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Enhanced thermal property measurement of a silver zinc battery cell using isothermal calorimetry

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ABSTRACT

The push for increased energy density of electrochemical cells highlights the need for novel electrochemical techniques as well as additional characterization methods for these cells in order to meet user needs and safety requirements. To achieve ever increasing energy densities and faster controlled release of that energy, all materials of construction must be constantly evaluated from electrode to casing and everything in-between. Increasing the energy density of the cell improves its utility, but it also increases the waste heat and maximum potential uncontrolled energy release. Design agents and system developers need new ways to monitor and classify the probability and severity of the catastrophic failures as well as the system characteristics during intended operation. To support optimization of these battery cells it is necessary to understand their thermal characteristics at rest as well as under prescribed charge and discharge cycles. One of the many calorimetric tools available to observe and record these characteristics is heat flow calorimetry. Typically, a heat flow calorimeter is operated isothermally and measures the sum heat released or consumed by a sample material inside of a calorimetric measuring cell. For this study an improved calorimetric measuring cell for a modified Hart 6209 precision temperature bath was designed and constructed to measure the heat flow of larger electrochemical cells ($18 \times 8 \times 16$ cm). This new calorimetric measuring cell is constructed to allow independent measurements of heat flow among each of the sample's six sides in contrast to the typical one measurement of the average heat flow. Heat flows from 0.01 to 7.00 Watts were measured by the calorimeter with an average signal noise less than 1 mW during the charge and discharge cycles of the batteries under test. The heat capacities of the samples were also determined with experimental deviation of less than 2%. This paper provides a description of the calorimeter, calibration test results on its performance, and test results from two cells tested.

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1. Introduction

Naval Surface Warfare Center (NSWC) Crane has a lengthy history of developing novel calorimeters to satisfy the unique requirements for users of other various size high energy density systems; mainly propellants, explosives, and pyrotechnic devices [1–4]. This enabled the materials analysis section at NSWC Crane to develop a calorimeter system able to accommodate multiple battery cell configurations and provide empirical system data for use in modeling and simulation, similar to that described by Pesaran at the National Renewable Energy Laboratory (NREL) [5]. The heat capacity, and thermal efficiency for each battery cell were determined, as well as the actual heat flow from each surface of the cell. The heat flow from each of six surfaces of the cell and overall thermal efficiency were obtained with the cell under a variety of prescribed charge and discharge cycles representative of typical lot acceptance testing of these cells. Testing was completed isothermally at 25 °C to capture the requirements necessary to remove the entire generated thermal load from the individual electrochemical cell. The electrochemical cells provided for this testing were silver zinc based secondary cells.

For the purposes of this study, the term "heat flow" refers to the measured transfer of heat from the sample cell through the sample chamber and then across the thermopiles and ending into the calorimeter heat sink. In contrast, the term "heat generation" will refer to the calculation of the total sum of heat transferred during an electrical cycle step divided by the time required to complete that charge or discharge step. This calculation accounts for the time lag of the heat transfer from the sample through its containment and across the thermopiles. The silver zinc electrochemical cells

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used in the calorimetry testing were previously part of cycle testing according to regular lot acceptance procedures. Therefore, they are not in a “like new” status prior to testing for this study and have had several charge and discharge cycles prior to being tested inside the calorimeter. The tested cells are from two different manufacturers built to the same specification and will be referred to as cells A and B.

2. Discussion

The modular and multi planar calorimeter measuring system was designed with the following constraints: the test system needed to accept two different sizes of silver zinc based battery cells. However for this study, only cells of one size and ampere hour capacity specification were used. The samples undergoing test needed to be subjected to constant physical restraint to hinder potential case swelling and to more accurately represent the end use environment of the cells. Case swelling of silver zinc electrochemical cells would cause premature failure of the battery and render the test samples useless. The cells under test must have access to their normal electrical test system at NSWC Crane through the use of extended charging cables passing through the access area of the calorimeter and minimizing any thermal leakage through this passageway.

This calorimeter test system was designed to approximate the best possible operational conditions in which the test cell is operated isothermally at 25 °C. However, the test system is capable of a wide operating temperature range. Maintaining the isothermal operating environment was achieved through the use of a Hart Scientific/Fluke precision temperature bath (model 91001). Additional temperature conditioning was provided by two VWR model 89202-966 circulating baths. The additional conditioning baths were set to control at 20 °C and connected to the main isothermal bath through independent heat exchangers.

The calorimetric measuring cell was designed such that each of the six surfaces of the cell was provided one thermal conduction pathway of least resistance. Each of these conduction pathways were isolated from the other five surfaces and channeled through a plurality of thermopiles. The thermopiles function according to the Seebeck effect and generate a voltage corresponding to the temperature difference on either side of the measurement device. The plurality of thermoelectric junctions in each thermopile amplifies the effect and thus lowers the minimum temperature differential required to generate a voltage to nearly isothermal values. Due to the size and anticipated thermal loading of the intended sample, this calorimeter was not designed to compare the heat flow from a matched reference chamber. Inclusion of a reference chamber would serve to decrease measurement noise for more precise measurements.

