Integration of Flow Batteries into Electric Vehicles: Feasibility and the Future

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ABSTRACT

Driving range, safety and cost remain the biggest hurdles in the way of mass electric vehicle (EV) adoption. To compete successfully with the flexibility and low cost of established combustion-engine vehicles, EVs need to have a highly flexible operating capability with minimum downtime. Innovative approaches to EV battery chemistries, designs and manufacturing could present the opportunity to bolster widespread adoption of EVs. In particular flow battery systems offer a unique refueling capability which can overcome both the limited autonomy and the high cost of advanced Li-ion batteries making EV's cost competitive.

Here we present novel rechargeable nanoelectrofuel flow battery technology that incorporates high energy density cathode and anode nanomaterials in a flowable battery format making them a very attractive energy storage media for EVs.

Keywords: electric vehicles, flow batteries, nanoelectrofuel, energy density

1 STATE-OF-THE-ART ENERGY STORAGE SOLUTIONS FOR EVs

Currently lithium ion batteries are considered the systems of choice for many mobile and stationary applications because of their relatively high energy and high power performance characteristics. Despite the progress in recent years Li-ion technologies are still facing cost and performance challenges, including barriers in specific energy density, short service life and low 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, whereby the discharged electrode is physically removed and replaced with the fresh one. Recycling or recharging of the reaction product is done remotely from the battery.

Redox flow batteries have multiple advantages over solid-state batteries, such as the separation of the power and energy components, rapid replenishment to fully charged state, long cycle life, low maintenance, and tolerance to overcharge/overdischarge. However, because of the low specific energy density of electrolytes (limited by the solubility of redox salts) flow batteries have not been seriously considered for transportation.

In flow batteries the energy is stored and released through a reversible electrochemical reaction between cathodic and anodic electrolytes that are stored externally to the battery and circulated through the reactor as required. 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 => I, and number of unit cells => V), while available capacity is determined by the volume of electrolyte in the charged state.

Currently, flow battery technology achieves an electrolyte energy density around 40 Wh/L (limited by solubility of redox salts), which is similar to that of industrial lead acid batteries, and so these batteries cannot match the more 60-mile range between charges achieved by Li-ion batteris. Because of the low energy density flow batteries have not been seriously considered for transportation are mostly developed for stationary applications.

2 FEASIBILITY OF FLOW BATTERIES FOR EV APPLICATIONS

Recently, a hypothetical feasibility study using currently available all vanadium redox flow battery (VRFB) technology has been carried out on the Ecobus design [1]. The Ecobus is a lead-acid battery powered minibus which is operating in European cities. Working within the existing battery envelope and based on the RE-fuel system with 30Wh/L electrolyte energy density, a city based minibus could cover a distance of 18 miles between refueling points giving 2 to 3 hours of city center operation. The refueling process could be carried out in 5-10 minutes fitting into a conventional diesel city bus schedule - the bus could operate for 24 hours a day if required. Other potential applications include taxis, delivery vans and 24 hour fork lift trucks. This model though is not applicable to mid-sized personal vehicles and transportation outside of the densely populated urban areas. At least 10 fold increases in the electrolyte energy density is required to make flow battery technology appealing to EV markets while maintaining current US driving patterns. To address the range anxiety issue a minimum requirement for EV battery energy density is set as 260 Wh/L (150 Wh/kg) at cost of no more than

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$125/kWh. In addition to range related anxieties are offset by lack of battery charging infrastructure and inconvenience of extended charging times (20 minutes minimum) vs. 3 minutes refill at a gas station.

Flow battery systems offer a unique refueling capability which can overcome both the limited autonomy and the high cost of advanced batteries making EV's cost competitive; they also offer a smooth interface with zero carbon renewable power and maximum use of off peak base load grid energy. If the energy density of liquid electrolytes can be increased, given all the positive characteristics of redox flow batteries, they are an excellent candidate to meet EV energy storage demands and could open much wider global markets in the future.

3 NANOELECTROFUEL FLOW BATTERY TECHNOLOGY

Although still in its early stages, nanotechnology is opening vast new territories for discovery and innovation. Scientists recently found, for example, that the unique properties of liquids known as nanofluids, which contain nanoscale particles in suspension, make them ideal candidates for a host of industrial and consumer applications.

