



Monolithically integrated electrochemical energy storage modules

Negar Sani^a, Ulrika Linderhed^a, Mats Sandberg^{a,b,*}

^aRISE Acreo AB, Bredgatan 33, SE-60117, Norrköping, Sweden

^bMid Sweden University, Holmgatan 10, 851 70, Sundsvall, Sweden

ARTICLE INFO

Article history:

Received 12 November 2017

Received in revised form 10 January 2018

Accepted 10 January 2018

Available online xxx

Keywords:

Monolithic integration

Printed serial modules

Supercapacitors

Balancing

Resistive dissipation

ABSTRACT

The concept of monolithic integration of electrochemical energy storage modules was tested on serially connected supercapacitor cells balanced by passive resistive dissipation. Five electrode pairs with collectors, interconnects, corrosion protection layers, electrode material and shunt resistors were printed on a single substrate. The printed patterns, lamination film, and a hot-sealing tool were designed so that upon folding, lamination, and electrolyte filling and sealing, five serial cells were formed with each having a shunt resistance. In an open circuit idling period following charge and discharge, the standard deviation of the individual cell voltages decreased, demonstrating the balancing function of this so called “*modulit*”, a short term proposed for a monolithically integrated electrochemical energy storage module.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

High cost is the main impediment for an increased use of electrochemical energy storage. Meanwhile, increased use of renewable but intermittent energy sources and smart energy solutions require lower cost of energy storage devices. The manufacturing and materials cost of discrete electrochemical storage cells is indeed decreasing [1–3]. However, as materials and manufacturing methods for electrochemical storage cells become cheaper, the cost share of integrating discrete storage cells into modules and systems is increasing. Lowering the cost of integration is therefore expected to become increasingly important.

When serial stacks of electrochemical storage cells are charged and discharged repeatedly, the state of charge of individual cells in the stack can drift apart. This is due to the differences between properties of individual cells such as capacity, leak resistance, and side reactions that may originate from differences in the manufacturing process or local temperature. This may lead to overcharging or over-discharging of cells in the stack, and ultimately cell damage. Circuits to protect cells from damage and to equalize the charge levels are therefore implemented to form a balanced and protected module.

Several types of circuitry have been applied and explored for balancing serial stacks of batteries and supercapacitors. Cao et al.,

Linzen et al. and Uno discussed active and passive balancing solutions [4–6]. The solutions differ in complexity, cost and performance. For electrochemical storage cells that can be fully discharged and work with low duty cycles, the simplest solution can be to connect a shunt resistor directly to each cell in the device. After charge and discharge cycling, the cells discharge by resistive dissipation to a common zero level during an idle period. This solution is simple and cheap. However, the shunt resistance increases the self-discharge of the cells as well as the charge time and current. More advanced solutions have controlled shunting, and there are solutions where charge is shuttled between the cells to equalize the charge levels [e.g., 7].

Here, we demonstrate a manufacturing scheme hitherto unexplored for the design and manufacturing of electrochemical storage modules: monolithic integration. Our approach is inspired by the development of monolithically integrated electronic circuits (ICs), which were first introduced in the early 1960s [8]. Monolithic integration simplifies and lowers the cost of integration compared with discrete integration, and has revolutionized the electronics industry for the last half century. The impact of monolithic integration in micro electronics reaches far beyond the electronics industry itself, and influences many aspects of modern life, such as mobile communication. Exploring manufacturing concepts for electrochemical energy storage modules with monolithic integration schemes would therefore be attractive.

Today, electrochemical energy storage modules are built by integration of discrete components. Modules are formed by connecting them in series and with circuits for balancing and protection by mounting on circuit boards or using lugs, nuts and cables. The large number of connections and soldering points

* Corresponding author at: RISE Acreo AB, Bredgatan 33, SE-60117, Norrköping, Sweden.

E-mail address: mats.sandberg@ri.se (M. Sandberg).

increases complexity, the probability of defects, and most importantly the cost of manufacturing of energy storage modules. The field of printed electronics has evolved in the last couple of decades [9,10], seeing energy storage devices, supercapacitors and batteries having been manufactured by printing methods [11,12]. In addition, a range of electronic transistors and circuits have been printed [13], including circuits that can be used for protection and balancing in electrochemical storage modules [14].

