

The vanadium redox reactions – electrocatalysis versus non-electrocatalysis

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Abstract

Catalytic effects of surface groups on porous carbon electrodes are claimed in literature for the redox reactions V(II)/V(III) and V(IV)/V(V). The literature is critically analysed also in relation to work of this group. A method how to overcome the problem of assessing the electrochemically active surface area on porous electrodes is presented. Applying this method, no catalytic effects for above reactions can be substantiated. It is further pointed out that the parameters electrochemical potential and temperature need to be used to assess electrocatalysis.

1) Introduction

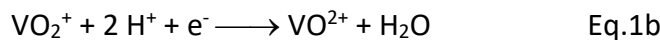
Electrocatalysis is one of the most important fields in electrochemistry since it decides if an electrochemical process is suitable for a technology development. Especially for energy related technologies electrochemical processes have clear advantages due to their generally sustainable nature. Electrochemical energy conversion can usually be performed with high efficiencies as compared to heat engine-based technologies, and it enables the use of non-carbon-based processes efficiently. In addition, energy storage as electricity is mostly based on electrochemical processes.

Because of the importance of energy science and technology today the enhancement of electrochemical processes is of high relevance and often results reported in literature claim catalytic effects. Where exactly does electrocatalysis come into play for e.g. energy storage? This paper will mainly focus on the redox flow battery (RFB) based on vanadium (VRFB). Since the work of Skyllas-Kazacos et al. [1, 2] a rapid increase in articles published on this topic has been observed. Special attention is obviously paid to the question of electrocatalysis based on possible effects of surface groups on the carbon felt electrodes on the kinetics of the vanadium redox reactions. This question is stimulated by the slow kinetics of both, the V(II)/V(III) and the V(IV)/V(V) reactions on the negative and the positive side of the VRFB, respectively.

The literature on this effect is reviewed under the aspect which electrocatalytic effects are reported, and what are the techniques the assessment of electrocatalysis is based on.

2) The kinetics of V(II)/V(III) and V(IV)/V(V) in literature

As pointed out above, the fact that the vanadium redox system, Eq.1, is technically important in the VRFB led to numerous investigations, specifically on possible catalytic effects of the carbon surface on the reaction rate [3-10].



In their seminal work McCreery et al. [11-13] investigated how different ways of pre-treating the carbon surface can influence the surface properties of carbon, either by changing the surface structural arrangement of the carbon atoms and/or the creation of functional groups. Both factors may influence the kinetics of the charge transfer reactions at such surfaces. So, an important task is to analyse the reaction rate of the vanadium redox reactions, both V(II)/V(III) and V(IV)/V(V) as a function of various kinds of surface treatment of carbon. Analysing the literature about previous results yields an obscure picture [14]. The rate constants of charge transfer, k_0 , of Eq.1a and 1b vary by orders of magnitude for different authors [3-10]. Even the influence of surface treatment can have opposite effects on the reaction rate. These results are shown in Fig.1. It seems that not only catalytic effects may be responsible for such a wide range of values of the rate constants. It can be noted from Fig.1 that for a given author the differences in rate constants between untreated, oxidised and reduced surfaces vary less than the results for the different authors. It is important to analyse the experimental procedure of pre-treating the electrode material, the surface condition of the electrode regarding porosity and the experimental techniques used to analyse the data. Such an analysis was done in [14]. It turns out that the porosity of the carbon surface and the way the reaction rate was evaluated have a significant impact on the value of the determined rate constant.