Working together, scientists from Argonne National Laboratory and the Illinois Institute of Technology (IIT) have developed a groundbreaking concept for the storage of electrical energy. Leveraging the properties of nanofluid technology and flow batteries, the team created a rechargeable battery in liquid form, whose convenience is comparable to that of gasoline. The battery design employs nanoelectrofuel – a unique liquid in which nano-scale battery-active particles are permanently suspended and can be charged and discharged multiple times in a customized flow battery cell. Operating at significantly greater capacity than conventional flow batteries, the nanoelectrofuel battery offers a host of other benefits, among them thermal safety, lower cost, higher efficiency, flexibility and adaptability. The use of the high-energy-density nanoelectrofuels offers fertile ground for scientific exploration across many disciplines and promises to revolutionize the practice of energy storage.

Rechargeable nanoelectrofuel technology capitalizes on the unique physical properties of electroactive (rechargeable) nanoparticles suspended in fluids: reduction/oxidation of nanoparticle material provides electrochemical energy storage; high surface area and nanoscale dimensions of particles allow fast response times, high charge/discharge efficiency and extended fuel life cycle. This approach is not limited by solubility of redox materials and with an appropriate surface treatment of nanoparticles volume concentration of up to 80 vol.% can be achieved while keeping the suspension pumpable. Thus nanoelectrofuels provide dramatic increase in volumetric energy density 10-30 times more than traditional redox electrolytes. Engineered nanoparticle suspensions also known as "nanofluids", have been extensively studied in the last decades due to their potential applications as advanced heat transfer fluids [2], but have not attracted attention for their energy storage capabilities. On the macroscale nanofluids are a liquid phase, 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 a rechargeable nanoparticle material is capable of storing/delivering energy through electrochemical (red/ox) reactions similar to solid-state batteries. It has been demonstrated that nano-sized battery materials provide significantly faster charge/discharge rates than micron-sized anode and cathode materials [3]. Suspensions of cathode or anode nanoparticles pumped through a porous stationary electrode can exchange electrons (charge/discharge) upon physical contact with the current collector.

The concept of a suspension electrode has been demonstrated more than 3 decades ago [4], but has not been applied to the redox flow battery until a recent publication from MIT [5], where the suspension of 30 micron cathode particles mixed with carbon nanotube conductive filler in a Li-ion electrolyte were successfully charged/discharged during passage though the flow battery half-cell. Challenges faced were high viscosity of the suspensions (>1000 times higher than the electrolyte alone) which incur pumping power penalties, limited power ratings, limited discharge rate, incomplete discharge, random electron conduction path, as well as passivation of the carbon nanotube solid/electrolyte interface, all resulting in extra cost, inactive battery weight, and short life cycle. Since 2011 several other groups have published results on different forms of suspension based energy storage media, including on electrochemical flow capacitor for fast energy storage and recovery [6]; use of reversible redox ions as mediators for Li intercalation/deintercalation into the $LiFePO_4$ nanoparticles [7]; demonstration of high charge retention of silicon/carbon dispersions in non-aqueous electrolytes [8], as well as few other molecular chemistries for nonaqueous Li Redox-Flow Batteries [9, 10]. The emergence of new publications in Li-based high energy density electrolytes for flow batteries confirms interest and demand in this new technology.

Nanoelectrofuel technology uses liquid electrolyte containing a large portion of redox nanoparticles to carry its charge, which increases its energy density while ensuring stability and low-resistance flow within the battery. Nanoscale electrode materials stably dispersed in electrolyte and effectively charge/discharge as they are pumped through custom-designed flow cell(s) and represent a high-energy-density rechargeable, renewable, and recyclable electrochemical fuel. They offer excellent flow and pump performance (the speed of repumping is comparable to that of gasoline refueling) that not only improves the convenience of refueling for users of electric vehicles, but also has minimal impact on the nation's existing electrical grid infrastructure. Nanoelectrofuel flow batteries could enable the separation of charging and storage of the liquid nanoelectrofuels, the long-term storage of charged fuel, and the improved energy distribution routes. Thus, nanoelectrofuel flow batteries could become a sustainable alternative to gasoline that can directly connect transportation energy demands to renewable energy sources through on-site power generation and freight or pipeline distribution.

