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Deconstructing three-dimensional (3D) structure of absorptive glass mat (AGM) separator to tailor pore dimensions and amplify electrolyte uptake

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ABSTRACT

Absorptive glass mat (AGM) separator is a vital technical component in valve regulated lead acid (VRLA) batteries that can be tailored for a desired application. To selectively design and tailor the AGM separator, the intricate three-dimensional (3D) structure needs to be unraveled. Herein, a toolkit of 3D analytical models of pore size distribution and electrolyte uptake expressed via wicking characteristics of AGM separators under unconfined and confined states is presented. 3D data of fiber orientation distributions obtained previously through X-ray micro-computed tomography (microCT) analysis are used as key set of input parameters. The predictive ability of pore size distribution model is assessed through the commonly used experimental set-up that usually apply high level of compressive stresses. Further, the existing analytical model of wicking characteristics of AGM separators has been extended to account for 3D characteristics, and subsequently, compared with the experimental results. A good agreement between the theory and experiments pave the way to simulate the realistic charge-discharge modes of the battery by applying cyclic loading condition. A threshold criterion describing the invariant behavior of pore size and wicking characteristics in terms of maximum permissible limit of key structural parameters during charge-discharge mode of the battery has also been proposed.

1. Introduction

Valve regulated lead acid (VRLA) battery has emerged as a key energy storage system that constitutes towards the largest part of the worldwide battery market share due to myriad of applications. Although, it is challenged by a large domain of other energy storage devices in terms of amount of energy stored, charge-discharge capacity, efficiency, durability characteristics, and cost [1]. To meet such a host of requirements, it becomes imperative to unravel the design aspects of key constituents of VRLA batteries. Absorptive glass mat (AGM) separator is the most important technical component in VRLA batteries with a view to fulfil the multi-functional requirements of separation of electrodes, retaining the electrolyte reliably, good contact force with the electrodes and easy transportation of H^+ ions and water molecules [2–4]. Majority of these requirements conform to the performance criteria of AGM separators pertaining to an effective gas and electrolyte transportation that essentially relies upon glass fiber properties, pore dimensions and degree of saturation or wicking characteristics [5]. In general, an AGM separator has a three-dimensional (3D) anisotropic structure both in terms of fiber alignment and pore dimensions [6,7]. Further, the pore morphology of AGM separators is analogous to that of thermoplastic nonwoven materials [5], which is deciphered by determining the differences in the entrance and exit pore dimensions, and often described as pore size distribution [8]. Some of the key experimental methods to determine the pore size distribution of an AGM separator are bubble point, liquid extrusion porometer and mercury intrusion methods [5,9]. These methods for determining pore size distribution alter the internal structure of a separator as a defined level of pressure is applied for quantifying the pore dimensions. Notably, the pore dimensions of an AGM separator are modulated with the applied pressure [7]. This means that the magnitudes of pore dimensions determined via these measurement techniques neither match with that of the pore sizes of an AGM separator in an unconfined state nor in the charge-discharge modes of the battery, indicating a departure from reality. On the other hand, various modeling approaches including capillary pressure, numerical, deterministic, stochastic and stereological or geometrical probability, have been applied to predict the pore size distribution of various types of nonwoven materials but not specifically intended for AGM separators [10–16]. Some of these modeling techniques are limited to two-dimensional (2D) random fiber networks

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[12,13,16], which do not match with the anisotropic characteristics of an AGM separator. Therefore, an analytical model of pore size distribution of 3D AGM separators is needed not only to simulate the realistic operating conditions within the battery but also directs us to relate with the key fiber and structural parameters to improve the state of art.

Pore dimensions play a pivotal role in the distribution of electrolyte within an AGM separator that effectively enables a stable electrode/electrolyte interface enhancing the overall cycle life [1]. Accordingly, small scale pores in the x-y plane of an AGM separator are primarily responsible for the distribution of electrolyte and inhibit acid stratification *whilst* larger pores assist in gas transportation via the z-direction to the negative plate [5,6,17,18]. The electrolyte movement between the separator and electrodes is normally assessed by wicking characteristics [5]. Classic Lucas-Washburn model [19,20] has been sporadically used for predicting the wicking behavior of AGM separators [3]. Recently, we have argued that the validity of the Lucas-Washburn model for AGM separators over longer time duration is questionable as the effect of gravity was not accounted in the original work [21]. However, Fries and Dreyer [22] approach included the effect of gravity and thus, successfully applied to predict the wicking characteristics of AGM separators [21]. The importance of gravity effect was also pointed out by Kamenev et al. [23] for computing the height and rate of capillary lift of the electrolyte through semi-analytical approach. Although, the realistic fiber and structural parameters (volume porosity, fiber orientation) of AGM separators have not been considered in the modeling approach. Ostensibly, the wicking characteristics of an AGM separator is dependent upon the structural parameters, wettability characteristics of fibers, and level of compression forces [5,24–26]. Specifically, the amount of compression forces should *ideally* conform to the level desired to simulate the charge and discharge capacity of battery which inevitably causes the separator to expand and compress, respectively [27]. Such charging and discharging of the battery alter the volume porosity and pore size characteristics of AGM separators leading to significant disparities in the saturation level of wicking heights [5]. Based upon the above listed gaps in the literature, analytical models of pore size distribution and wicking characteristics of AGM separators are required to be developed such that the 3D structural characteristics can be incorporated. Most importantly, the variations in pore size distribution and wicking characteristics should be simulated during the charging and discharging of the battery. To address these challenges, the presented work was designed to serve the multifaceted objectives such that the 3D analytical models of pore size distribution and wicking characteristics of AGM separators were proposed under unconfined and confined states. Here, the analytical models were combined with our recently developed model of compression-recovery behavior of AGM separators [28] to predict the pore size distribution and wicking characteristics under cyclic loading conditions in order to simulate the charging and discharging modes of the battery. To compare between the theory and experiments, 3D data of fiber orientation distributions have been obtained from X-ray microcomputed tomography (microCT) analysis, as determined in our previous work [28]. Through theoretical modeling, the maximum permissible limit of the structural parameters under cyclic loading conditions was also predicted beyond which the pore size distribution and wicking characteristics of AGM separators became invariant.

