



Kinetic studies at carbon felt electrodes for vanadium redox-flow batteries under controlled transfer current density conditions



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ABSTRACT

In this work we present a combination of mathematical modeling and experimental kinetic characterization of carbon felt electrodes in positive electrolyte (PE) and negative electrolyte (NE) of vanadium redox-flow batteries. The mathematical model is applied to check for homogeneous transfer current density within a radially connected carbon electrode intensively flown through by the electrolyte. Transfer current homogeneity depends mainly on electrolyte conductivity, electrode thickness and charge transfer coefficient. The transfer current inhomogeneity of the investigated electrode samples is below 5%, when single layers of carbon electrodes (415 μm thickness at 89% porosity and 210 μm thickness at 75% porosity) are applied and high electrolyte conductivities ($>800 \text{ mS}\cdot\text{cm}^{-1}$) are maintained by low vanadium concentrations ($<15 \text{ mM}$). Experimental results show charge transfer coefficients for high overpotentials of 0.26 ± 0.03 for the reduction reaction in NE and 0.37 ± 0.04 for the oxidation reaction in NE. The charge transfer coefficients of the PE are 0.13 ± 0.02 for reduction and 0.30 ± 0.04 for the oxidation reaction. Application of the Butler-Volmer equation to describe the polarization behavior shows adequate agreement with the experimental results at states of charge between 25% and 75%. The rate constants for the PE reaction are nearly two times higher than for the NE reaction.

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1. Introduction

Vanadium redox-flow batteries (VRFB) might be an attractive energy storage technology, due to their long cycle life and high energy efficiencies. Further development is vital to increase the power density of the cells and to yield lower power specific costs of the system. Development in the area of cell design and cell setup deals with the improvement of the three main components: the bipolar plate, the separator and the carbon felt.

The development of thin “zero-gap” cells lead to dramatic gain of the achievable power density of VRFBs, since they reduce ohmic resistance within the porous electrode significantly [1]. But the application of single layer carbon paper electrodes, instead of carbon felt electrodes, reduces the surface area as well. Thus, an optimum between thin electrodes with low ohmic potential drop and low surface area leading to high overpotential and thick

electrodes with high ohmic potential drop but high surface area that enables low overpotential [2,3] must be found. The optimized thickness is depending on the porosity, electrical conductivity and kinetic behavior of the carbon paper, giving rise to a need for precise information about the kinetic characteristics of the carbon paper.

The modeling of VRFBs is another important field, which is dependent on accurate kinetic data of carbon felt electrodes. Several models use assumed charge transfer coefficients $\alpha = 0.5$ for both half cell reactions [4–11]. Knehr et al. adjusted the coefficients in order to describe experimental results, but the obtained charge transfer coefficients still remained close to 0.5 [12]. This is in contrast to published data, especially for the positive half cell reaction, as can be seen from Table 2.

First characterization of the kinetics of the $\text{V}^{2+}/\text{V}^{3+}$ reaction (abbreviated as NE reaction) and the $\text{V}^{4+}/\text{V}^{5+}$ reaction (abbreviated as PE reaction) were performed by Skyllas-Kazacos group [13,14] using cyclic voltammetry with a stationary disc electrode for both reactions and a rotating disc electrode for the PE reaction only. These authors used glassy carbon as well as gold and platinum electrodes. Since only the glassy carbon electrode showed peak currents and because of its wider potential window without

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hydrogen or oxygen evolution, carbon electrodes were the recommended choice for vanadium redox-flow batteries. The charge transfer coefficient determined for the NE reaction was found to be 0.55 but had a large uncertainty (± 0.32). Further cyclic voltammetric studies were published by Kaneko et al. [15], who reported charge transfer coefficients of 0.30 to 0.35 for the reduction and 0.52 to 0.59 for the oxidation of the NE reaction. Instead of using cyclic voltammetry Fabjan et al. [16] performed polarization curve measurements on a smooth surface composite electrode in a usual three electrode assembly under vigorous stirring for sufficient mass transport. Orij et al. [17] applied potential step experiments on a glassy carbon electrode to overcome mass transport resistances, but their results allowed determining charge transfer coefficients for the NE reaction only. Gattrell et al. [18,19] studied the PE reaction at a rotating disk electrode and reported very high Tafel slopes of 350–450 mV per decade (corresponding to values of 0.13 to 0.17 for the charge transfer coefficient) for the V^{5+} reduction at high overpotentials. Aaron et al. measured the NE kinetics in situ [20] by applying a dynamic hydrogen reference electrode within a VRFB, that operated with a diluted electrolyte of only 0.1 M vanadium in 5 M sulfuric acid. The high exchange current density for the PE reaction lead to small overpotentials for the PE electrode. Therefore, no linear behavior in the Tafel plot could be observed and no charge transfer coefficient could be estimated for this reaction. Agar et al. [21] performed cyclic voltammetry on untreated and heat treated carbon felt electrodes. Since no reduction peak current density was obtained for the NE reaction at untreated electrodes, no evaluation for the NE reduction was possible. Wang et al. [22] performed polarization curves on glassy carbon and pyrolytic graphite rotating disk electrodes to investigate the oxidation of V^{4+} . Additionally they investigated the reduction of V^{5+} [23] and found charge transfer coefficients for cathodic and anodic PE reaction that were comparable to the results published by Gattrell et al. [18,19].