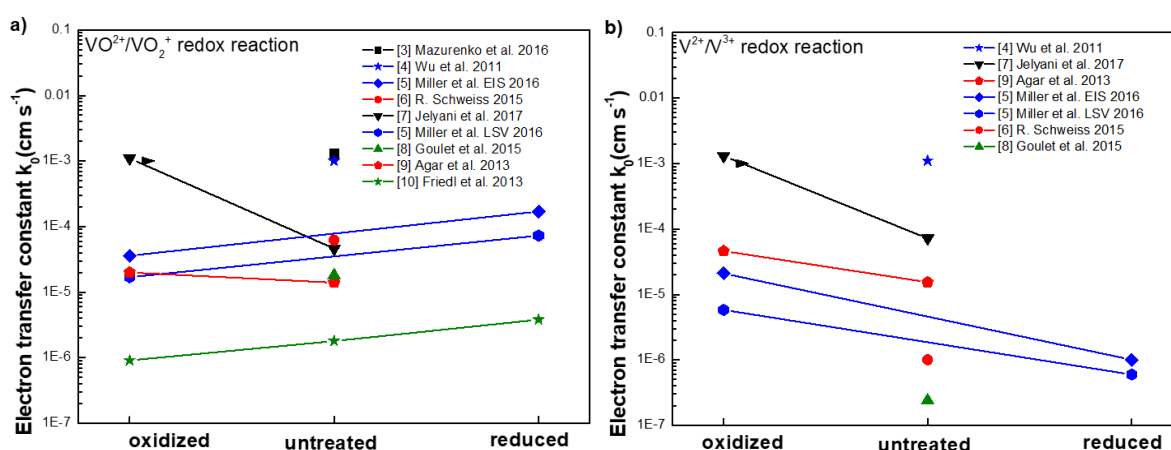


Fig.1. Electron transfer constants on various porous carbon electrodes for a) $\text{VO}_2^{+}/\text{VO}_2^{+}$ redox reaction and b) $\text{V}^{2+}/\text{V}^{3+}$ redox reaction [14].

A big factor is the accuracy of the determination of the electrochemically active surface area in porous electrodes. Usually, assumptions are made on the basis of BET surfaces, but the degree of hydrophilicity may vary considerably depending on the pre-treatment. This may

account for the large variation of the data in Fig.1. An additional point of consideration is that the active surface area may be a function of the current density that flows through the electrode; since the electrolytic pathway in the porous structure may vary considerably in size and consequently the Ohmic drop as a result, the overpotential for the reaction may be lower in pores with larger Ohmic drop yielding a lower current density. Some of these problems can be overcome with an approach using impedance spectroscopy and plotting the inverse of charge transfer resistance versus the double layer capacitance. The slope of such a plot is proportional to the exchange current density, j_0 [10]. Using Eq.2 one can calculate j_0 without any assumption regarding the active electrochemical surface area.

$$R_{CT}^{-1} = \frac{nF d_{DL}}{RT \epsilon_r \epsilon_0} j_0 C_{DL} \quad \text{Eq.2}$$

In Eq.2 R_{CT} is the charge transfer resistance, d_{DL} is the thickness of the double layer, j_0 is the exchange current density, and C_{DL} is the double layer capacitance.

For diluted electrolytes (i.e. ionic strengths below 0.01 mol dm^{-3}) d_{DL} can be estimated as three times the Debye length, which in turn can be calculated according to the Gouy-Chapman theory, as in Eq. 3 [15-16].

$$\kappa = (3.29 \times 10^7) z_i c^{1/2} \quad \text{Eq. 3}$$

Where $1/\kappa$ is the Debye length, z_i is the positive and negative ionic charge, and c is the bulk electrolyte concentration.

In concentrated electrolytes the double layer structure can be approximated with the Helmholtz model and d_{DL} can be estimated from the sizes of the solvent molecules and ionic species. For a detailed discussion of the structure of the electric double layer the reader is referred to standard textbooks such as [15-16].

Using EIS data from the slope of a R_{CT}^{-1} vs. C_{DL} plot one can calculate the current density which is unaffected by any ambiguity of the surface area. In such a way the values in Fig.1 for the data points of [10] were obtained. As can be seen from Fig.1 all other results yield a largely overestimated reaction rate.