2. Theoretical framework

As aforementioned, an AGM separator has a 3D network of fibers that can result in an anisotropic structure both in terms of fiber alignment and pore dimensions [6,7]. Since, an AGM separator has similar structural characteristics as that of thermoplastic nonwoven materials [5]. Thus, our previously developed models of pore size distribution of nonwoven materials can be tailored for 3D AGM separators [8,29–31]. Using our recently developed model of compression-recovery characteristics [28], we also account for the cyclic loading conditions in order to simulate the charging and discharging of the battery. Accordingly, some of the key assumptions have been accounted for the development of theoretical framework in order to predict the pore size distribution of AGM separators.

1. In an AGM separator, the fibers are assumed as cylinders with centers of gravity uniformly distributed in a 3D system [32]. The cylinders have uniform geometrical properties in terms of length and diameter [29,32].
2. The AGM separator can be divided into elementary planes of equal thickness, and each of these planes exhibit identical fiber orientation distribution characteristics [13,29].
3. Glass fiber segments between the two consecutive contacts are considered to be straight entities with linearly elastic characteristics [4,17].
4. The properties of 3D AGM separator in any given direction are dependent upon the proportion of fibers involved in the corresponding direction such that the contribution of the air within the pore is neglected [33].

2.1. Pore size distribution of AGM separator

Typically, the alignment of fiber segment in a network such as an AGM separator can be represented by the in-plane (azimuthal) (φ) and out-of-plane (polar) (θ) orientation angles [32,34]. Based upon the spherical co-ordinate system, the probability of finding the fiber segment in the infinitesimally small range of angles, θ and $\theta + d\theta$, and φ and $\varphi + d\varphi$ is given by $\Omega(\theta, \varphi)\sin\theta d\theta d\varphi$, which is further constrained by the following normalization condition.

$$\int_0^\pi d\varphi \int_0^\pi \sin\theta\,\Omega(\theta, \varphi) d\theta = 1 \tag{1}$$

where $\Omega(\theta, \varphi)$ is a probability density function.

Suppose the fiber network of an AGM separator is sectioned by an imaginary arbitrary (secant) plane, whose normal is defined by an orientation (Θ, Φ), as shown in Fig. 1. Due to the anisotropic nature of the fiber segments in an AGM separator, the fiber cut-ends on the plane are projected as ellipses. The empty spaces in the form of apex circles, which are not occupied by the fibers are represented by pores. The variation in apex circle dimensions yields pore size distribution, which inevitably depends upon the total number of intersections of fibers on a unit area of the plane, $\upsilon(\Theta, \Phi)$, which is given by [32,34],

$$\upsilon(\Theta, \Phi) = \frac{L}{V} B(\Theta, \Phi);\ B(\Theta, \Phi) = \int_0^\pi d\theta \int_0^\pi d\varphi |\cos\Psi| \Omega(\theta, \varphi) \sin\theta \tag{2}$$

$$\text{where } \cos\Psi = |\sin\theta \sin\Theta \cos(\varphi - \Phi) + \cos\theta \cos\Theta| \tag{3}$$

where L is the total length of a fibers in a defined volume, V, and Ψ is the angle formed between the fiber and the sectioning plane directions, (θ, φ) and (Θ, Φ).

In a VRLA battery, the transportation of gas takes place in the z-direction, which is primarily dictated by thru-plane pores. This directs us to consider the arbitrary plane being aligned in a manner such that it is parallel to the in-plane direction, i.e. $\Theta = 0$, hence $\cos\Psi = |\cos\theta|$ using equation (3). Accordingly, equation (2) is simplified as shown below:

$$\upsilon(\Theta, \Phi) = \frac{L}{V} \int_0^\pi d\varphi \int_0^\pi |\cos\theta \sin\theta| \Omega(\theta, \varphi) d\theta \tag{4}$$

These planes consisting of defined intersections of fibers are collated to form a 3D model of an AGM separator. Here, the pores were assumed as circular discs or conduits with axes perpendicular to the plane. The sieving percolation theory thus allowed us to assume that the circular pores of diameter (d) followed gamma distribution [29]. Consequently,