



Determining Electron Transfer Kinetics at Porous Electrodes



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ABSTRACT

Porous carbon materials are of tremendous importance for electrochemical energy storage. Their low cost, wide potential window and high surface area make them ideal electrodes for many applications. The activity of the electrode towards a certain reaction is given by both the available wetted surface area and the electron transfer constant k_0 . The present study investigates which electrochemical methods are suitable to determine k_0 on porous carbon electrodes. For this purpose, we investigate the ferric/ferrous redox couple on a porous carbon nanotube electrode as model system. We show that results from cyclic voltammetry (CV) can yield an apparent catalytic effect and elucidate its origin. Chronoamperometry and electrochemical impedance spectroscopy are shown to produce consistent values for the exchange current density I_0 , which can then be normalized to k_0 . Limitations of both methods in terms of k_0 and diffusion constants are discussed.

The gathered insights in terms of validity of methods on porous electrodes are harnessed to review the recent literature on the vanadium redox reactions. Reported k_0 values spread over four orders of magnitude and there is no consensus on the influence of heat- or acid-treatment on the kinetics. Taking into account the difficulties of CVs on porous electrodes we conclude that reasonable values for the vanadium reactions are $k_0 < 1.210^{-4} \text{ cm s}^{-1}$ and that oxidation of the samples increases surface area, catalyzes the V^{2+}/V^{3+} redox reaction but impedes the VO^{2+}/VO_2^+ redox reaction.

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1. Introduction

Porous carbon electrodes are ubiquitous in energy storage applications due to their high surface area (500–2000 m²/g) [1]. They are employed as electrodes in supercapacitors as the capacitance increases (mostly) linearly with the surface area A accessible to electrolyte ions [2]. In applications for which electron transfer is important, e.g. batteries or fuel cells, a high surface area A decreases the required current density j to achieve a current I and therefore reduces charge transfer overpotentials. Other advantages of porous carbon electrodes “include low cost, wide potential window, relatively inert electrochemistry, electrocatalytic activity for a variety of redox reactions” [3].

To increase the current that can be obtained from a battery electrode or fuel cell one has two options, either to increase the surface area A or to increase the exchange current density j_0 . Enhancing j_0 is equivalent to increasing the catalytic activity of an electrode towards a reaction (or partial reaction) [4–7]. To assess

whether a certain electrode composition, the size or dispersion of catalyst particles, the coordination of surface atoms or the substrate improve the catalytic activity of an electrode, j_0 has to be determined unambiguously.

Electrochemical experiments, however, always yield the exchange current I_0 , which is the product of A and j_0 . Therefore, in order to determine either A or j_0 , the other one has to be known.

On noble metal electrodes used for fuel cells there a number of experimental methods to determine the electrochemical active surface area A [8,9]: H₂ adsorption and desorption and CO and Ag deposition.

For high surface area carbons the gases typically chosen for adsorption studies are N₂ or CO₂ [10]. Watt-Smith et al. found a good correlation between the surface area A^{BET} determined from the Brunauer-Emmett-Teller (BET) method and values obtained from small-angle X-ray scattering for two out of three carbon samples with $A^{BET} \leq 796 \text{ m}^2 \text{ g}^{-1}$ [10]. Interaction of chemical species with the adsorbing gas led to complex surface layers and A^{BET} could not be determined for one of the samples [10]. For very high surface area carbons, from around $A^{BET} = 1000 \text{ m}^2 \text{ g}^{-1}$, the surface area accessible to the electrolyte becomes almost constant whereas A^{BET} can increase further [1]. As the size of molecular

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probes used in BET experiments (N_2 , CO_2) differs from the size of solvated ions in the electrolyte a discrepancy between A and A^{BET} is not surprising.

Another possibility to determine A is via the double layer capacitance C_{DL} and the specific capacitance of the electrode material c_{DL} [F/cm^2]. Values for c_{DL} are given in the literature ($<2 \mu F/cm^2$ for basal plane HOPG, $\sim 60 \mu F/cm^2$ for edge plane HOPG and $24\text{--}36 \mu F/cm^2$ for GC [3,11,12]) and can be used to determine A by dividing C_{DL} by c_{DL} . Two caveats exist to this method: First, the ratio between edge plane and basal plane might be unknown, and therefore the large difference between the two values makes a recalculation difficult. Second, the C_{DL} is potential dependent which is not considered in above literature values [13].

Microscopy techniques such as tapping mode atomic force microscopy [14] and scanning tunneling microscopy can be used to obtain an image of the electrode surface and then deduce the roughness from it [15], but these tools will not reveal the porosity of the bulk of the electrode interior.