3) The effect of functional groups on carbon on the charge transfer kinetics

Since the work of McCreery [11-13] the formation of surface groups is discussed as a source of catalysis of redox reactions, including V(II)/V(III). Solvated metal ions, such as Fe(II)/Fe(III) and V(II)/V(III) show a strong effect of the solvation shell upon charge transfer which expresses itself as a large solvent reorganisation energy, λ , which directly influences the reaction rate. Fig.2 illustrates this dependence and shows, e.g. for iron, how with increasing size of the ligands around the iron ion the solvent reorganisation energy decreases and the rate constant of the electron transfer reaction increases. The relation between the rate constant of the electron transfer k_{ET} can be approximated by Eq.4 [17].

$$k_{ET} \approx A \cdot \exp\left(-\frac{\lambda}{4 k_B T}\right) \quad \text{Eq.4}$$

In Eq.4 the pre-exponential factor, A , contains the electron frequency ν_n , λ is the solvent reorganization energy, and k_B is the Boltzmann constant. For the iron based redox couples it can be clearly seen the larger and stiffer the ligands become the smaller is the solvent reorganisation energy and thus the higher is the rate constant.

Because of the low rate constant of the metal ions that are only surrounded by solvent molecules, and not ligands, they are more prone for reaction pathways involving surface groups via a bridging mechanism. Thus, the results of McCreery do not come as a surprise. The question that remains is to which extend this understanding can be transferred to porous carbon surfaces. As pointed out above the assessment of the active surface area is a crucial point.

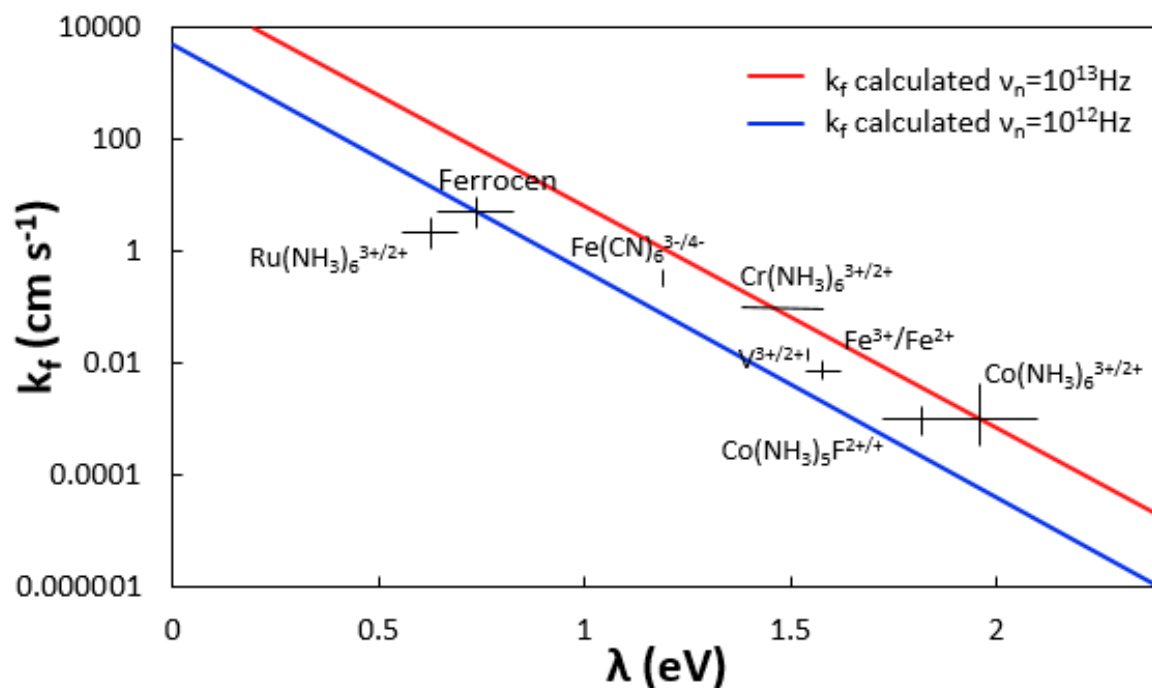


Fig.2. Rate constant vs. reorganisation energy for various redox reactions. ν_n denotes the electron frequency, the two values, indicated by the red and blue lines, illustrate the effect of which value is chosen.

