

Rechargeable Nanofluid Electrodes for High Energy Density Flow Battery

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ABSTRACT

Nanomaterial suspensions in liquids (nanofluids) are the new expanding area in nanotechnology, with applications as wide as biomedical, lubrication, thermal management, energy generation, energy conversion, and energy storage. Variety and unique characteristics of nanomaterials allow for engineering the multifunctional fluid media with new desired characteristics. We will present experimental results demonstrating applicability of rechargeable nanofluid electrodes for high energy density flow batteries. The rechargeable nanofluid technology is a transformational advancement of redox flow battery concepts, where energy is stored and released through a reversible electrochemical reaction in two electrolytes. Use of stable dispersions of solid electroactive nanoparticles in the liquid electrolyte allows increasing volume concentrations of electroactive nanoparticles therefore dramatically (up to 30 times) increasing the energy density in flow batteries.

Keywords: flow battery, nanofluid, suspension electrode, XAS, in situ experiment.

1 INTRODUCTION

The limited performance of current electrical energy storage devices is the bottleneck for deep penetration of renewable energy into transportation, industrial and residential sectors of the economy. The need to transition from petroleum-based liquid fuels to renewable sources has been realized a long time ago, however the reality of the situation is that none of the existing alternative energy storage technologies can match the convenience, low mass per delivered energy and overall economy of petroleum-based fuels. The battery with performance that will enable electric vehicles to attain higher speeds and greater ranges will lead to the wider acceptance of electric vehicles for transportation.

In the last decade a number of different battery systems were found to meet some of the requirements for electric vehicles (EV), among which are the nickel-metal hydride (Ni-MH), the sodium-sulfur (Na-S) and the lithium-ion systems. Currently lithium ion batteries are considered the systems of choice for many mobile and stationary applications because of their high energy and high power performance characteristics. The two major arguments for using the Li-ion battery is that lithium is the lightest that

can be safely handled in electrochemical processes and it exhibits the highest oxidation potential of any element.

A typical commercialized Li-ion cell uses lithiated carbon material as negative active material. A lithiated transitional metal intercalation compound is used for the positive active material, and electrolyte is either a liquid aprotic organic solution or a solid polymer electrolyte. Lithium ions move back and forth between the positive and negative electrodes during charge and discharge.

Despite this progress Li-ion technologies are still facing cost and performance challenges, including barriers in specific energy, energy density, service life, and charge efficiency at high rates.

Another category of EV prospective battery systems are the metal-air batteries. These batteries are noted for their high specific energy as they utilize the ambient air as the positive active material and light metals (Al, Zn, Na, Li) as the negative active material. Except for the iron/air battery on which earlier development work for EV applications has now been abandoned, metal-air batteries have limited capability for recharge. For EV and other applications it is being developed as a “mechanically” rechargeable battery, where the discharged electrode is physically removed and replaced with the fresh one. In this fashion recycling or recharging of the reaction product is done remotely from the battery.

2 REDOX FLOW BATTERIES

Redox flow battery technologies have been developed since 70's with the focus on stationary applications because of the low volumetric energy density, which is limited by solubility of reacting salts. In redox flow cell cathode and anode reactions take place in solution on the surface of inert electrodes acting as current collectors. The reactants flowing across the electrodes come from the containers outside of electrochemical cell and they are prevented from mixing in the electrochemical cell by the ion-selective membrane or micro-porous separator. The cathodic and anodic electrolytes are stored externally to the battery and circulated through the cell(s) of the reactor as required, providing almost limitless number of charging and discharging cycles since red/ox transfer occurs at atomic/molecular level.

In such a system the electrochemical reactor unit is decoupled from the storage unit, leading to a decoupling between power and capacity, because the available power is determined by the size of the stack (surface area of the electrodes and number of unit cells), while available

capacity is determined by the volume of electrolyte in the charged state. Given all the positive characteristics of redox flow batteries, they could be a good candidate to EV energy storage demands if the energy density can be increased.

3 NANOFLUIDS

Nanomaterial suspensions in liquids (nanofluids) have been expanding area in nanotechnology over last two decades, with applications as wide as biomedical, lubrication, thermal management, energy generation, energy conversion, and energy storage. A unique variety of nanomaterials' physical characteristics allow for engineering multifunctional fluid media with new and desired characteristics. Engineered nanoparticle suspensions known as “nanofluids”, have been extensively studied in the last decades due to their potential applications as advanced heat transfer fluids [1-3], but have not attracted much attention for their energy storage capabilities. On the macroscale nanofluids are a liquid phase, which are easy to store, transport and maintain. At the nanoscale they possess a huge area of solid/liquid interface represented by electrical double layers (capacitors), while rechargeable nanoparticle material is capable of storing/delivering energy through electrochemical (red/ox) reactions similar to solid-state batteries. Suspensions of rechargeable nanoparticles pumped through the porous stationary electrode can charge/discharge upon physical contact exchanging electrons with a circuit (Figure 1).

