25 ± 2) °C and oxygen free atmosphere maintained by blowing nitrogen through electrolyte solution for 30 min prior measurements.

Impedance spectroscopy, EIS, data were recorded at different fixed bias potentials using 1255B FRA and 1287 ECI (Solartron Analytical, UK) under the Z<sub>plot</sub> software (Scribner Associates Inc.) control. Sine wave  $ac$  signal of 10 mV amplitude, frequency,  $f$ , ranged between 10<sup>5</sup> and 0.02 Hz and 10 frequency points measured per decade were applied. For impedance data fittings, the complex non-linear least squares, CNLS, program of Z<sub>view</sub> software (Scribner Associates Inc.) in the impedance modulus weighting mode and appropriate electrical equivalent circuits were used. Contributions



**Fig. 1.** EECs for an electrode showing A) battery-like; B) pseudocapacitive in combination with battery-like; C) pseudocapacitive charge storage mechanisms. Definitions of elements are given in the text.

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