Particle based method and X-ray computed tomography for pore-scale flow characterization in VRFB electrodes

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ARTICLE INFO

ABSTRACT

Porous electrodes are pivotal components of Vanadium Redox Flow Batteries, which influence the power density, pressure drop losses, activation overpotentials, limit current density, bulk and contact resistance, and ohmic losses. The quantification of the fluid-mechanic efficiency of porous electrodes based on their real geometry is a useful measure, as it primarily affects the mass transport losses and the overall battery performances. Although several studies, both numerical and experimental, have been devoted to the electrode enhancement, most analyses are carried out under the simplifying assumption of linear, macrohomogeneous and isotropic behavior of the fluid mechanics in the porous material. We present an original approach built on the Lattice-Boltzmann Method and Lagrange Particle Tracking that makes use of pore-scale accurate geometrical data provided by X-ray computed tomography with the aim of studying the dispersion and reaction rates of liquid electrolyte reactants in the flow battery porous electrode. Following this methodology, we compare the fluid-dynamic performances provided by a commonly used carbon felt and an unconventional material, that is, a carbon vitrified foam. Surprisingly, results unveil the possibility of achieving higher fluid-mechanic efficiencies with the foam electrode, whose intrinsic microstructure promotes higher reaction rate.

1. Introduction

Stationary energy storage has a key role in the expansion of decarbonized renewable energy sources, which are typically intermittent, and of smart grids provided with distributed energy-management capability. Energy storage systems are required to provide a variety of services with response times ranging from milliseconds to minutes and discharge duration ranging from minutes to several hours. Seasonal storage implies the capability of preserving energy storage over some months with limited self-discharge. Electrochemical Energy Storage is the solution of choice for fast power quality services, for small power/energy ratings, and for the general distributed exploitation that is required in smart grids. In fact it has grown fast in last years, its rated power passing from 0.1 GW as of 2007 to 1, 7 GW as of 2017 [1]. Even if Lithium-ion batteries are presently the most successful technology in the stationary market, after gaining a dominant position in the portable electronics and electric mobility sectors, beyond-lithium forecasts indicate that Redox Flow Batteries (RFBs) will have a major boost for stationary energy storage in the next future [2].

They feature a unique combination of advantages including: very fast response times, of the order of millisecond in stand-by mode; independent sizing of power and energy allowing for discharges long at will; a single reversible device performing energy storage and delivery; good round-trip efficiency; and virtually no self-discharge in off-mode. The Vanadium RFB (VRFB), that is the only widely marketed version at present, presents extremely long calendar and cycle lives, in excess of 20 years and 20,000 cycles, respectively, thanks to the use of the same metal in the two electrodes, that prevents cross-contamination and limits membrane aging. However, VRFBs also suffer from some drawbacks which limit their present market competitiveness, notably low energy density, due to limited solubility of the electrolyte in the sulphuric acid solution, and low power density, related to the limited

current density generated in the electrodes. Industrial-size cells have average current densities much lower than top values obtained in experimental small-size single-cell devices.

1.1. Mass transport losses in VRFB

The main sources of losses in a VRFBs are electrochemical, ohmic and concentration polarizations. While the former two are significant at low current densities, the latter mainly affect the battery behavior at high current densities. Concentration polarization occurs since in the electrolyte diffusive mass transport ($\mathcal{D}_m \sim 10^{-3}$ mm^2/s) is much slower slower than momentum diffusivity ($\nu \sim 1$ mm^2/s) and the fluid-mechanic efficiency of the system is poor. The too-slow mass transport of reactants limits the battery current density. A proper design of the cell and porous microstructure can mitigate this technological issue. This work focuses on this important issue.

Two arrangements for distributing the solutions inside the electrodes are typically considered: the flow-through and the flow-by design. The former requires thick, highly porous and little compressed electrodes characterized by relatively high bulk and contact resistances [3]. Instead, in the latter, liquid electrolytes are distributed into thin paper electrodes from channels engraved in thicker current collectors which provide better contact resistance. Nevertheless, this solution typically shows poor electrochemical behavior and smaller active surface areas [4]. An extensive literature deals with flow field design documenting the much work done in order to increase the uniformity of the electrolyte distribution along the cell area, making use of alternative design concepts [5–7]. Typically, the aforementioned analyses adopt the macrohomogeneous porous electrode approach. In this view, permeability and diffusion in the porous electrode are modeled through homogeneous equivalent parameters, e.g. by means of the Bruggeman approximation. [8].