Fig. 1 is a CAD generated image of the tested battery cell inside the calorimetric measuring unit installed in the precision bath. The battery sample is the center most rectangle with cylindrical terminal posts on the top surface. Representative thermopiles can just be seen between the containment vessel holding the battery cell and the heat sink. There are additional thermopiles, not shown, between every surface of this inner containment vessel and system heat sinks. The heat sinks, thermopiles, and inner containment are removably coupled together such that the entire calorimeter measuring cell assembly can be removed via the eye bolt fastened to the uppermost heat sink. Alternative, the uppermost surface of the calorimeter measuring cell can be removed while the bulk of the calorimeter measuring cell remains in place. This allows for rapid and simplified test sample exchanges. Beyond the heat sink is the outer stainless steel containment which is immersed in the fluid bath.

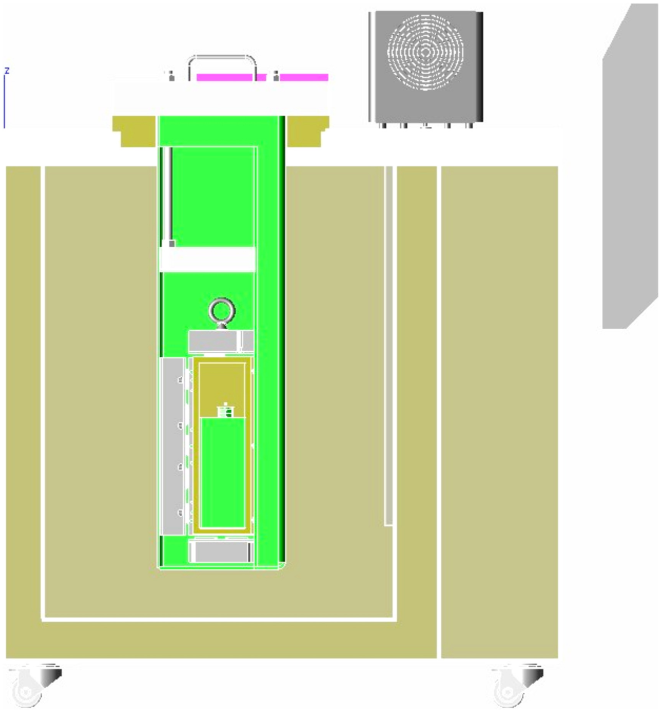

Fig. 1. Right side cutaway of installed cell.

The positioning of the calorimetric measuring cell in the fluid bath can be seen more clearly in Fig. 2. The system fits together so that there is an uninterrupted conduction path from the test sample, through the inner containment, across the thermopiles,

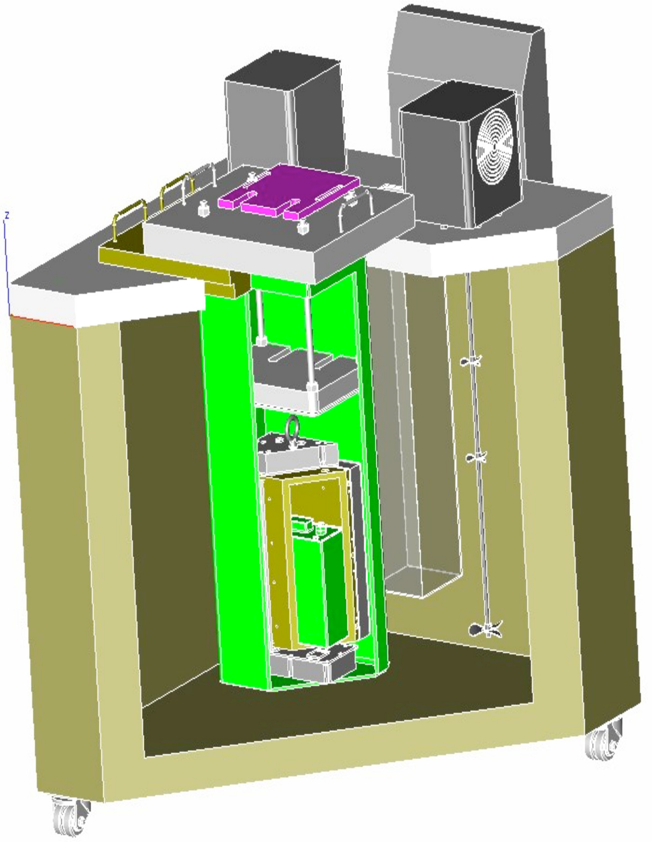

Fig. 2. Isometric view of installed cell.