The resulting charge transfer coefficients for the NE and PE reaction are summarized in Tables 1 and 2. The data show a broad variation, probably due to the different methods and different carbon materials applied for characterization. Characterization of porous carbon felt and carbon paper electrodes would be advantageous instead of planar glassy carbon or pyrolytic graphite electrodes, since only the porous electrodes are applied in VRFBs. However, Goulet et al. argued [24] that typical characterization methods as cyclic voltammetry or Tafel analysis on rotating disk electrodes suffer from diffusion limitations if porous electrodes are employed. In situ methods might overcome this problem, but asymmetric exchange current densities impede sufficiently high overpotentials to determine Tafel slopes for the PE reaction. Goulet et al. [24] published a method for direct measurements of the

Table 2

Published charge transfer coefficients for the PE reaction.

	α_{cat}	α_{an}	Electrode	Method	Ref
PE	0.33–0.39		composite electrode	polarization curve	[16]
PE	0.13	0.42	glassy carbon	polarization curve	[18,19]
PE	0.23	0.23	raw carbon felt	cyclic voltammetry	[21]
PE	0.14	0.13	heat treated carbon felt	cyclic voltammetry	[21]
PE		0.53	graphite	polarization curve	[22]
PE	<0.15		pyrolytic graphite	polarization curve	[23]
PE	>0.14	0.32	carbon paper	polarization curve	[24]

reaction kinetics on porous electrodes utilizing a flow through setup. They performed experiments with a Toray carbon paper electrode placed within a microfluidic electrochemical cell. Flow velocities as high as $0.1 \text{ m}\cdot\text{s}^{-1}$ should enhance the mass transfer, so that only kinetic effects would dominate the charge transfer. This technique offers the possibility to determine exchange current densities and charge transfer coefficients at constant operation conditions (state of charge, flow rate) for both NE and PE reaction. However, the Tafel slopes for the PE reaction did not reach a constant value independent of the flow rate. Therefore Goulet et al. [24] stated that further development is required to quantify the influence of the electrode dimensions, which might cause edge effects.

In this work, we present a model to describe the liquid and solid phase potential distribution as well as the transfer current density distribution within a porous electrode. The model is used to quantify the effects of different kinetic parameters, electrolyte conductivities, electrode resistivities and dimensions on the homogeneity of transfer current density. The results are applied to an experimental setup and two different carbon electrodes are characterized at different states of charge (SoC). The kinetic parameters of these materials are then determined at carefully controlled conditions.

2. Experimental

2.1. Materials

The investigated carbon electrodes were SIGRACET[®] GDL10AA carbon paper (SGL Carbon GmbH, Germany) and Freudenberg H2315 carbon felt (Freudenberg FCCT KG, Germany), which were used as received without any pretreatment. The initial electrolyte was a 1:1 mixture of V^{3+} and V^{4+} supported by GfE (Gesellschaft für Elektrometallurgie, Germany) with a total vanadium concentration of 1.6 M and a total sulfate concentration of 4 M. The electrolyte was charged within a conventional redox flow battery to a SoC of approximately 95%. The precise SoC of charged negative electrolyte

Table 1

Published charge transfer coefficients for the NE reaction.

	α_{cat}^a	α_{an}^b	Electrode	Method	Ref
NE	0.55 ± 0.32	$1 - \alpha_{cat}^a$	glassy carbon	cyclic voltammetry	[14]
NE	0.30–0.35	0.52–0.59	GRC ^c	cyclic voltammetry	[15]
NE	0.4	0.26	composite electrode	polarization curve	[16]
NE	0.50	0.43	glassy carbon	potential step	[17]
NE	0.30	0.29	carbon paper	full cell polarization ^d	[20]
NE		0.21	raw carbon felt	cyclic voltammetry	[21]
NE	0.26	0.31	heat treated carbon felt	cyclic voltammetry	[21]
NE	0.54	0.49	carbon paper	polarization curve	[24]

^a α_{cat} – cathodic charge transfer coefficient.

^b α_{an} – anodic charge transfer coefficient.

^c GRC – graphite reinforced carbon.

^d full cell polarization – polarization curves recorded in a working VRFB using dynamic hydrogen reference electrode to examine kinetic behavior.

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