Systematic experiments to evaluate the effect of surface treatment on the kinetics of the Fe(II)/Fe(III), the V(II)/V(III) and the V(IV)/V(V) reactions were performed using Eq.2 to determine the rate constants [10, 14]. In addition, it was evaluated which experimental techniques are suitable (or not) to determine reaction rates on porous surfaces [14].

Starting with the latter question cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were compared. An important result is that CV may suggest catalytic effects based on an analysis of the peak separation in the CV data which was deduced after pre-treatment of the carbon felts. It was clearly shown that the shape of CV curves is strongly influenced by the porosity of the surface but is not influenced by the charge transfer kinetics. This result confirms earlier work by Punckt et al. [18] who declared CV unsuitable for the determination of charge transfer kinetics on porous surfaces. On the other hand, using EIS gives the advantage to determine in one measurement charge transfer resistance and double layer capacity and use this data to determine the rate constant according to Eq.2, without any ambiguity regarding the electrochemically active surface area.

In a separate set of experiments CNT covered surfaces were subjected to oxidation and reduction and then rates of various redox systems were determined. The results were compared with the untreated carbon surface [10]. In addition, various kinds of pre-treatment were performed on CNTs, various degrees of oxidation and defunctionalisation (by heating at 1000 °C for 3 h in Ar) and then the rate of the redox reactions were compared to the pristine surface.

The results show that the surface treatment has quite different effects on the redox systems Fe(II)/Fe(III), V(IV)/V(V), and V(II)/V(III). For Fe(II)/Fe(III) the oxidative treatment of the carbon with a mixture of sulfuric and nitric acid yields the highest rate constant and the defunctionalised (clean) surface gives the lowest with the pristine (unaltered) surface being in between. For V(IV)/V(V) the opposite is observed, the defunctionalised surface of carbon gives the highest values [10]. Also, for V(II)/V(III) a similar situation was found: oxidising the carbon yields lower rate constants while the reduced surface shows the highest reactivity for the redox reaction. Another effect of the pre-treatment needs to be taken into account; the oxidative pre-treatment generates oxygen containing surface groups such as -OH, -CO and -CHO that increase the hydrophilicity of the carbon surface. So, the pre-treatment will increase the electrochemically active surface area and concurrently the current even at a given rate constant. This is not electrocatalysis - although it has been interpreted this way - but just a mere increase of the active surface area. Applying the EIS-based procedure described above (Eq.2) avoids this pitfall.

4) How strong is the evidence of electrocatalysis for the vanadium reaction?

While the results on the vanadium redox systems are quite contradictory if one reviews the literature, still a few conclusions can be drawn considering the specific aspects of the experiments. As stated above, redox systems with high solvent reorganisation energies can easily change their reaction path from outer-sphere to inner-sphere if suitable molecules on the electrode surface are available. The case of Fe(II)/Fe(III) clearly shows this [10]. As Fig.3a illustrates the highest rate constant for this redox reaction was observed when oxygen containing surface groups are present and the lowest for the reduced surface. It is also well known that even minute amounts of chloride enhance the rate of the redox reaction Fe(II)/Fe(III). On the other hand, for the vanadium based redox system this does not hold true although they have an equally large solvent reorganisation energy and thus low rate constants [10]. Fig.3b shows the highest rate for the reduced surface where no functional groups are present. There are effects of pre-treatment on the rate, but they seem to influence merely the hydrophilicity of the carbon, thus changing the electrochemically active surface area. For such a case the change of current should not be denoted as electrocatalysis. In addition, cyclic voltammetry is not suitable to investigate electron transfer reactions on porous electrodes, it leads to erroneous conclusions.

