Development of carbon nanotube and graphite filled polyphenylene sulfide based bipolar plates for all-vanadium redox flow batteries

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HIGHLIGHTS

- Injection molded bipolar plates are evaluated for all-vanadium redox flow battery.
- Carbon nanotubes possess promising features as secondary conductive filler.
- Titanate coupling agent increases the electrical conductivity of bipolar plates.
- Developed bipolar plates show favorable surface structures for redox reactions.

ARTICLE INFO

ABSTRACT

In this study, synthetic graphite and carbon nanotube (CNT) filled polyphenylene sulfide (PPS) based bipolar plates are produced by using co-rotating twin-screw extruder and injection molding. Graphite is the main conductive filler and CNTs are used as bridging filler between graphite particles. To improve the dispersion of the fillers and the flow behavior of the composite, titanate coupling agent (KR-TTS) is used. The concentration effect of CNTs and coupling agent on the properties of bipolar plates are examined. At 72.5 wt.% total conductive filler concentration, by addition of 2.5 wt.% CNT and 3 wt.% KR-TTS; through-plane and in-plane electrical conductivities increase from 1.42 S cm^{-1} to 20 S cm^{-1} and 6.4 S cm^{-1} to 57.3 S cm^{-1} respectively compared to sample without CNTs and additive. Extruder torque value and apparent viscosity of samples decrease significantly with coupling agent and as a result; the flow behavior is positively affected. Flexural strength is improved 15% by addition of 1.25 wt.% CNT. Differential scanning calorimeter (DSC) analysis shows nucleating effect of conductive fillers on PPS matrix. Corrosion measurements, cyclic voltammetry and galvanostatic charge–discharge tests are performed to examine the electrochemical stability and the performance of produced bipolar plates in all-vanadium redox flow battery.
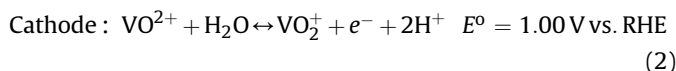
1. Introduction

All-vanadium redox flow battery (VRFB) is a secondary type battery which uses the electrolyte of vanadium (V) element in both half-cells [1]. It was invented almost three decades ago and has gained considerable attention and used in applications such as; uninterruptible power supply, battery for wind turbine generator, load leveling of electrical power stations and remote area power sources due to its highly efficient and reliable energy storage characteristics [2]. In VRFB, on the contrary to conventional batteries, electrolyte is stored in tanks and pumped into the related half-cells. This design gives opportunity to the control of power density and energy density independently. While the higher volume and concentration of the electrolyte are increasing the energy density, power density is dependent on the surface area of the electrode and the reaction rate on the electrode surface [3]. Oxidation and reduction reactions occur on the surface of porous carbon-electrode and the H$^+$ ion balance between half-cells is controlled by the proton exchange membrane. Produced electrons are transferred to the following cell or out of the battery to complete the circuit by bipolar plates. The anode and cathode reactions of VRFB are as follows and standard electrode potentials are given vs. reversible hydrogen electrode (RHE):

$$\text{Anode}: \quad V^{2+} \leftrightarrow V^{3+} + e^- \quad E^o = -0.26 \text{ V vs. RHE} \tag{1}$$
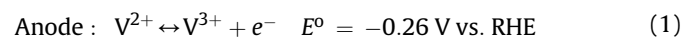
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$$\text{Cathode}: \text{VO}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{VO}_2^+ + e^- + 2\text{H}^+ \quad E^{\text{o}} = 1.00\,\text{V vs. RHE}$$
$$(2)$$

Bipolar plates are one of the main components of VRFB. They should possess high electrical conductivity, good mechanical stability, corrosion resistance and electrochemical durability in the electrolyte [4]. Polymer based conductive composites are promising materials for the production of bipolar plates. Due to their structural stability against acidic medium of the electrolyte, they do not demand protective layer deposition unlike metallic bipolar plates. Polymeric composites are produced in relatively short cycle times by processes like injection molding and machining of proper final structures costs less time and capital compared to carbon–carbon composites. As polymer matrix itself is an insulator, the main afford is given to increase the electrical conductivity of composites by addition of conductive fillers such as graphite [5] carbon fiber [6], carbon black [7] and carbon nanotubes [6]. Dispersion and distribution of fillers, their aspect ratio, purity and the interaction between filler and polymer matrix are crucial to have high electrical conductivity and good mechanical properties. Carbon fibers and carbon nanotubes have lower percolation thresholds due to their high aspect ratios however graphite and carbon black filled polymers need more filler to achieve certain electrical conductivities [6]. Fillers like carbon nanotubes tend to agglomerate due to their van der Waals forces between individual particles therefore, to benefit from their unique properties, they must be well-dispersed inside the polymer. This may be achieved by optimizing process parameters of compounding [8] or using suitable additives to increase the interaction between the filler and the polymer [9].

