

Investigation of the Electron Transfer Kinetics of the $\text{VO}^{2+}/\text{VO}_2^+$ -reaction on Multi-Walled Carbon Nanotubes

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Introduction

The Vanadium Redox Flow Battery (VRB), invented and developed by Maria Skyllas-Kazacos and her co-workers at the University of New South Wales, represents one of the possible options for efficient energy storage [1]. However, one of the contemporary challenges of VRBs is their low power density and therefore catalysis of the redox reactions is desirable [2]. This work investigates the influence of surface functional groups attached to multi-walled carbon nanotubes (MWCNTs) on the heterogeneous electron transfer kinetics of the $\text{VO}^{2+}/\text{VO}_2^+$ - reaction.

Experimental

Since it is difficult to determine the charge transfer kinetics of mesoporous structures such as MWCNTs a new method is proposed in this study. Employing Electrochemical Impedance Spectroscopy (EIS), the double layer capacity C_{DL} and charge transfer resistance R_{CT} for varying amounts of MWCNTs on a glassy carbon (GC) disk electrode were determined. Both variables are functions of the electrochemical interface area and a plot of R_{CT}^{-1} vs. C_{DL} is proportional to the exchange current density j_0 . Therefore it is possible to compare the charge transfer kinetics without knowing the electrode-electrolyte interface area, which is an inaccessible parameter for mesoporous structures.

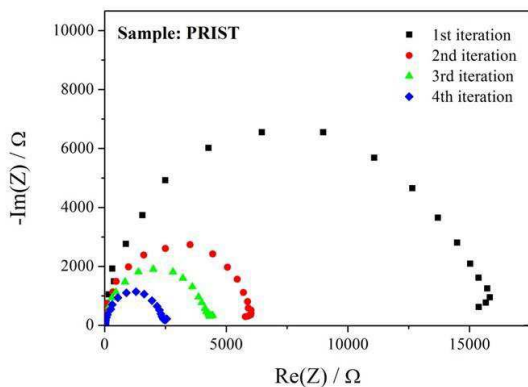


Figure 1: Impedance data for different coating thicknesses of the untreated Nanocyl 3100 MWCNT sample and the $\text{VO}^{2+}/\text{VO}_2^+$ redox system

The activity of untreated Nanocyl 3100 MWCNT (NC 3100) is compared to the performance of NC 3100 which were subjected to different treatments which increase or reduce the amount of surface functional groups. To validate the sensitivity of this method towards alteration of charge transfer kinetics caused by surface functional groups a suitable redox system, the ferrous/ferric electrode reaction, was also investigated. It is well known that this redox reaction is facilitated by oxygen containing surface functional groups [3].

All experiments are performed in a custom built three-electrode glass cell. The properties of the pristine and (de-) functionalized MWCNTs were determined by Fourier Transform Infrared Spectroscopy, Thermogravimetric Analysis coupled with Mass Spectroscopy and Raman Spectroscopy.

Results and Discussion

As can be seen in figure 1, which shows the Nyquist representation of EIS measurements of the $\text{VO}^{2+}/\text{VO}_2^+$ -redox reaction on pristine NC3100 MWCNTs, the amount of nanotubes under investigation changes the absolute values of C_{DL} and R_{CT} . Plotting R_{CT}^{-1} over C_{DL} yields a straight line, as seen in figure 2. The slope is proportional to j_0 .

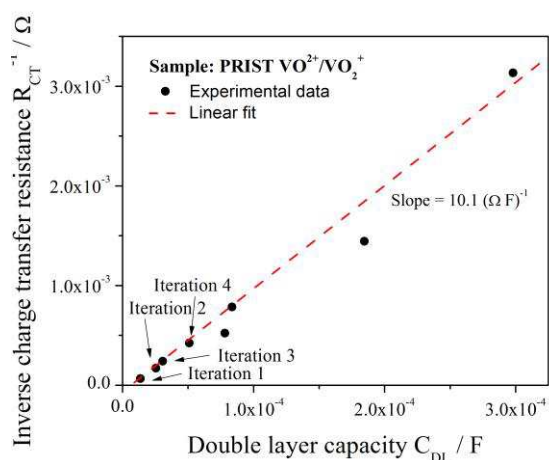


Figure 2: Inverse charge transfer resistance R_{CT}^{-1} vs. double layer capacity C_D for the sample PRIST obtained from EIS. The data points are fit linearly, the slope is $10.1 (\Omega F)^{-1}$. The iterations 1-4 which are shown in fig. 1 are marked.

The analysis of the slopes for the two redox systems and the different MWCNTs yields interesting results. While for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ - system heavily functionalized MWCNTs feature a j_0 which is more than 15 times higher than for thermally defunctionalized MWCNTs, the $\text{VO}^{2+}/\text{VO}_2^+$ - reaction is fastest on defunctionalized MWCNTs. With increasing amounts of surface functional groups the reaction becomes more sluggish. We will give an explanation for this unexpected behavior and discuss the applicability of this method to other electrode materials.

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