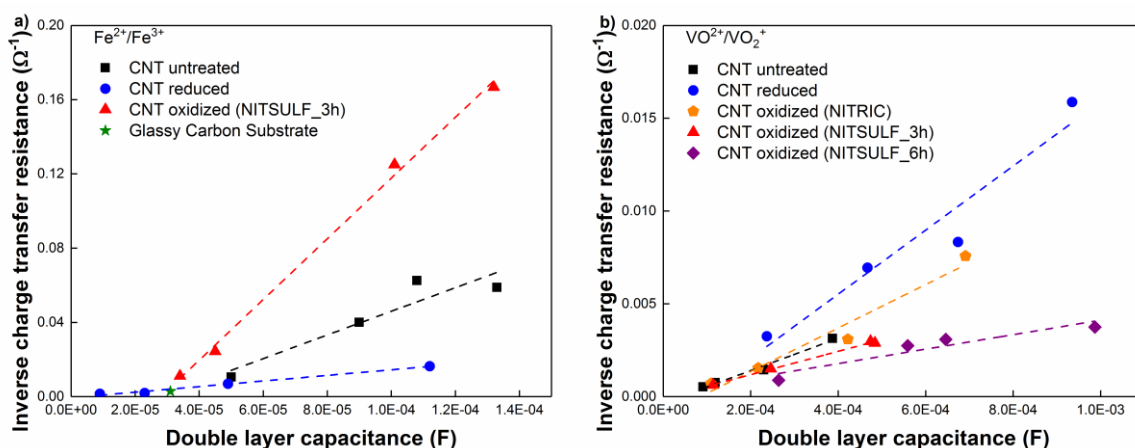


Fig.3. Inverse charge transfer resistance over double layer capacitance obtained from EIS for a) the Fe²⁺/Fe³⁺ and b) VO²⁺/VO₂⁺ redox reaction on CNT samples [10].

Table 1. Extracted slopes and electron transfer constant k_0 for the Fe²⁺/Fe³⁺ and VO²⁺/VO₂⁺ redox reaction on CNT samples [10].

Sample name	VO ²⁺ /VO ₂ ⁺	Fe ²⁺ /Fe ³⁺
	Slope (F ⁻¹ Ω ⁻¹)	Slope (F ⁻¹ Ω ⁻¹)
Untreated	8.1 ± 1.5	(8.1 ± 3.8) × 10 ²
Reduced	17.5 ± 2.8	(1.5 ± 0.26) × 10 ²
Oxidized (NITRIC)	7.8 ± 1.2	
Oxidized (NITSULF_3h)	6.2 ± 1.2	(18.3 ± 5.9) × 10 ²
Oxidized (NITSULF_6h)	4.2 ± 1.1	

However, an electrocatalytic effect can be described for the V(IV)/V(V) system which would rather be denoted as homogeneous catalysis. If one substitutes the base electrolyte of sulfuric acid for phosphoric acid the reaction is enhanced by about one order of magnitude (Fig.4 and Table 2 [19]). It was suggested that the phosphate ion may form a complex that would have a higher rate constant [19]. Since the phosphate would not be consumed this could be considered a homogeneous catalytic effect of the phosphate. There is, however, no effect of phosphate on the reaction rate of the V(II)/V(III) reaction. As can be seen from Table 2 for a 1:1 mixture of sulphuric and phosphoric acid the rate constant takes an intermediate value.