Even though such efforts have been rewarded with improved performances, few studies focus on the phenomena occurring at microscopic scales which are at the base of the VRFB fluid-dynamic efficiency. X-ray computed tomography (CT) was early used for investigating VRFB electrodes by Qiu et al. [9,10], who proposed a methodology for modeling the transport mechanisms of species and charge in the VRFB at the pore scale. They used CT data as geometry input for the flow field of electrolyte that was modeled using the Lattice-Boltzmann Method (LBM). Transport of species and charge was formulated by means of the finite volume method (FVM) with the Butler-Volmer equations which model the species and charges coupling at the active surface sites. They obtained local concentration, overpotentials, current density and cell voltage, finding a cell voltage increase with increasing electrolyte flow rate due to decreasing concentration gradients. Trogadas et al. [11] combined CT of voltage-cycled graphite felts, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) to capture the changes in felt structure and properties such as porosity, characteristic tortuosity and volume specific surface area, during operation. Jervis et al. [12] designed a miniature flow cell that allowed the use of CT to study carbon felt materials *in situ* and *operando*, in both lab-based and synchrotron CT. Their bespoke cell can be used to observe felt fibers, electrolyte and pore phases, enabling non-destructive characterization of an array of microstructural parameters during the operation.

However, to the best of our knowledge such diagnostic techniques where not yet used to compare effects and performances of different porous microstructures of real VRFB electrodes. In this paper we present an original approach that resorts to the Lattice-Boltzmann Method and Lagrange Particle Tracking and makes use of material geometry data obtained using a X-ray CT system to investigate the dispersion and reaction rates induced by different microstructure of the VRFB porous electrode. Through this technique we obtain a pore-scale non-homogeneous anisotropic analysis and parametrization of the flow filed inside

two different materials for VRFB electrodes: a commonly used carbon felt and a carbon vitrified foam. The surprising results of this analysis show that the foam microstructure induces higher dispersion and reaction rates which in turn can increase VRFB fluid-mechanic performances.

2. Methodology

The fluid-dynamic performance of porous electrodes strongly depends on the microstructure of the media. From an experimental point of view only global properties can be measured. Local flow features, e.g. electrolyte dispersion or velocity, are very difficult to measure since optical accesses through porous electrodes are difficult to use without altering the local geometry. Recent computational methods and resources open new perspectives in the detailed analysis of these devices. The procedure we propose aims to evaluate the performance of different porous electrode microstructures mixing state-of-the-art metrology and numerical simulation techniques.

In particular, we use X-ray CT to reconstruct the real microstructure of porous media, a Lattice-Boltzmann flow solver to simulate the microscopic flow behavior through the pores of the electrodes and a Lagrangian Particle Tracking method to evolve the electrolyte dispersion and reaction through the medium. The synergy of all these different competences is used to evaluate electrode performance at fixed pump power in terms of electrolyte dispersion and reaction rate in the limit of fast chemistry. The main advantage of the proposed methodology is a detailed characterization from microscopic to macroscopic properties of the media which is presently unfeasible with a pure experimental approach. In fact, by means of the present methodology, we are able to obtain: (i) a geometrical reconstruction of the electrode with high resolution that allows to capture the typical small length scale of the pores (the voxel size ~ 5 μm is one/two orders of magnitude smaller than the mean pore size diameter in VRFB electrodes, see e.g. [13]) and (ii) a full characterization of the electrolyte flow field at the same length scale (the LBM computational cell size corresponds to the X-ray CT voxel size). Each technique forming the procedure is described in one of the following sections.

2.1. X-ray computed tomography

Dispersion and reaction mechanisms in porous and/or fibrous media are connected to the specific material properties, including the internal configuration (i.e. spatial disposition and volume of interconnected pores and fiber orientation). In order to fully understand how such mechanisms can affect the performances of real electrodes of flow batteries, an analysis of the internal material characteristics should be conducted. However, analyzing non-accessible features is impossible with conventional methods. For example, internal porosity is commonly investigated by the Archimedes method, which measures only the percentage content of pores, or by optical analyses, which require destructive operations and are limited to few cut-sections [14]. Also the fiber orientation can be studied using destructive techniques from the geometry of elliptical cross-sectional shape of fibers, in correspondence to specific consequential cut-planes of the specimen [15].

An advanced technology capable of overcoming the limitations of the above mentioned methods is X-ray CT, which enables non-destructive analyses of both external and internal features [16,17]. In particular, material porosity can be evaluated in terms of spatial distribution, size and morphology [14] and the fiber orientation can be successfully assessed from CT data throughout the entire part [18]. Another advantage of CT is that soft and fragile parts, as the samples investigated in this paper, can be scanned without risks of damages or deformations. Furthermore, CT systems specifically developed for coordinate metrology are currently available to perform accurate measurements [19]. Given these features, X-ray CT has been already used for characterizing porous electrodes [9,10] but it has been never used for investigating innovative materials.