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On charge percolation in slurry electrodes used in vanadium redox flow batteries

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A B S T R A C T

In vanadium redox flow battery systems porous carbon felts are commonly employed as electrodes inside the flow channel. Recently, slurry electrodes (or flow suspension electrodes) were introduced as a potentially viable electrode system. Such electrode systems are little understood so far. Mass, momentum and charge transfer phenomena co-occur, interactions with each other are nearly impossible to capture experimentally. We present a novel discrete model of the particulate phase combining theories from fluid dynamics, colloidal physics, and electrochemistry with a coupled CFD-DEM approach. The methodology allows to visualize local phenomena occurring during the charging of the battery and to compute the net current of the slurry electrode system. We demonstrate that an increasing particle volume fraction enables the formation of conducting networks in the flow electrode until a threshold is reached. Our study concludes, that the assumption of all particles participating in the charge transfer as assumed in pure CFD investigations is not necessarily valid.

1. Introduction

Vanadium redox flow batteries (VRBs) currently become the prominent technology of choice for long-term and large scale stationary electrical energy storage [1-6]. By now, multiple energy storage systems based on the vanadium redox flow battery have been introduced worldwide not only in research but for industrial applications [7]. State-of-the-art VRB commonly employ a static porous carbon felt in the flow channel in the form of a no-gap configuration to achieve a maximum contact area to the electrolyte [8,9]. However, the optimization of the active electrode surface area which directly correlates to the systems power output remains a challenge. Recently, we introduced a novel slurry electrode - or flow suspension electrode - within the VRB cell providing an independent dynamic electrode system [10].

Slurry electrodes comprise solid particles suspended in the electrolyte rather than of a static solid matrix between the current collector and the separator membrane. They have been introduced in multiple electrochemical systems such as Li-ion batteries [11], supercapacitors [12] and have attracted attention for capacitive deionization [13-16]. For the application as conducting electrodes, the ability to form a conductive percolating particle network has to be ensured [17]. The particles must maintain contact to the electrode, contact between each other and contact between particle and electrolyte. For the experimental investigation [18,19] and deconvolution of the many physical phenomena co-occurring during charge transfer, the translation of microscopic events into macroscopic behavior represents today's bottleneck in comprehension and design.

Computer-aided simulations are necessary to describe the fundamental charge transfer effects within the slurry electrodes. Current numerical investigations describe slurry electrodes by the mean field theory that is derived from Newman's model [20]. Here, the fluid flow phase and the particles are considered both as a single continuous phase by the Euler-Euler approach [21-23]. Profound knowledge of the particle movement and particle charge distribution is crucial for the verification of the charge transfer phenomena for slurry electrodes. Using the Euler-Euler approach, a detailed description of the single particle cannot be made. Hence, the Eulerian approach cannot realistically describe the percolation induced transition phenomena. Microscopic features of the charge transfer are insufficiently described. Another approach to model semisolid redox flow batteries in static mode by Monte Carlo-based mechanistic models was reported for Li-ion systems [24,25]. Here the particle dynamics (growing of the particles), the

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diffusive suspension dynamics (movement of the particles) and the electrochemical effects are investigated. However, in an all-vanadium redox flow battery with slurry electrodes the suspended particles are charge carriers only. The particle percolation and charge transfer effects are influenced by viscous flow. In this study, we extend the description beyond previously made studies by defining the multiphase flow not only by computational fluid dynamics (CFD). The description is extended by a coupled discrete element method (DEM) to describe the particle flow within the vanadium electrolyte including the electrical charge transfer between particles and current-collector.

This study proposes a novel discrete model of the particulate phase within the electrolyte based on an Euler-Lagrange approach with a coupled CFD-DEM concept to depict the percolation induced transition phenomena. Our approach combines theories from fluid dynamics, colloidal physics, and electrochemistry to investigate microscopic as well as macroscopic slurry electrode properties. We aim to visualize the charge transfer of the colloidal particles of the half cell and to compute the net current transferred via the particles in the suspension.

