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The study of electrical conductivity and diffusion behavior of water-based and ferro/ferricyanide-electrolyte-based alumina nanofluids

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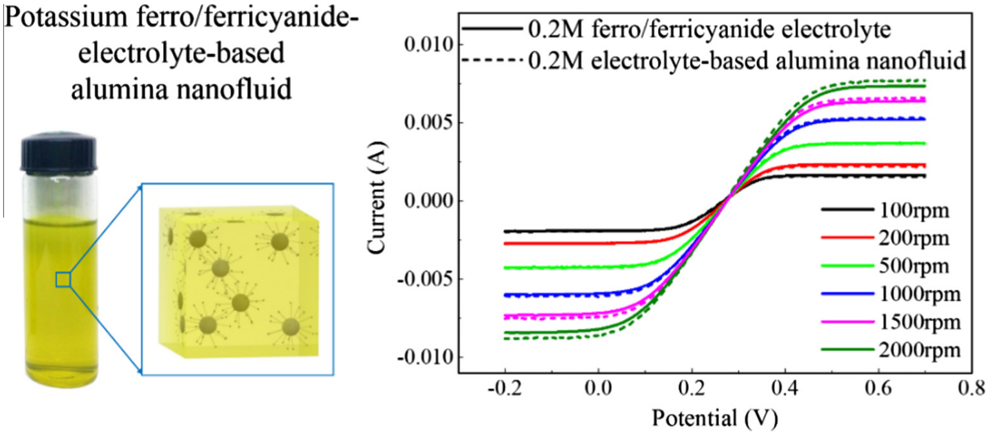
GRAPHICAL ABSTRACT



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ABSTRACT

Nanofluids are liquids containing suspensions of solid nanoparticles and have attracted considerable attention because they undergo substantial mass transfer and have many potential applications in energy technologies. Most studies on nanofluids have used low-ionic-strength solutions, such as water and ethanol. However, very few studies have used high-ionic-strength solutions because the aggregation and sedimentation of nanoparticles cause a stability problem. In this study, a stable water-based alumina nanofluid was prepared using stirred bead milling and exhibits a high electrical conductivity of 2420 μS/cm at 23 °C and excellent stability after five severe freezing–melting cycles. We then developed a process for mixing the water-based nanofluid with a high-ionic-strength potassium ferro/ferricyanide electrolyte and sodium dodecyl sulfate by using stirred bead milling and ultrasonication, thus forming a stable electrolyte-based nanofluid. According to the rotating disk electrode study, the electrolyte-based alumina nanofluid exhibits an unusual increase in the limiting current at high angular velocities, resulting from a combination of local percolation behavior and shear-induced diffusion. The electrolyte-based alumina nanofluid was demonstrated in a possible thermogalvanic application, since it is considered to be an alternative electrolyte for thermal energy harvesters because of the increased electrical conductivity and confined value of thermal conductivity.

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1. Introduction

Nanofluids, suspensions of nanosized particles in liquids, have been extensively investigated [1] because they enhance heat transfer and have potential applications in energy technologies. Considerable attentions have been devoted to using nanofluids for augmenting mass transfer in colloidal systems [2–4]. Increased mass transfer is anticipated to have evolving repercussions on conductivity and diffusivity in a wide range of applications in cooling devices, nanometer-sized transformers, microsensors, fuel cells, and industrial devices [5]. Whereas, the presence of nanoparticles in base fluids challenges not only the validity of theoretical models of mass transfer enhancement [6–8] but also the stability and reproducibility of nanofluids. Thus, the ionic strength of the base fluid, pH, zeta potential, preparation method, and nanoparticle concentration become major factors required to formulate a stable nanofluid without precipitation [9]. In particular, nanoparticle aggregation and sedimentation cause a stability problem in high-ionic-strength solutions. Therefore, most studies on nanofluids have used low-ionic-strength solutions (e.g., water, ethanol, and ethylene glycol), and very few studies have used high-ionic-strength electrolytes [10,11]. Beiki et al. studied turbulent mass transfer in a circular tube by using 0.00985 M potassium ferro/ferricyanide as an electrolytic base fluid containing suspended titanium oxide and alumina in volume concentrations of 0.01%–0.05% and 0.005%–0.025%, respectively [12]. Sara et al. [13,14] studied the effect of suspended copper oxide nanoparticles on mass transfer behavior and used 0.00985 M ferro/ferricyanide ($K_4Fe(CN)_6/K_3Fe(CN)_6$) as an electrolyte. These nanofluid-based electrolytes were required to undergo an immediate test to prevent nanoparticle sedimentation in the electrolyte. The incorporation of nanoparticles into electrolytes is anticipated to improve the diffusivity and electrical conductivity for some potential electrochemical applications, such as electrochemical capacitors [15] and thermogalvanic cells (TGCs), which are limited by the diffusion of electrolyte and the thermodynamics property (Se) of the system [16]. However, the low concentration of $K_4Fe(CN)_6/K_3Fe(CN)_6$ used in previous studies is not feasible for practical operations.

