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Ultrasonic enhancement of battery diffusion

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ABSTRACT

It has been demonstrated that sonic energy can be harnessed to enhance convection in Galvanic cells during cyclic voltammetry; however, the practical value of this approach is limited due to the lack of open volumes for convection patterns to develop in most batteries. This study evaluates the ability of ultrasonic waves to enhance diffusion in membrane separators commonly used in sandwich-architecture batteries. Studies include the measuring of open-circuit performance curves to interpret performances in terms of reductions in concentration overpotentials. The use of a 40 kHz sonicator bath can consistently increase the voltage of the battery and reduce overpotential losses up to 30%. This work demonstrates and quantifies battery enhancement due to enhanced diffusion made possible with ultrasonic energy.

1. Introduction

If ultrasonic energy can be used to enhance diffusion in batteries, batteries with shorter charging times and longer overall lifetimes can be designed. Since high charge times limit the use of batteries in applications like battery electric vehicles, batteries enhanced with sonication can ease this drawback, making such technologies more desirable.

In this research the performance of zinc–alkaline batteries using various separator materials are evaluated in a 40 kHz sonicator bath. The goal is to improve the understanding of how ultrasonic energy can be used to enhance battery performance. In particular, data are taken to quantify overpotential losses and thereby allow the reduction in overpotential to be quantified in a manner that will assist in modeling and extrapolating performance to optimal applications.

2. Background

Sonication has been shown to enhance mixing in the studies of Murugan and Nagarajan [1]. In their research, they investigated the effect of ultrasonic pulsing on the mixing of hot and cold liquid layers in storage tanks with different dimensions. Mixing was faster and more efficient when ultrasonic pulses were added more regularly. Higher intensity (higher power) pulses made the mixing more efficient than lower intensities. Similar to the setup used in this research, they had the liquid layers in a cylinder immersed in a lukewarm water bath, and the ultrasonic pulses were sent through the water bath.

Pohl et al. [2] provide an example application on ultrasonic waves. In their work, the production of nanoparticles was expedited by increasing the rate of generation of a homogenous triiodide concentration.

Merken et al. [3] have shown that the application of an ultrasonic probe to an electrochemical system can yield a small decrease in the size of the diffusion layer in a cell (the area where the concentration of the electroactive species increases from that of the bulk fluid to that of the solid electrode) as well as a large increase in the mass transport-limited current. Increasing the intensity of the ultrasonic vibrations resulted in more cavitation bubbles. This cavitation further enhanced mass transfer but also caused erosion of electrodes [4].

In practice, there have generally been two methods of applying an ultrasonic pulse to an electrode, and both involve the use of a sonic probe. The first method is known as the ‘face on mode’, in which the sonic probe sends a pulse to the electrode from a distance of a few millimeters, in order to agitate the diffusion layer near the electrode. The other method involves an apparatus known as a ‘sonotrode’, which involves the combination of the sonic probe and the electrode in one system [3]. Both produce notable increases in transport-limited currents of the respective electrochemical cells [5].

Compton et al. [4] compared a voltammogram of a cell without sonication and with sonication. The system studied is the sonication of ferrocene at a 2 mm diameter platinum disc-electrode in acetonitrile solution with a supporting electrolyte. Upon the application of sonication, the voltammogram becomes hydrodynamic (i.e. no hysteresis). Also, the sonicated current is higher than that

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of the silent system by a factor of about 10. This increase in current is due to the enhancement of electroactive species movement by way of the ultrasound, which significantly reduces concentration overpotential. Zhu et al. [6] performed studies using Lithium cobalt oxide cells with a lithium hydroxide solution, and found dendrite formation to be virtually eliminated via the use of powerful ultrasonic cavitation. Several other studies have also shown the positive effects sonication has on current [7,8].

Banks et al. [9] determined the dependence of transport limited current in sonic-probe electrodes to correlate with the square root of the power of the sonicator as summarized by Eq. (1).

$$I_{\lim} = C(h, \upsilon)D^{2/3}AC_{\text{bulk}}P_w^{1/2} + I_{0-\lim} \qquad (1)$$

where A is the electrode area (m^2),

C_{bulk} is the concentration of electroactive species (kg/m^3),

D is the diffusion coefficient (m^2/s),

P_w is the ultrasound power (W), and

C is a function of the kinematic viscosity, υ, and of the electrode-to-horn separation, h, which decreases sharply as h increases.

The most important aspect of this equation is continuous increase in $I_{\lim}$ with $P_w^{1/2}$ Practical limitations of this relation include: (a) limited utility of the respective electrochemical cell designs, (b) increasing erosion with increasing power, and (c) increasing rates of temperature increase with increasing power.