2. Modeling approach

2.1. CFD-DEM modeling

To describe the multiphase flow of moving conductive particles in a vanadium electrolyte flow field inside the Vanadium Redox Flow Battery, we apply a CFD-DEM approach (Computational Fluid Dynamics - Discrete Element Method). The properties of the particles are based on non-porous carbon. Therefore, we use the open source software CFDEM © which combines OpenFOAM © (CFD) and LIGGGHTS © (DEM). A coupling algorithm between fluid and particle phase determines the particles trajectories inside the vanadium electrolyte flow field. This procedure based on a momentum exchange between the liquid and the particulate phase. Further, a force and a momentum balance determine the interactions between the individual particles. We assume a simplified Newtonian model to determine the fluid viscosity. A more detailed description of the modeling approach is provided in the supplementary material.

2.2. Modeling the electrochemical half cell

A cell section maps the electrochemical half cell to minimize computational effort. The mapped domain is displayed in Fig. 1. The considered half cell is a rectangular channel with a dimension of 250 μm × 375 μm × 800 μm.

Slurry electrodes base on the principle of charging conductive particles [26] which are utilized for an electrochemical conversion. To describe the electrochemical processes of the VRB, the model combines charge transfer, charge storage, and a redox reaction. The charge transfer takes place during contact of particles with the current collector or among one another. We assume an instant charge transfer during the contact of surfaces. On contact between a particle with the current collector, we assume that the particle adopts the potential of the current collector. In case of a particle-particle contact, both particles adopt the arithmetic average of their potentials before the contact.

The conductive particles store electrical charge in the electrostatic double layer [27-29]. The double layer persists of a rigid part of counterions with capacitor-like behavior, also called the Stern layer, followed by a diffusive part obeying the laws of the Poisson-Boltzmann theory. VRB batteries usually contain a high molar concentration of electrolyte whereby the majority of counterions are located in the rigid part. This phenomenon is confirmed by the development of the double layer capacity [27,28]. Therefore, Eq. (1) derived from the model of the parallel plate capacitor [27,28,30]