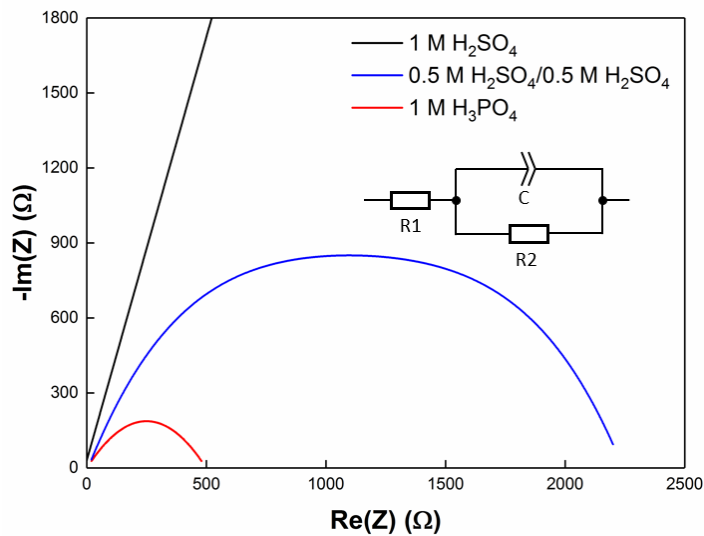


Fig.4. Nyquist representation of fitted impedance data for plot of 50 mM VO²⁺ and 50 mM VO₂⁺ in various electrolytes [19].

Table 2. Fitted parameters of EIS of 50 mM VO²⁺ and 50 mM VO₂⁺ in various electrolytes [19].

	1M H ₃ PO ₄	1M H ₂ SO ₄	0.5M H ₂ SO ₄ /0.5M H ₃ PO ₄
R _{Ohm} /Ω m ²	7.8 × 10 ⁻⁵	1.2 × 10 ⁻⁵	5.0 × 10 ⁻⁵
R _{CT} /Ω m ²	8.8 × 10 ⁻⁴	6.0 × 10 ⁻²	4.4 × 10 ⁻³
α	0.824	0.856	0.858
Q/Fs ^(α-1)	5.7 × 10 ⁻⁶	3.6 × 10 ⁻⁶	3.6 × 10 ⁻⁶
C _{DL} /F	4.4 × 10 ⁻⁷	4.3 × 10 ⁻⁷	4.6 × 10 ⁻⁷
j ₀ /A m ⁻²	29.3	0.44	5.87
k ₀ /cm s ⁻¹	6.1 × 10 ⁻⁴	9.2 × 10 ⁻⁶	1.2 × 10 ⁻⁴

5) What is important about electrocatalysis

The common view of catalysis is that the catalyst, in homogenous and heterogeneous catalysis, lowers the activation barrier for a reaction but is not consumed in the reaction. Considering the Eyring equation (Eq.5) catalysis would be given when the Gibbs Free energy of the activated complex, ΔG^\ddagger , is lowered. At the same time the pre-exponential factor, which describes the rate at infinitely high temperature, should be unaltered. ΔG^\ddagger can be split into an enthalpic and entropic part (see also below) which results in the temperature dependence of the rate only dependent on ΔH^\ddagger .

$$k = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad \text{Eq.5}$$

In Eq.5 κ is the transmission coefficient and the other quantities have their usual meanings.

In electrocatalysis the electrode potential and temperature are the main parameters that determine the reaction rate of an electrochemical reaction. So, the Gibbs Free energy of activation ΔG^\ddagger is a function of the electrode potential U (see. Eq.6) and both, the enthalpy of activation and the entropy of activation could possibly be potential dependent. The usual assumption, however, is that ΔS^\ddagger does not depend on the electrode potential and the electrochemical potential only affects ΔH^\ddagger . This can be verified by performing temperature dependent measurements from which using equation Eq.5. ΔH^\ddagger is evaluated as a function of electrode potential. This, unfortunately, is rarely done, often with the argument that the temperature range available in aqueous solutions allows a variation of temperature by only 30%. Such a small variation may increase the error of assessment but still gives valuable information on the fundamental question if ΔS^\ddagger is potential dependent. So, it can easily happen that a potential dependence of the current is associated with the activation energy, although entropic contributions influencing the pre-exponential factor can cause a potential dependence as well. Looking at the potential dependence of the current, the current density for a one-step, one-electron process can be described by the Butler-Volmer equation (Eq.6):

$$j = j_0 \cdot \left\{ \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta}{RT}\right) \right\} \quad \text{Eq.6}$$

with j , the current density, α_a and α_c the anodic and cathodic transfer coefficients, respectively and η , the overpotential given by $U - U_0$, the difference between the actual potential U and the equilibrium potential U_0 . Note that Eq.6 is only valid if there are no concentration changes due to the reaction.

