Composite Structures 145 (2016) 113–118

Contents lists available at ScienceDirect

Composite Structures

journal homepage: www.elsevier.com/locate/compstruct

Development of a fluoroelastomer/glass fiber composite flow frame for a vanadium redox flow battery (VRFB)

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ARTICLE INFO

Article history:
Available online 27 February 2016

Keywords:
Vanadium redox flow battery (VRFB)
Flow frame (FF)
Fluoroelastomer composite
Gasket-less

ABSTRACT

The stack of a vanadium redox flow battery (VRFB), which is a promising energy storage system (ESS), is composed of flow frames (FFs), carbon felt electrodes, bipolar plates (BPs) and membranes. The components of VRFB are assembled and compacted using flat gaskets or O-rings to seal the highly concentrated vanadium sulfuric electrolyte. The reliable sealing of the stack is a crucial issue because the highly concentrated sulfuric acid will damage the system when it leaks.

In this work, a gasket-less FF composed of fluoroelastomer/glass fiber composite was developed to prevent leakage without using gaskets or O-rings. The fluoroelastomer layer, which has high chemical stability under an acidic environment, was formed at the surface of the composite, which worked as a sealant of the FF owing to its resilience. Glass fiber reinforcement into the matrix was employed to provide mechanical properties for use as a flow frame structure under the compaction pressure.

The surface treatment and fabrication methods for the fluoroelastomer/glass fiber composite were developed. Based on the measured mechanical properties and sealability test of the composite with respect to the curing conditions, the zero-leakage compaction pressure for the gasket-less FF was investigated.

1. Introduction

The energy storage system (ESS) is widely considered to be an effective approach to improve the reliability, power quality, and economy of renewable electrical energy. A vanadium redox flow battery (VRFB) is the most promising technology among the various ESSs such as lithium-ion, lead-acid, and supercapacitors [1]. VRFBs have several advantages including non-explosiveness, high energy efficiency, short response time, low self-discharge and a long lifetime. In addition, the most important advantage is that the power generation capacity and electricity storage capacity can be designed independently, which simplifies scale-up for large-scale ESS [2]. As shown in Fig. 1, a unit cell of VRFB consists of electrodes, an ion exchange membrane, bipolar plates (BPs) and positive and negative electrolytes circulated by pumps. The energy conversion between the chemical potential of vanadium electrolytes and electrical energy occurs at the electrodes when liquid electrolytes are flowing through the cell.

Because VRFBs are operated by the viscous flows of strong sulfuric acid-based electrolytes, the carbon felt electrodes are compacted less than 0.1 MPa to provide flow permeability, which makes the sealability of FFs difficult [3]. Therefore, avoiding the leakage of electrolytes is a main concern when constructing the stack because leakages of electrolytes result in an unbalanced concentration between positive and negative electrolytes, which reduces energy efficiency.

A typical unit cell of a VRFB stack is illustrated in Fig. 2(a); it is composed of carbon felt electrodes, flow frames (FFs), BPs, a current collector and an ion-exchange membrane. Additionally, rubber gaskets and O-rings are inserted between all components to seal the stack, and the whole stack is compressed by endplates and tie-bars as shown in Fig. 1. However, the achievement of perfect sealing is difficult with conventional gaskets or O-rings because a VRFB stack consists of several hundred unit cells that require a high level of alignment of the components. The rubber gaskets and O-rings should be replaced regularly during long-term operation (10–20 years) to maintain the sealability against creep deformation under the compaction pressure.

In this work, the concept of gasket-less composite FFs was developed to overcome the technical problems of rubber gaskets

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http://dx.doi.org/10.1016/j.compstruct.2016.02.052
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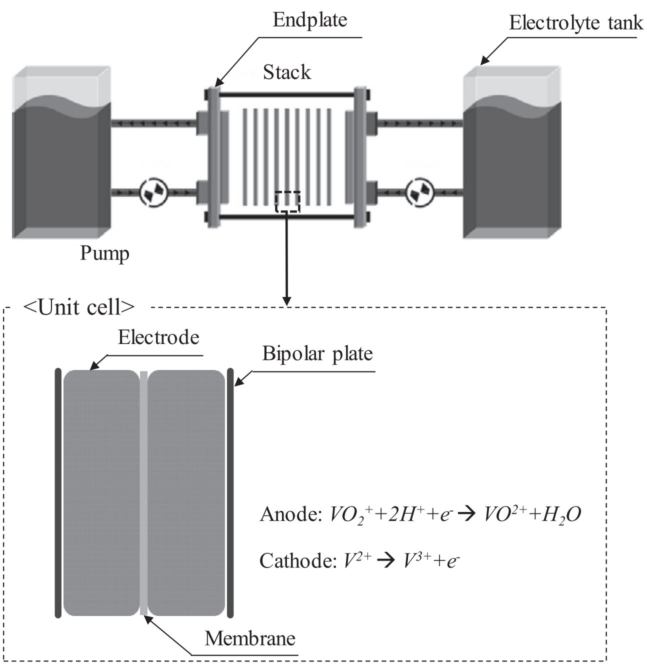

Fig. 1. Schematic diagram of a VRFB system and the chemical reactions in the unit cell.