$$\sigma = \frac{\epsilon_r \epsilon_0}{d_{HH}} \psi \tag{1}$$

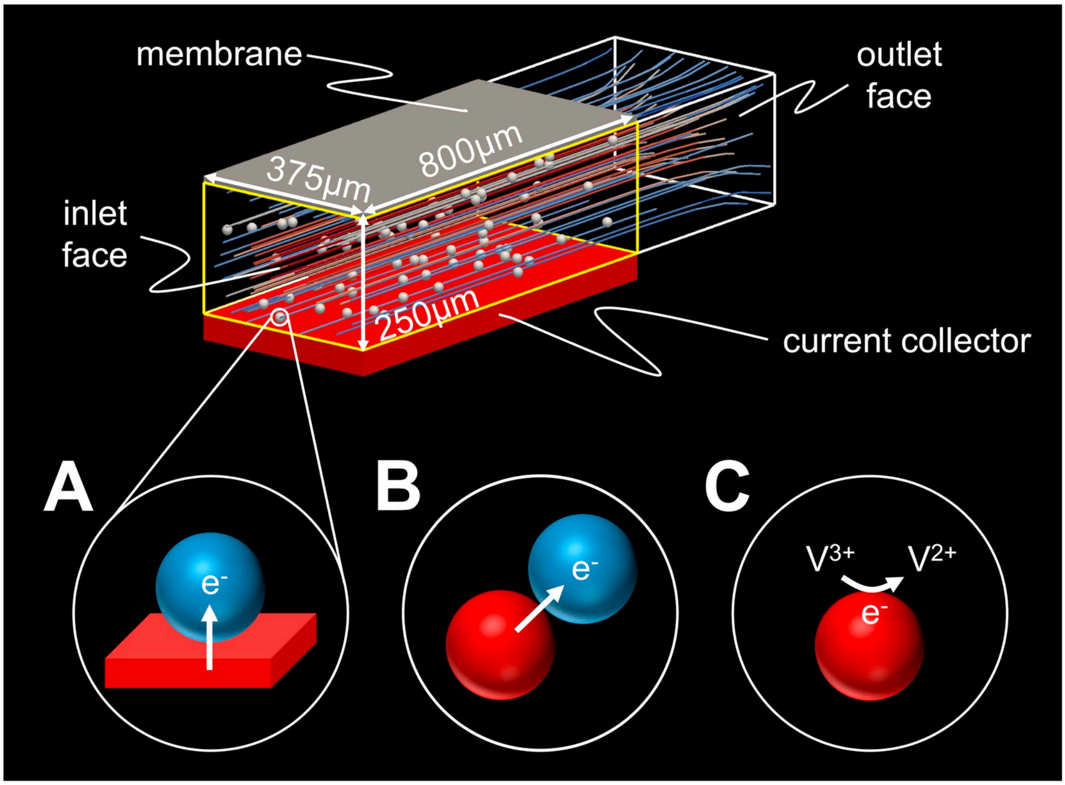

Fig. 1. The simulation domain of the slurry electrode particles in the vanadium redox flow battery, showing the contact and charge transfer phenomena (A) between particles and the current collector, (B) the particles themselves and (C) between the particles and the electrolyte. The stream lines in the simulation domain indicate the flow profile.

determines the correlation between charge and potential of the particles. Here, σ is the charge density of the considered body, ϵ_r the relative permittivity of the surrounding medium, ϵ_0 the electric constant, d_{HH} the size of the Stern layer and ψ the potential.

The redox pair V^{2+}/V^{3+} is utilized for charge operation. The modified Butler-Volmer equation describes the reaction kinetics in the electrochemical cell

$$i = A_s F k c_{II}^{\alpha_c} c_{III}^{\alpha_a} \left[\frac{c_{III}^S}{c_{III}} \exp\left(-\frac{\alpha_c F \eta}{RT}\right) - \frac{c_{II}^S}{c_{II}} \exp\left(\frac{\alpha_a F \eta}{RT}\right) \right] \tag{2}$$

where the Roman indices stand for the equivalent vanadium species and the exponent S denotes their concentration at the electrode surface, α is the charge transfer coefficient, F the Faraday constant and k the transfer rate. We assume the conductive particles as non-porous spheres. The active area A_s is the surface area of the particles. The overpotential η represents the potential difference between the inner electrode surface and the electrolyte concentration at its outer surface, which is non-zero due to excess concentration of ions. We assumed that the mass transfer of V-ions is much faster than the reaction kinetics leading to $\frac{c_i^S}{c_i} = 1$. The simulation parameters are listed in the supplementary material. Choosing a slurry electrode system influences the active surface area A_s and the overpotential η. Carbon particles are rough and incorporate a porous structure as opposed to ideal particles with a uniform spherical surface. Therefore, the active surface of those particles is larger. However, the mass transfer of ions into the porous structure of the particles limits the charge transfer. Additionally, the overpotential is influenced by the particle material properties. For further development of the model, the model has to incorporate mass transfer, ohmic resistances as well as contact resistances. Contact resistances may reduce the performance of the charging. The contact resistances are relatively low in the simulation domain used. This assumption is based on the relatively small dimensions of the simulated half cell. However, for a real half cell which is significantly larger, the contact resistances have to be considered.

2.3. Simulation settings

The performed simulations refer to the charging operation of the one-half cell at a constant state of charge (SoC). The potential of the current collector is modeled more negative than the potential of the electrolyte in accordance with the potentiostatic battery mode. Consequently, the particles are negatively charged when they collide with the current collector and transfer electrons to the electrolyte phase. The simulation is subdivided into homogeneous mesh elements with a size set to two times the particle diameter of the conducting particle for the calculation of the vanadium electrolyte flow. The no-slip condition is applied for the membrane and the electrode boundary. On the outlet face, the flow channel is virtually enlarged compared to the half cell in which all particles are located, whereby inlet effects are reduced, and a constant flow rate is ensured. The simulation conditions are summarized in the supplementary material.