According to Eqs.5 and 6 the transfer coefficient α is given by

$$\alpha = \partial \Delta G^\ddagger / \partial \eta \quad \text{Eq.7}$$

The transfer coefficient given by $\partial \Delta G^\ddagger / \partial \eta$ can be expanded to

$$\partial\Delta G^\ddagger/\partial\eta = \partial\Delta H^\ddagger/\partial\eta - T \partial\Delta S^\ddagger/\partial\eta \quad \text{Eq.8}$$

So, the change of the activation barrier ΔG^\ddagger can be seen from the transfer coefficient and its potential and temperature dependence.

In a semi-logarithmic plot of $\ln |j|$ vs. U , following Eq.6, the current-voltage curve should change slope with varying temperature for a constant α according to Eq.6. However, α can be temperature dependent if the entropic part of the Gibbs Free energy of activation is potential dependent. This can be evaluated from a temperature dependence of the current according to Eq.6.

Based on Eqs.7 and 8 one can define

$$\alpha = \alpha_H + T\alpha_S \quad \text{Eq.9}$$

The relative contributions of the enthalpic and the entropic part of the transfer coefficient can be determined from a plot of α vs. T . One can distinguish two limiting cases, α is T independent which means $\alpha = \alpha_H$ and α_S is zero or the curve $\alpha(T)$ is a straight line going through zero, then $\alpha = \alpha_S$ and α_H is zero. Any intermediate case is possible as well, where α_H is found at the condition $\alpha(T=0)$ and α_S is given by the temperature dependent portion (see Fig.5)

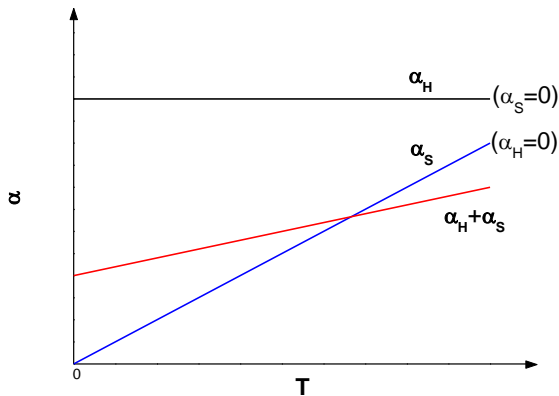


Fig.5. Relative contributions of the enthalpic and the entropic part of the transfer coefficient.

So, there are two different ways to evaluate experimental data of the temperature dependence of current-voltage curves. One can use plots according to Eq.5 and evaluate the potential dependence of the slope and the pre-exponential factor (see Fig.6, Fig.7, and Fig.8). In addition, one can use the temperature dependence of α according to Eq.9 to evaluate the enthalpic and entropic contribution to the transfer coefficient. Such a treatment of data of temperature dependent electrochemical reactions has been described in literature [20-23].

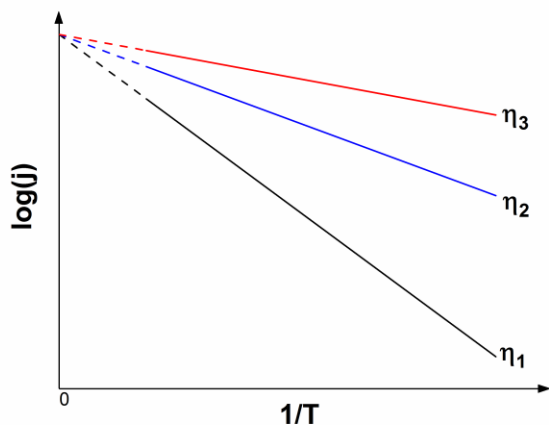


Fig.6. Contribution only from $\partial\Delta H^\ddagger/\partial\eta$.