Determination of I_0 on porous electrodes is also not a simple task. A number of studies showed that porosity alters electrochemical responses compared to flat model electrodes [16–22]. The planar diffusion model does not hold and it was stated that the electrode effectively does not have a constant active surface area A [21]. However, one could also argue that there is a dispersion of diffusion coefficients and this is responsible for the inapplicability of textbook electrochemical equations: The high surface area electrode material hinders diffusion of redox species from the bulk electrolyte into the pores. With distance from the outer electrolyte-electrode interface, deeper within the porous structure, the diffusion constants will decrease. Porosity might further influence the effective viscosity of electrolyte [23]. Therefore, to determine I_0 on porous electrodes, a measurement technique has to be chosen that has access to a time regime in which the redox species within the pores are not depleted yet and therefore diffusion plays a negligible role. In general, both the redox kinetics and the mass transport contribute to the overpotential for a given redox reaction. In practical electrochemical energy storage or conversion devices it is crucial to obtain reaction conditions under which both kinetics and mass transport are fast. However, the presented study only deals with the determination of the electron transfer constant k_0 in a time regime in which mass transport limitation is less important. For the combined treatment of both kinetics and mass-transport in electrochemical cells the reader is referred to other studies [24–30].

In this study, we will investigate a model system, the ferric/ferrous couple on a multi-walled carbon nanotube (MWCNT)-modified GC electrode, to obtain and compare values for I_0 from three different measurement techniques: Cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). Possible ways to obtain A and therefore j_0 and the electron transfer constant k_0 are discussed then. We will also present a method that normalizes the charge transfer resistance R_{CT} by the C_{DL} , both values are obtained from EIS [17].

With the insights obtained regarding the suitability of CV, CA and EIS for porous electrode materials we will review the recent literature on the kinetics of the vanadium redox reactions (V^{2+}/V^{3+} and VO^{2+}/VO_2^+). These two redox reactions are employed in the commercially important All-Vanadium Redox Flow Battery (VRB) [31,32] and are mostly investigated on porous electrodes. In the literature, k_0 values for these two redox reactions spread over four orders of magnitude (see Fig. 5) and we will review how these strongly deviating values were obtained [33–35]. The additional benefit when combining the study on the electrochemical techniques and the review on the vanadium redox reactions is that we will be able to show that this discrepancy in k_0 values can be explained by the selection of electrochemical techniques unsuitable for high surface area carbon electrodes.

2. Comparison of experimental methods to obtain kinetic information on porous electrodes

In this section, three electrochemical methods are compared. The working electrode is a porous MWCNT structure on glassy carbon and the redox system under investigation is $50 \text{ mM } Fe^{2+}$ and $50 \text{ mM } Fe^{3+}$ in $1 \text{ M } H_2SO_4$. For CV, CA and EIS the raw data will be presented and it will be discussed how the exchange current I_0 can be obtained from these measurements. After that I_0 will be converted to k_0 by estimating the surface area by using BET and the specific capacitance.

2.1. Experimental methods and materials

To generate porous electrodes MWCNTs NC3100 from Nanocyl were deposited onto glassy carbon electrodes as reported previously [17]. Variable amounts of MWCNTs were suspended in Hexane and ultrasonically dispersed. With a pipette $20 \mu\text{l}$ of this solution was then drop-cast onto glassy carbon facets and dried at

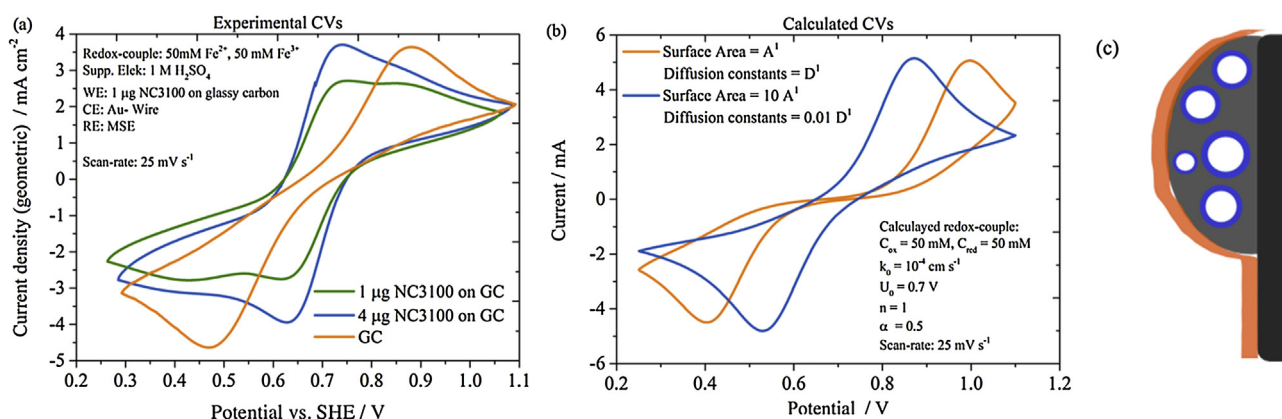


Fig. 1. Cyclic voltammograms of $50 \text{ mM } Fe^{2+}$ and $50 \text{ mM } Fe^{3+}$. (a) Experimental curves on a GC electrode (orange curve), GC electrode with $1 \mu\text{g}$ of MWCNTs (green curve) and $4 \mu\text{g}$ of MWCNTs (blue curve). (b) Calculated CVs for two systems. The surface area of system 2 (blue curve) is ten times higher and its diffusion coefficient is 100 times lower than that of system 1 (orange curve). All parameters are given in the graph. (c) Cartoon of a porous carbon structure on a flat electrode. The porous surface area that will have a small diffusion coefficient compared to the freely accessible electrode area (orange) is marked blue.

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