At the initialization of the simulation, all particles are inserted at once in the half cell. The inlet and the outlet for the particles are selected as the periodic boundary where every particle leaving the domain reenters at the inlet. The particle's volume fraction was varied between $10 vol.\% - 35 vol.\%$ to analyze the percolation of particles. A $35 vol.\%$ particle volume fraction corresponds to a weight fraction of $20 wt.\%$ non-porous carbon particles. The corresponding experimental results are presented in our previous study by Percin et al. [10]. In cell operation, it is important to verify whether the volume fraction is above the percolation threshold and still flowable. In CFD studies it is generally assumed that both conditions are fulfilled. In the following, we present that the CFD-DEM model can verify this assumption.

Two distinct SoC of the vanadium electrolyte are evaluated with different particle volume fractions. Only distinct states are modeled due to the high computational effort. The symmetrical Butler-Volmer reaction kinetic describes the maximal and minimal impact of the SoC on the charging process at 2% and 50%, respectively.

3. Results & discussion

Simulations are performed to investigate the role of the conductive particles in the charging process of the battery half cell. Simulations mainly focus on the interplay between particle percolation and charge transfer and its effect on the current density. The question addressed here is the existence and the magnitude of a critical particle volume fraction at which the charge transfer rises disproportionately in a sigmoid-shaped trajectory indicating percolation.

Fig. 2 visualizes the charge distribution of the particles at 50% state of charge with 10, 20, 27.5 and $35 vol.\%$ particle volume fraction. The chosen images represent a characteristic time-step during the simulation. The complete charging behavior over time for each particle volume fraction is provided in Video format in the supplementary material. The Fig. 2 reveals a higher amount of charged particles with increasing particles concentration. At $10 vol.\%$ particle volume fraction, only particles in the vicinity of the current collector are charged. The majority of the particles do not contribute to the charge transfer in the cell. At $20 vol.\%$ particle volume fraction, a percolation network develops ranging from the current collector to the membrane. Due to the percolation network, particles from the current collector to the membrane of the half cell participate in the charge transfer. However, the majority of particles do not contribute to the charging process. A further increase in particle concentration leads to a transition. At $27.5 vol.\%$ and $35 vol.\%$ particle volume fraction, a multitude of percolation networks develop and the majority of particles passing through the channel are involved in the charging process.

In the following, the influence of the percolation on the charge transfer is analyzed. The current in the half cell is determined by summing over every particle the current according to the modified Butler-Volmer equation (cf. Eq. (2)). Fig. 3 A shows the net current of the suspension at $35 vol.\%$ particle volume fraction as a function of time. Initially, the current increases up to an almost asymptotic level. Due to the spontaneous formation and disintegration of the percolation networks, the current fluctuates in the half cell. Such microscopically observed fluctuation average out in real cell applications due to their bigger cell size. For further current density analysis, the current after 1 s of simulation is assumed to represent steady-state mode, and an average value is extracted over the rest of the simulation period. Peaks in the signal represent breakage of the large charged clusters. These events are fast, and the slurry electrodes percolate swiftly afterwards.