Our approach to high energy density electrolytes for flow batteries uses nanoparticle suspensions (<100 nm) that have significantly higher stability than micron-sized suspensions due to relative balance of Brownian motion and gravity. Nanoparticle suspensions can be prepared with as high as 60 vol.% solid loading in electrolytes. Viscosity of the nanofluid electrolyte affects charge/discharge efficiency and power ratings of the flow battery, and can be controlled by appropriate surface modification of the redox nanoparticles. Unsupported nanoparticles in suspensions provide additional advantage to any intercalation based redox chemistry: volume expansion during lithiation/delithiation doesn't affect the integrity of the electrode unlike in the electrode materials attached to the current collectors that suffer permanent loss of capacity because of this. At the same time if nanoparticles are smaller than the self-healing threshold for a given material [11] the defects resulting from volume changes in the nanoparticles can self-repair, minimizing the loss of capacity and providing an extended battery life cycle.

The concept of nanoelectrofuels is generally chemistry agnostic [12] and can be applied to any redox couple where both reduced and oxidized form is solid (insoluable) in the electrolyte i.e. will remain in nanoparticle form.

Figure 1 shows a flow battery schematics with nanoelectrofuel made out of typical Li-ion battery chemistry with $LiCoO_2$ (LCO) cathode and carbon anode (Figure 1).

The nanoelectrofuel charges/discharges suspended nanoparticles as they are pumped through the corresponding chambers. Electrical energy is stored in redox nanoparticles included in the nanoelectrofuels. In battery discharge mode nanoelectrofuels undergo a spontaneous electrochemical reaction with cathodic nanofluid being reduced and anodic nanofluid being oxidized. The difference between electrochemical potentials for cathodic and anodic redox reactions defines the cell potential. Under steady-state rest conditions, the cathodic and anodic nanoelectrofuels are stored in two separate reservoirs or half-cell bodies which are separated by an ion conducting, but electron insulating membrane. Therefore nanoelectrofuels cannot be discharged without a closed circuit. The spontaneous electrochemical reaction of the battery discharge only occurs when there is a path for electrons to flow from the first half-cell cell body to the second half-cell cell body (closed circuit). Once the circuit is closed, the electrons start flowing from anode current collector to cathode current collector through the circuit, while ions are flowing through the ion conductive membrane for compensation of charge created at the cathode. When the cathodic and anodic nanoelectrofuels flow through an electrochemical cell at closed circuit, electron movement from anodic to cathodic material is effected and an electrical current is generated. In battery charging mode the flow of cathodic and anodic fluids is reversed and corresponding redox reactions are reversed under the application of an external energy source. The nanoelectrofuel may be stored in charged or discharged form separate from the electrochemical device.

$$CoO_2 + LiC_6 \Leftrightarrow LiCoO_2 + C_6$$

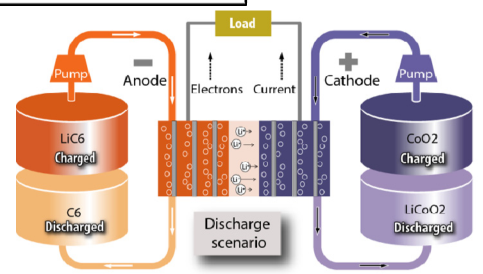

Figure 1. Schematic diagram showing a flow battery with LCO/C nanoelectrofuels as one of potential chemistries to meet an EV metric of 100 kWh energy storage at 400V power.

Figure 2 shows the breakdown for the total volume of LCO and C nanoelectrofuels that would be required to provide 100 kWh storage at 400V power output, typical for a consumer EV. Two scenarious were considered – for full lithiation of CoO_2 to $LiCoO_2$ and to half lithiation $Li_{0.5}CoO_2$, which is the more realistic scenario.

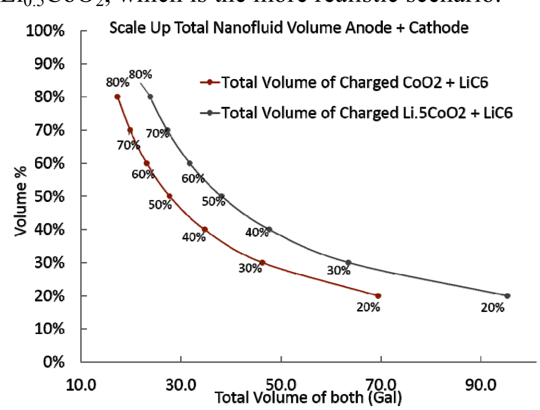

Figure 2. Estimation of the total volume of anode and cathode nanoelectrofuels in gallons for LCO/Carbon battery materials.