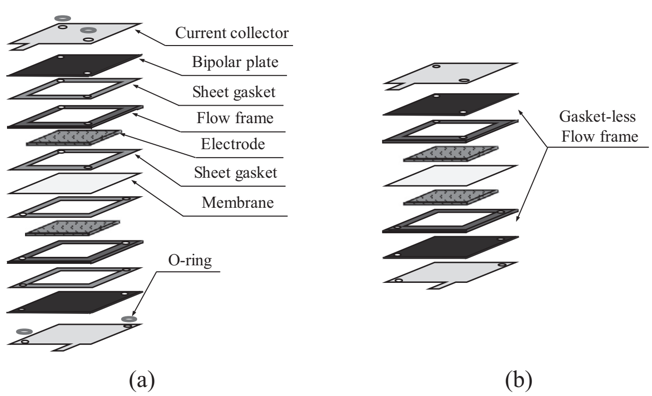

Fig. 2. Components of VRFB unit cell: (a) conventional components; (b) reduced components with gasket-less composite flow frame.

and O-rings. A schematic drawing of the developed gasket-less composite FF structure is illustrated in Fig. 3, which is composed of fluoroelastomer matrix and glass fabric reinforcement. The fluoroelastomer layers, which are resin rich layers, are formed at the surfaces of the composite structure, whose resilience allows it to function as a gasket. The glass fiber fabric reinforcement provides required mechanical properties for the composite to be used as a structure under the compaction pressure and to retard creep deformation. With the gasket-less composite FF concept, the number of components in a stack can be reduced by half as shown in Fig. 2(b).

The components of VRFBs have been studied by many researchers. Carbon cloth, carbon paper and carbon felts have been investigated and suggested for the electrode materials [4–6], and

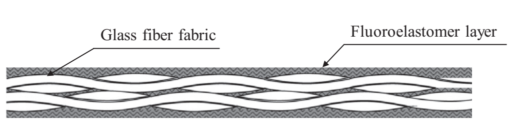

Fig. 3. Concept of gasket-less composite flow frame for VRFB.

pretreatment methods to increase the performance of the electrodes were also investigated [7–9]. Including the conventional graphite plate BPs, recently developed carbon composite BPs have been widely investigated by many researchers [10–16]. Research has been conducted on perfluorinated membranes owing to the high conductivity and good chemical stability in the oxidizing electrolyte environment [17–19]. Regarding the FF structure, most research has focused on the channel design and materials that can endure the oxidizing electrolyte environment. Nam et al. studied the FF-BP assembly by co-curing carbon/epoxy and glass/epoxy composite structures to reduce the leakage path between the components [20].

Research on the fluoroelastomer composite has been performed primarily to improve the properties of the fluoroelastomer such as its thermal resistance, electrical properties, wear resistance, crack retardation and curing time [21–23].

Previous studies on the components of VRFBs have mostly focused on the electrode, BP and membranes, which are directly related to the electrochemical performance of the stack. Most fluoroelastomer composites have been studied to increase the thermal, electrical and mechanical properties as sealing materials rather than for use as structural materials. In this work, a fluoroelastomer/glass fiber composite structure was developed for the FFs of VRFBs. To increase the bonding between fluoroelastomer matrix and glass fiber fabric reinforcements, surface treatment methods were investigated. A cyclic pressurizing cure process was introduced to impregnate the highly viscous fluoroelastomer into the glass fiber fabrics. The fluoroelastomer/glass fiber composite FF specimens were fabricated with respect to the number of glass fiber fabric layers and curing pressure to investigate the composition of the composite. The mechanical properties of fabricated specimens were measured. In addition, the sealability test was performed by measuring the zero-leakage compaction pressure of each fabricated specimen. Based on the mechanical properties and sealing performance, the fabrication condition of fluoroelastomer/glass fiber composite for the FFs of VRFBs was investigated.

2. Experimental

2.1. Concept and material selection

The concept of gasket-less FFs is illustrated in Fig. 3. During the fabrication process of the composite structure, the elastomer layer, which is a resin rich layer, is formed on the surface, and the glass fiber reinforcements provide the required mechanical properties.

Materials for VRFB components should be chemically stable owing to the highly oxidizing environment under strong, acid-based electrolytes. In this work, fluoroelastomer (Dai-El G327, Daikin, Japan) was selected because of its high chemical stability in acidic environments. Plain weave glass fiber fabric (GEP126, SK Chemicals, Korea) of 0.3 mm in thickness was used as reinforcement to increase the mechanical properties. Generally, fluoroelastomer compounds are composed of a curing agent such as bisphenol, metal oxides (magnesium oxide and calcium hydroxide) and fillers such as carbon black, silica or carbon nanotubes. Although fillers are used to improve the mechanical or electrical properties of fluoroelastomer, they increase the viscosity of the compound. In this work, fillers were not adopted when fabricating the fluoroelastomer compound to reduce the viscosity of the compound.

2.2. Surface treatment methods

Co-curing of the fluoroelastomer compound and glass fibers is difficult owing to the fluorine in the compound. From the