The average current is shown in Fig. 3 B as a function of the particle volume fraction (10, 20, 27.5 and $35 vol.\%$) for 2% and 50% state of charge. The sigmoidal shape of the current curves corresponds with the charge distribution of the particles shown in Fig. 2. At low particle volume fractions, only particles located at the current collector are charged leading to a small current. At higher particle volume fraction disproportionately more particles participate in the charge transfer due to the percolation leading to a significant increase in the current. After crossing the percolation threshold, percolation networks develop over the whole domain the current again increases slower with increasing particle volume fraction. We identify this transition effect as the percolation threshold for a slurry electrode with the current identifying the charge percolation. The threshold is observed at slightly lower particle volume fractions as for thresholds for 3D continuum models of spheres [31]. We asses this shift due to the presence of a flow field and the strong boundary effects within the small cell domain. The physical behavior resulting in the sudden increase of current is also observed

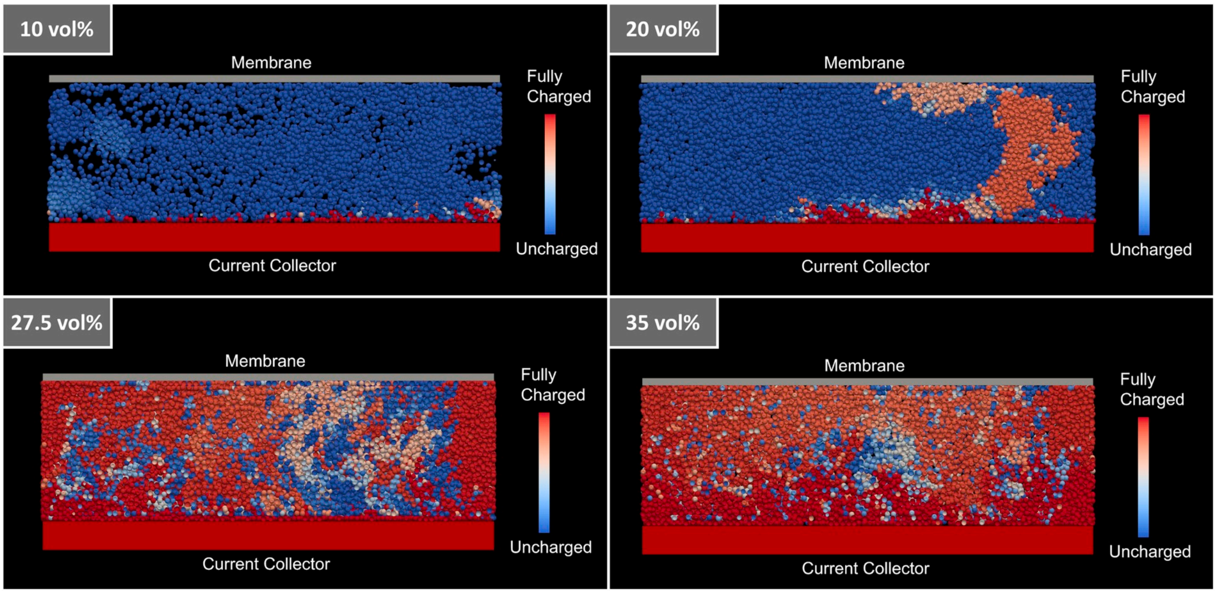

Fig. 2. Visualization of the charge distribution on the slurry electrode particles at 50% state of charge and 10, 20, 27.5 and 35*vol.%* particle volume fraction. The state of charge corresponds to the charge state of the vanadium electrolyte. The legend ranging from fully charged to uncharged corresponds to the charge of the individual slurry electrode particles. The images represent one characteristic time-step during cell operation. Visualized is a mid plane cross-section of the simulated domain.