In this study, polyphenylene sulfide was selected as the matrix material due to its higher stability in acidic medium and possibility to be used in high-temperature applications. Synthetic graphite was the main filler with spherical particle shape to obtain isotropic electrical properties. Carbon nanotubes were chosen as secondary filler to act as bridge between graphite particles to improve especially electrical conductivity of bipolar plates. Titanate based monoalkoxy coupling agent was used to decrease the overall viscosity of the composites to ensure the breakage of CNT agglomerates and to facilitate the processing of mixture both in extruder and injection molding.

2. Experimental

2.1. Materials

Polyphenylene sulfide (PPS) was Ryton V-1 grade commercial polymer from Chevron Phillips with melt flow 5000 g 10 min^{-1}. PPS was used in powder form. Synthetic graphite with low anisotropy in particle shape, KS5-75TT (d90 = 70 μm) was purchased from TIMCAL Graphite & Carbon. NC7000 grade multi-wall carbon nanotubes (average diameter = 9.5 nm, average length = 1.5 μm, 90% carbon purity) was obtained from Nanocyl, Belgium. KR-TTS, titanate-based monoalkoxy coupling agent (Titanium IV 2-propanolato, tris isooctadecanoato-O) was supplied from Kenrich Petrochemicals, Inc. Conventional bipolar plate from Schunk Company (FU 4369) with a thermoset binder was used as a commercial reference for the produced bipolar plates. According to the data sheet, FU4369 grade bipolar plate has in-plane electrical conductivity of 111 S cm^{-1} and through-plane electrical conductivity of 53 S cm^{-1}.

2.2. Production of bipolar plates

Polyphenylene sulfide was dry mixed with conductive fillers and coupling agent in two steps. In the first step, PPS was filled into

Table 1
The composition of produced bipolar plates.

Samples	PPS wt.%	Graphite wt.%	CNT wt.%	Titanate wt.%
S-1	27.5	72.5	0	0
S-2	27.5	71.25	1.25	0
S-3	27.5	70	2.5	0
S-4	24.5	72.5	0	3
S-5	24.5	71.25	1.25	3
S-6	24.5	70	2.5	3

a Papenmeier mixer and the 3 wt.% coupling agent was added by direct syringing on the dry polymer for samples S-4 to S-6. To obtain homogenous dispersion of coupling agent into PPS matrix, they were mixed during 8 min at 1000 rpm. Secondly, samples with coupling agent and the pure PPS were filled into plastic bags and the calculated amount of graphite and carbon nanotubes were added separately. The final mixture was prepared by hand-mixing. Total filler concentration was fixed to 72.5 wt.% in order to avoid the negative effects of high viscosity in injection molding. Graphite was substituted with by CNTs at different concentrations: 0, 1.25 and 2.5 wt.%. The compositions of the produced bipolar plates are given in Table 1. The prepared masterbatches were processed with Berstroff ZE 25 × 48D co-rotating twin-screw extruder with 2.5 kg h^{-1} throughput and 300 rpm screw speed. Temperature profile was: 60 °C–315 °C–320 °C, at feeding, mixing and die respectively. Granules were collected into water-bath and dried in vacuum-oven overnight. To produce bipolar plates; granules were fed into the hopper of Demag Ergotech 100/420-120 El-Exis S type injection molding machine. Plates were injected into a mold cavity with 600 mm s^{-1} injection speed and mold temperature was held at 140 °C. The temperature profile of barrel was; 345–340–340–330 °C from feeding through the die. Bipolar plates were produced in the size of 100 mm × 100 mm × 3 mm. Specimens for electrical, mechanical and electrochemical tests were prepared by laboratory scale, water-cooled saw.

2.3. Characterization of bipolar plates

Electrical conductivity of samples was tested both in through-plane and in-plane (bulk) directions. In-plane electrical conductivity was tested according to ISO 3915 standard method. Samples were cut into 70 mm × 10 mm × 3 mm size. When current flows from one side to another, voltage drop was measured from the middle of the specimen with 1 cm electrode-span. Test setup for through-plane measurement (Fig. 1) was prepared with gold coated-copper plates (electrodes) which were protected by poly-vinyl chloride (PVC) covers and samples were cut in the dimensions of 10 mm × 10 mm × 3 mm. GDL paper (35 AA) from SGL Carbon was used to decrease the contact resistance between electrodes and bipolar plates. Both in through-plane and bulk conductivity
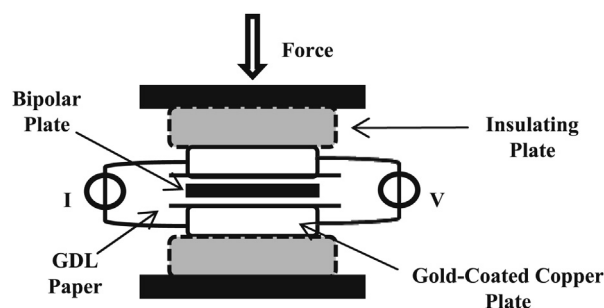
Fig. 1. Through-plane electrical conductivity setup.