Eq. (2) relates temperature increase to power [9].

$$\Delta T(t) = \frac{P_w}{C_{\text{sys}}m}\left(\frac{1 - e^{-at}}{\alpha}\right) \qquad (2)$$

where ΔT is the change in temperature of the sonicated electrolyte solution,

t is time sonication is applied,

C_{sys} is the heat capacity of the electrolyte solution (J/kg*K),

m is the mass of the electrolyte solution (kg),

P_w is the power of the sonicator (W), and

α is a parameter describing heat exchange between sonicated liquid and surroundings.

3. Experimental procedure

Both the electrochemical cells and the battery chemistry of the study presented in this paper differ from those of previous work on sonic-enhanced electrochemistry. The battery chemistry used in these experiments is the zinc manganese oxide chemistry, described by Eqs. (3)–(5), using a 2M potassium hydroxide solution as the electrolyte.

Anode reaction:

$$Zn + 2OH^- \rightarrow ZnO + 2e^- + H_2O \qquad (3)$$

Cathode reaction:

$$H_2O + 2e^- + 2MnO_2 \rightarrow Mn_2O_3 + OH^- \qquad (4)$$

Net reaction:

$$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3 \qquad (5)$$

A cathode electrode mixture is prepared as a powder consisting of Aldrich Chemical 325 mesh 99% manganese oxide (30% by mass), 150–225 μm Acros graphite powder (35% by mass), and 4 K activated carbon (35% by mass) for which the production process is illustrated by Fig. 1 [10]. A solution of 6% (by mass) polyvinylidene fluoride (PVDF) and 94% *n*-methylpyrrolidone (NMP) is added to the powder to form a paste (1.5 g solution/g of powder). Exactly 70 mg of this paste is spread across a thin 0.5 × 2 cm strip copper and allowed to dry in an oven at 120 °C overnight. The anode is simply a 0.5 × 2 cm strip of 99.9% Zinc from Aldrich Chemical Company.

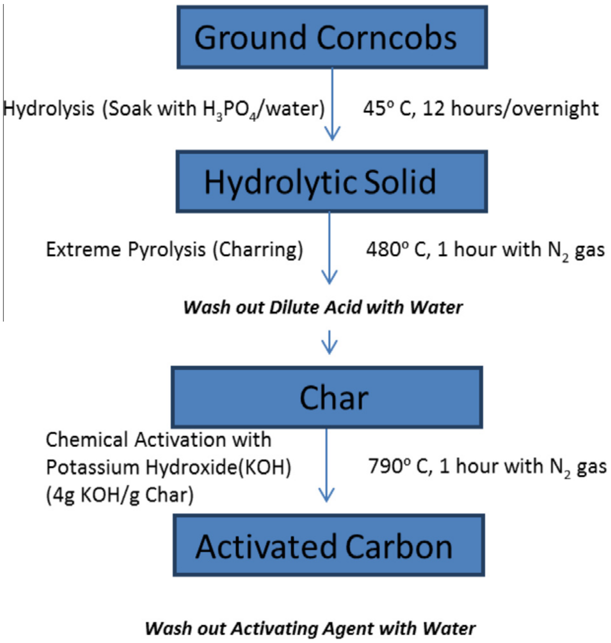

Fig. 1. Summary of 4 K activated carbon production process.

Alligator clips are attached to one end of the strips to connect the battery to a control circuit designed to provide a constant current load with data monitoring by a National Instruments PCI-6229 data acquisition card connected to a National Instruments SCB-68 shielded connector block. Voltage measurements and control were operated by National Instruments LabVIEW software using custom created virtual instrument files. Both electrodes are suspended within a glass vial, and electrolyte solution is poured into the vial until the anode paste is completely submerged.

The foil electrodes are configured in one of two design configurations within the glass vial as illustrated by Fig. 2. In Design A, the two electrodes are suspended in the electrolyte solution, separated by 2–3 mm. In Design B, the electrodes are in the sandwich cell configuration with a membrane between them, and the electrodes are held together by electrical tape. Three different membranes

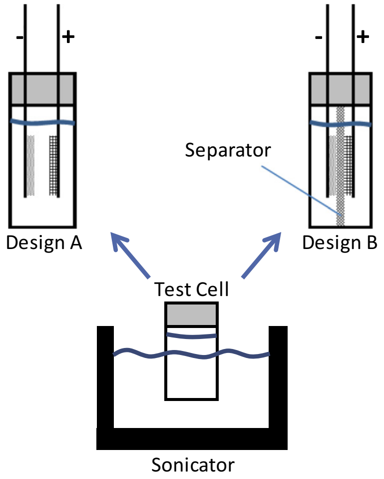

Fig. 2. Contrasting Design A and Design B.