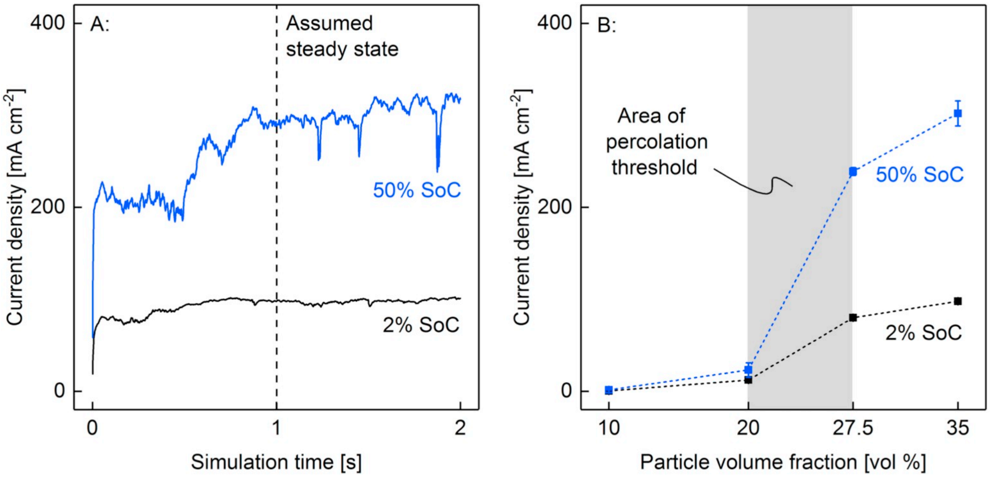

Fig. 3. Net currents based on the summation of the corresponding particle current flow, showing (A) the net currents of the slurry electrode at 35*vol.%* particle volume fraction at 2% and 50% state of charge (SoC) indicating the assumed steady state currents. In (B) the corresponding assumed steady state currents are averaged for the particle volume fraction 10, 20, 27.5 and 35*vol.%* indicating a percolation threshold. Crossing the percolation threshold, the active electrode area is significantly increased by the conducting particle network.

experimentally in our previous work by Percin et al. in 2018 [10]. The effect of charge percolation becomes more predominant with increasing state of charge due to the faster reaction kinetics. The symmetry of the Butler-Volmer indicates a decay after reaching 50*%SoC*. The presented results indicate interesting features for the slurry electrode processes: (a) Particle percolation networks strongly impact the charge transfer and (b) a critical percolation threshold between 20% and 27.5% in the slurry electrode system. The existence and importance of a charge percolation threshold in a slurry electrode system were recently demonstrated by our working group [32]. The modeling approach presented here enables a detailed insight into charge percolation phenomena.

So far, the model describes two distinct state of charges of the battery operation with different volume fractions of particles. Hereby, we qualitatively assess the effect of the particle percolation on the battery operation in a small section of the electrochemical cell. Due to the extensive computational effort of solving the model, a number of simplifications were made. Beyond the microscopic details discussed in this communication, the presented methodology also motivates further detailed studies on questions such as

- How does network break-up and percolation depend on process properties?
- How does the shape and size distribution of the conducting particles influence the cell operation?
- How do the mass transfer limitations influence the charging process when considering porous particles?
- Do contact resistances limit the up-scaling of the electrode system?
- What is the particle charge distribution in galvanostatic operations?

4. Conclusion

Slurry electrode systems present potential enhancements within a vanadium redox flow battery cell. This study evaluates the microscopic events during charge transfer responsible for the macroscopic charging during operation. The formation of conductive particle percolation networks is analyzed. Contrary to mean field theories, with the discrete description of the particle behavior the simulations reveal that an increasing particle volume fraction favor percolation networks which strongly impact the charge transfer. With increasing particle volume fraction there exists a critical percolation threshold in the slurry electrode system. Not all particles in the cell contribute to the charge transfer. This effect is especially crucial for experimental considerations. The increase in the number of particles leads to an increase in the viscosity of the suspension. Crossing the critical percolation threshold might lead to an unfeasible operation in an electrochemical cell. This study enables a systematic and closer look at the charge transfer phenomena of the slurry electrode. We presume that the assumption of a fully developed percolation in mean field approaches is not necessarily valid. The results suggest that percolation theory can be used directly in dimensioning of slurry electrode systems. The detailed view enhances the observation of physical particle interaction effects, which can be used in the development and understanding of this promising electrode system. This study can be easily adapted to other slurry electrode systems, such as flow capacitive deionization.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2019.02.013.

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