One can see that as the nanoparticle loadings go up, the total volume required to achieve the EV capacity reduces dramatically and at ~50 vol% particle loading it would take 25-40 gallons of total (anode and cathode) nanoelectrofuels. Considering the other system level savings from replacing the combustion engine to electric engine the results are encouraging.

The volumes of nanoelectrofuels and system level energy density can be further improoved in cathode and anode materials with higher capacity are used.

The growing demand for better performing battery materials has dictated the development of experimental strategies using in situ electrochemical (EC) cells towards those experimental techniques which are noninvasive during data collection at battery operating conditions. An early EXAFS investigation demonstrated the lithiation mechanism in a nanofluid flow regime during an *in-situ* multimodal measurement.

Recording the energy dependence of the x-ray absorption coefficient μ(E) across the absorption edge of a particular element allows for measured changes within the scope of an individual battery active material. The XAS data enables an element by element reconstruction from which bond length, electronic configuration, valence occupancy changes are determined.

The nanoelectrofuel with intermetallic anode nanoparticles was charged inside the glovebox for 4 hours at potential ~0.0 V vs Li^+/Li reference and then the samples of as prepared "unlithiated" suspensions and electrochemically lithiated nanoelectrofuel were tested ex-situ with XAS and compared to the same materials . Apparent changes in x-ray absorption spectra were observed before and after electrochemical treatment of both nanofluids, indicative of successful redox changes in unsupported nanoparticles (Figure 3).

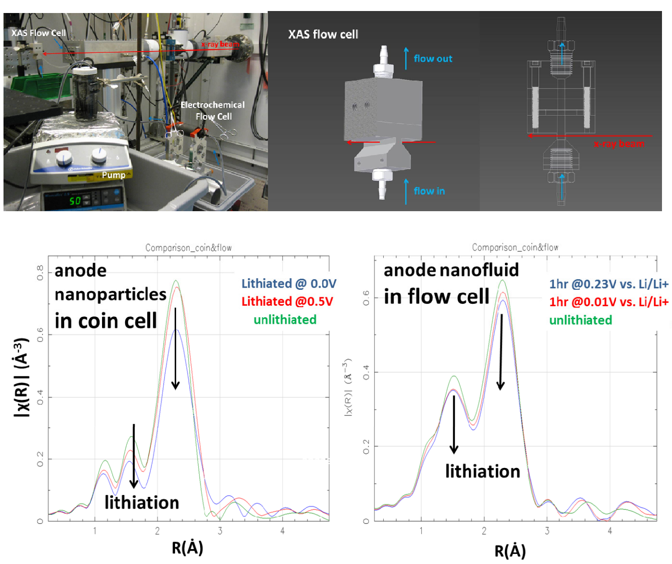

Figure 3. (Top) The insitu experimental set up at the 10BM APS synchrtron beamline. (Bottom) Fourier transformed x-ray absorption spectra for intermetallic anode nanoparticles show that similar changes to the structure occur when nanoparticles are lithiated in conventional coin cell assembly (left) and in nanoelectrofuel flow cell (right).

4 SUMMARY

The rechargeable nanoelectrofuel innovation in battery technology provides a key advantage over conventional batteries: its energy-storing material—that is, the nanoelectrofuel—can be separated from its charging device, the flow cell. For example, Nanoelectrofuels can be charged at solar plant locations and transported to market by specially designed trucks or by rail. The fuel can be deployed in a variety of uses such as fueling an electric vehicle or power tool, supplying electricity to homes and more. To recharge the fluid, the user plugs into the grid or replaces the spent fuel with charged Nanoelectrofuel at a station that recycles discharged liquids. Taking advantage of Nanoelectrofuel's unique properties, the flow cell design can be easily optimized by adjusting such variables as the size and composition of the nanoparticles and the size and shape of the flow cell materials. The Nanoelectrofuel can be stored externally to the flow cell and charged or discharged while passing through the cell in a closed circuit. Novel flow-through cells use inexpensive conductive materials.

The battery system itself is highly flexible: Nanoelectrofuel storage tanks of any shape or size can be used, and can be positioned as desired with respect to the flow-cell stack. In electric vehicles, this is particularly important. Currently, electric vehicles must be "designed around" the battery's requirements. Flow batteries with Nanoelectrofuel, on the other hand, can be located virtually anywhere in an electric vehicle and in any shape—enabling a storage tank to be placed, for example, in the safest place in case of collision.

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