4 RECHARGEABLE NANOFLUIDS

Thus stable rechargeable nanofluids (dispersions of solid electroactive nanoparticles in the liquid electrolyte) used in flow battery configuration could dramatically increase the energy density. Cathode or anode nanoparticles dispersed in electrolyte represent high energy density rechargeable, renewable and recyclable electrolyte. The rechargeable nanofluid technology capitalizes on the unique physical properties of rechargeable nanoparticles suspended in fluids: (1) reduction/oxidation of nanoparticle material provides electrochemical energy storage; (2) the electrical double layers at the solid/liquid interfaces enables supercapacitor energy storage; (3) high surface area and nanoscale dimensions of particles allow fast charge/discharge. These phenomena make rechargeable nanofluid technology a transformational advancement of redox flow battery concepts, which combines the best attributes of rechargeable solid-state batteries, flow batteries and capacitors. Nanofluids applied in flow cell configuration provide higher energy densities per volume than conventional electrolyte in redox flow batteries and opens the opportunity for separating the charging, storage, and discharging in time and location and can become a gasoline alternative for transportation and portable devices.

The concept of a suspension electrode has been demonstrated more than 3 decades ago [4], but has not been applied to redox flow battery until recent publication from MIT [5], where the suspension of 30 micron cathode particles mixed with carbon nanotubes conductive filler in Li-ion electrolyte were successfully charged/discharged during the passage through the flow battery half-cell. Challenges that are faced in this proof of concept experiment are extremely high viscosity of suspensions (> 1000 times higher than electrolyte) that incur pumping power penalties, limited power ratings, limited discharge rate, incomplete discharge, random electron conduction path, and passivation of carbon nanotube solid/electrolyte interface, which all results in extra cost, inactive battery weight, and short life cycle.

Use of nanoparticle suspensions instead of micron-sized suspensions can significantly improve dispersion stability due to relative balance of Brownian motion and gravity forces. Nanofluids can be prepared with high solid loading at manageable viscosity increase. Low viscosity of nanofluid electrolyte adds to higher efficiency and power ratings of the flow battery. It has been demonstrated that nanosized electrode materials provide significantly faster charge/discharge than micron sized anode and cathode materials [6]. Because of nanoscale dimensions of suspended particles in nanofluids the volume expansion and irreversible changes in crystalline structure during ions intercalation/deintercalation become less of an issue resulting in an extended life cycle of the nanofluid battery electrolyte.

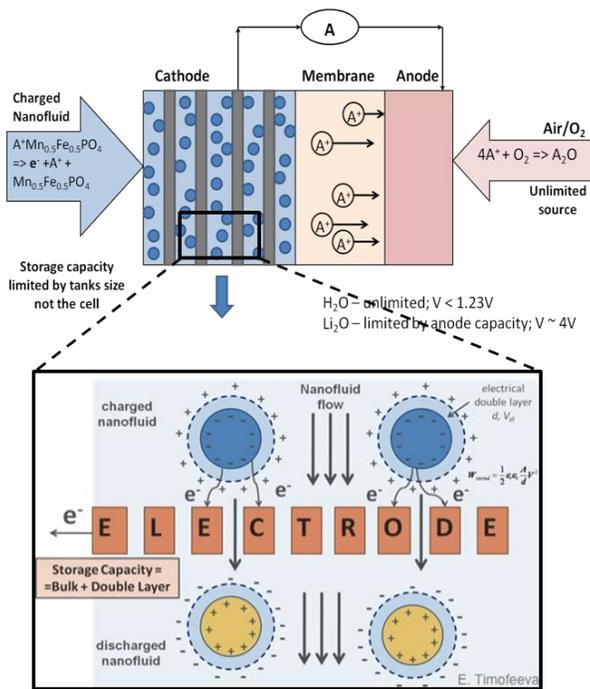


Figure 1. (top) An example of battery with nanofluid cathode and air anode; (bottom) schematic illustration of nanoparticle discharge at porous electrode.

5 CHARACTERIZATION OF NANOFLUID ELECTRODES

In order to improve the flow battery performances and to bring innovation in rechargeable batteries detailed knowledge of the battery reactions is indispensable. Therefore we have formulated and tested two types of rechargeable nanofluid systems: (1) water-based graphite nanoparticle suspension (Figure 2) and (2) Li-ion electrolyte based nanofluids with intermetallic anode nanoparticles (Figure 3). We achieved stable suspensions of these nanoparticles in electrolytes by using appropriate surface modifiers that mediate the electron and Li^+ ion transfer, while improving the miscibility of nanoparticles with electrolyte.