In this study, a uniform and stable suspension of alumina was prepared in water (5% acetate buffer solution) by using stirred bead milling. The high stability of this water-based alumina nanofluid was verified according to its zeta potential. A severe cyclic freezing–melting test was conducted to confirm the formation of the stable water-based alumina nanofluid. To prepare stable electrolyte-based alumina nanofluids, sodium dodecyl sulfate (SDS) was first added to a buffer solution and then mixed with alumina nanoparticles through stirred bead milling, resulting in a stable nanofluids. The intermediate water-based alumina nanofluid was blended with a $K_4Fe(CN)_6/K_3Fe(CN)_6$ electrolyte through ultrasonication. This fabrication procedure enables preparing a stable $K_4Fe(CN)_6/K_3Fe(CN)_6$-based alumina nanofluid. High electrical conductivity and stability are attainable only if the alumina nanoparticles and the $K_4Fe(CN)_6/K_3Fe(CN)_6$ electrolyte are functionalized in this sequence. To investigate the mass transfer of electrolyte-based nanofluids at different convection intensities, electrical conductivity and a rotating disk electrode (RDE) experiments were performed. In addition, we used a model that describes the joint effect of local percolation behavior and nanoscale convection caused by the Brownian motion (BM) to explain an increase in mass transfer [6–8,17]. According to the diffusivity of electrolyte-based nanofluids with respect to a homogeneous standard electrolyte under convection, we propose that forced convection exerted by the RDE induces local redistribution of nanoparticles in a shear flow, leading to both shear-induced diffusion and an increase in the fraction of nanoparticles in the near region of the electrode. Consequently, higher diffusivity and more conductive percolation paths are attainable. Our experiments on electrolyte-based alumina nanofluids elucidated the transport phenomenon of nanofluids under the joint effect of local percolation and convection. The optimization of $K_4Fe(CN)_6/K_3Fe(CN)_6$ electrolyte via the addition of alumina nanoparticles improved both the electrical conductivity and the diffusivity under convection. The prospect for being an alternative electrolyte of thermal energy harvesters was demonstrated in a possible thermogalvanic application.

2. Experimental

2.1. Preparation of water-based alumina nanofluids

Water-based alumina nanofluids were prepared by dispersing 10-nm γ-alumina nanoparticles (>99.99%; Nanostructured and Amorphous Material, Inc., USA) in an acetate buffer solution (0.082 M acetic acid–0.018 M sodium acetate buffer solution) with pH 4.3. This solution was processed using stirred bead milling (JBM-B035) for 2.5 h to ensure the formation of a well-dispersed nanoparticle suspension. The acetate buffer solution was used as the base fluid for maintaining a deviant pH value from the isoelectric point of alumina nanoparticles. The stability of water-based alumina nanofluids was verified using a particle size and zeta potential analyzer (Microtrac, Nanotrac Wave, USA) and cyclic freezing–melting test. Transmission electron microscopy images indicated that alumina nanoparticles deagglomerated after stirred bead milling, and the average nanoparticle size was approximately 20 nm.

2.2. Preparation of ferro/ferricyanide-electrolyte-based alumina nanofluids

SDS was dissolved in an acetate buffer solution through stirring for 1 h and served as a surfactant for stabilizing alumina nanoparticles [18]. Alumina nanoparticles were dispersed in the buffer solution, and the solution underwent stirred bead milling for 2.5 h. The water-based alumina nanofluids were mixed with 0.4 M $K_4Fe(CN)_6/K_3Fe(CN)_6$ in a 1:1 ratio and subjected to ultrasonic dispersion to prepare $K_4Fe(CN)_6/K_3Fe(CN)_6$-electrolyte-based alumina nanofluids. The fabrication flow diagram is shown in Fig. S1.

2.3. Material, electrochemical characterization, and thermogalvanic application test

A conductivity bench meter (Five Easy FE30-K), and thermal conductivity meter (KD2-Pro) were used to measure the electrical conductivity and thermal conductivity of the water-based and $K_4Fe(CN)_6/K_3Fe(CN)_6$-electrolyte-based alumina nanofluids, respectively. An insulating cell was designed for measuring thermal conductivity to minimize the error caused by thermal fluctuation (Fig. S2). In addition, a viscosity meter (NDJ-9S) was used to measure the viscosity of the nanofluids. To examine the effects of the mass fraction of nanoparticles on conductivity and viscosity, samples with various mass fractions were prepared. Furthermore, each sample was measured in quintuplicate. After processes and measurements, the electrolyte-based alumina nanofluids were subjected to an RDE test (RDE PTE Platinum Disk Electrode 600C) at room temperature (23 °C) to obtain the limiting currents of the electrolyte at various intensities of convection, and, in turn, determine the diffusion coefficient of the electrolyte-based alumina nanofluid. The possible thermogalvanic application was conducted to identify the effectiveness of $K_4Fe(CN)_6/K_3Fe(CN)_6$-electrolyte-based alumina nanofluids by using a double-deck device equipped