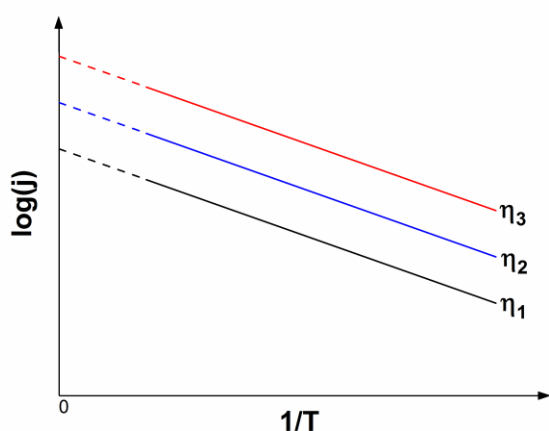


Fig.7. Contribution only from $\partial\Delta S^\ddagger/\partial\eta$.

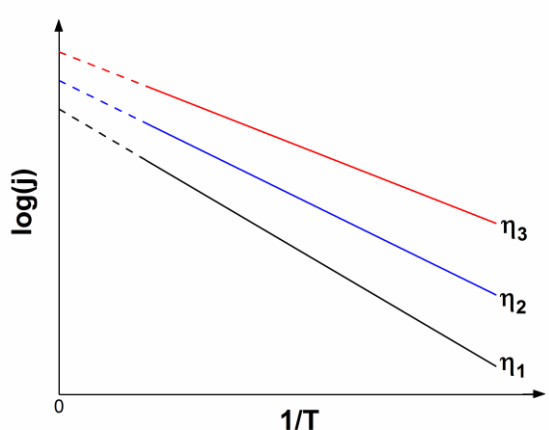


Fig.8. Contribution from both $\partial\Delta H^\ddagger/\partial\eta$ and $\partial\Delta S^\ddagger/\partial\eta$.

The above discussion illustrates that the main parameter determining the rate of an electrochemical reaction is the Gibbs free enthalpy of activation, ΔG^\ddagger , in contrast to ΔH^\ddagger for e.g. a heterogeneous surface reaction. This would suggest to clearly define electrocatalysis as the “lowering the activation barrier, ΔG^\ddagger , in an electrochemical reaction” where, in fact, the lowering of ΔG^\ddagger can result from a change in ΔH^\ddagger and/or ΔS^\ddagger . An analysis according to the

above-discussed procedures would pin down which quantity is responsible for the lowering of ΔG^\ddagger that may allow for a better interpretation of the electrocatalytic effect.

Coming back to the vanadium redox system the differences of evaluated rates by the different authors is rather due to in-adequate consideration of the active surface area of the porous carbon and/or unsuitable electrochemical techniques for evaluating the kinetics at porous surfaces. In summary, a catalytic effect of functional groups on the carbon surface on the redox reaction V(II)/V(III) and V(IV)/V(V) is hard to argue for.

Conclusions

Using the example of the redox reactions V(II)/V(III) and V(IV)/V(V) the literature was analysed regarding possible catalytic effects of functional groups on carbon electrodes. The conclusion was that no electrocatalysis of either of these reactions can be confirmed. In more general terms, the criteria for electrocatalysis were described. Experimentally, an investigation should contain both, measurements of the potential dependence and the temperature dependence since the main parameter in electrocatalysis is the lowering of ΔG^\ddagger . Only then, the respective influence of ΔH^\ddagger and ΔS^\ddagger can be assessed.

Acknowledgments

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Keywords

charge transfer kinetics, electrocatalysis, porous carbon electrodes, temperature dependence, vanadium redox reactions

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