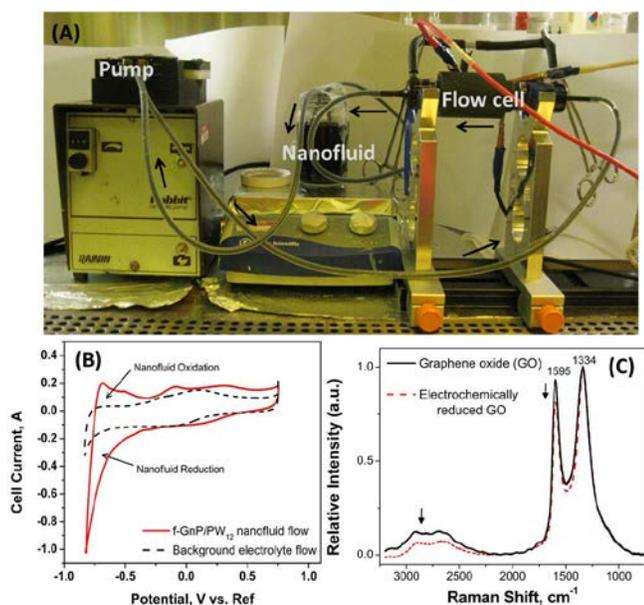


Figure 2. (A) Bench-scale flow cell for testing water-based nanoparticle suspensions in half cell configuration. (B) Cyclic voltammogram shows additional current for reduction/oxidation of nanofluid flow. (C) Raman spectroscopy of nanoparticles before and after electrochemical treatment shows changes in the peak ratio which indicate partial reduction of graphene oxide to graphene.

Our experimental approach involves in-situ x-ray adsorption spectroscopy (XAS) of electroactive nanofluids prepared from dispersed battery anodes (nanofluid electrode) and comparing the results to in-situ XAS of the same electroactive nanoparticles in conventional coin cell configuration (i.e. solid state battery). Custom electrochemical flow cells were developed to accommodate the efficiency of nanofluid electrode. In situ XAS, specifically extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) combined with electrochemical characterization

of the anode material indicate lithiation of unsupported nanoparticles in suspension similar to the lithiation of the electrode nanoparticles in coin cell.

The water-based system (Figure 2) was selected for the ease of handling and testing of nanofluids, even though they have low energy density. With Raman spectroscopy we have observed reduction of Graphene oxide to graphene upon the passage of the electrochemical flow cell chamber.

The knowledge gained in the water-based system was transferred to the Li-ion-based nanofluid with intermetallic nanoparticles as the prospective high-energy-density formulation. A combination of electrochemical testing, Raman spectroscopy, and XAS were used to obtain electronic and atomic structural information on the materials. *Ex situ* XAS experiments demonstrated that both types of studied nanofluids can be charged/discharged upon passage through the flow cell.

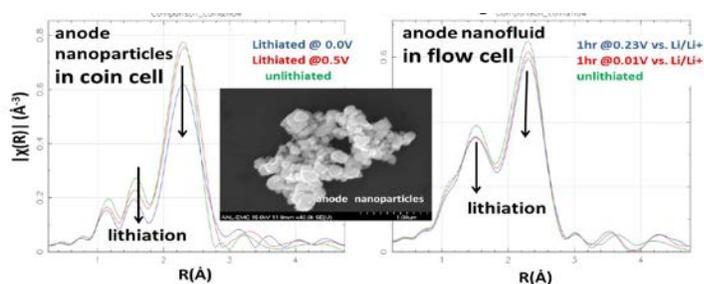


Figure 3. Fourier transformed x-ray adsorption spectra for intermetallic anode nanoparticles show that similar changes to the structure occur when nanoparticles are lithiated in conventional coin cell assembly (left) and in nanofluid flow cell (right). SEM image shows sizes of anode particle of 50-300 nm.

EXAFS of intermetallic nanoparticles lithiated in the coin cell and in flow cell show similar changes, indicating extrusion of one of the metals out of the crystalline structure upon lithium intercalation (Figure 3).

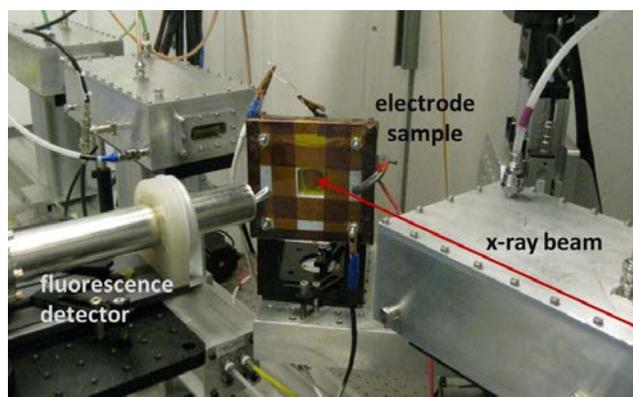


Figure 4. Experimental setup for in-situ XAS tests of the battery electrode material in the coin-cell assembly.

Further *in situ* XAS investigation of these and other nanofluid electrode systems will facilitate comparisons between charging/discharging of the same electrode material in the flow cell and in the solid-state battery assembly. This information on the kinetics of charge/discharge in both forms of batteries could accelerate the progress in both fields.

The rechargeable nanofluid batteries could provide unique flexibility for variety of applications, and are especially attractive for transportation industry as it offers high energy densities and a convenience of gasoline. Cathode and anode nanoparticles dispersed in electrolyte represent high energy density rechargeable, renewable and recyclable electrochemical fuel. The rechargeable nanofluids concept opens the opportunity for separating the charging, storage, and discharging steps in time and location and could become a gasoline alternative for the transportation. "Refueling" will be possible in plug-in configuration or simply by replacing discharged fluid with charged fluid which is recycled at the "gas stations" with virtually no wait time to the end customer.

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