Here, we demonstrate a supercapacitor modulit prototype where balancing is achieved by simple passive resistive dissipation. By monolithic integration of electrochemical modules, we mean that collectors, interconnects and components for balancing are printed on a single substrate. The choice of supercapacitors is motivated by their ability to fully discharge, in contrast to most batteries. In addition, they can be manufactured under ambient conditions from commercially available low-cost and harmless materials. We printed ten supercapacitor electrodes and five resistors on a substrate in a geometry such that upon folding, lamination, and filling of the cells with electrolyte, a supercapacitor module with five serial cells, each connected to a parallel resistor, was obtained. The selected number of cells, five, was motivated as the five cell modulit can be charged from a 5 V USB-port to an average cell voltage of 1 V.

The modulit was tested for a low duty-cycle hypothetical use case in which the module is repeatedly charged and discharged, followed by a resting period when resistive leakage through the shunt resistor balances the states of charge in the serial stack. The shunt resistances were thereby patterned to be large enough to permit reasonable charge retention and discharge over a load for a period after charging, while providing a substantial contribution to the discharge current.

2. Design and manufacturing scheme for modulit prototypes

A set of screen printing patterns was designed to form five electrode pairs, such that a five-cell serial stack with shunt resistors on each electrode pair is obtained after folding along a center line followed by lamination, as shown in Fig. 1. A patterned hot-melt film onto which separator sheets were mounted, was used to laminate the cells with a hot-sealing tool shaped to form cells and leave an inlet channel open, see Supplementary Fig. S1 and S2. After lamination, the electrolyte was injected into the cell compartments through the inlet channels before sealing to form a working modulit, shown in Fig. 2. The outlines of the screen printing patterns shaping the collectors, leads, protecting carbon, resistances and electrodes are shown in Supplementary Fig. S3.

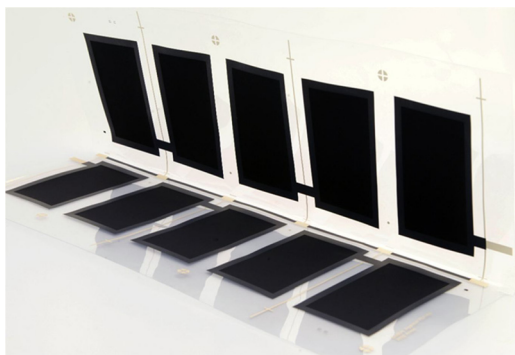


Fig. 1. The printed layers in the five-cell supercapacitor modulit prototype. Folding forms five aligned electrode pairs with interconnects and shunt resistors. Lines and markings of the silver interconnect pattern aid alignment and enable contacting individual cells for measurements.

Manufacturing under ambient conditions and less-than-perfect barriers influenced the choice of materials and manufacturing methods. The electrode material was based on previously reported printable compositions [15]. As we found that this material has limited long-term stability in aqueous electrolytes, we chose a room temperature ionic liquid as electrolyte. The metal material forming the collector was selected for corrosion stability. With the chosen ionic liquid, we found that printed silver collectors with a printed conducting carbon coating were sufficiently stable towards corrosion for evaluation of the modules. The modulit was designed to form five serial cells with $45 \times 87 \text{ mm}^2$ electrodes, each shunted by a 64 mm long and 3 mm wide resistor.

3. Materials and methods

3.1. Materials

The modulits were printed on 100 μm thick AutostatTM CT4 films purchased from MacDermid Autotype, Ltd. DuPont 5000 screen printable silver ink, purchased from DuPont was used to print collectors and interconnects. Carbon based conducting ink DuPont 7102, purchased from DuPont, was used to print corrosion protection layers on top of the silver collectors, and to form the shunt resistors. Activated supercapacitor grade shell carbon (AC) HCE 202 was kindly provided by Haycarb PLC of Sri Lanka. Carbon black (CB) EnsacoTM 250G was kindly provided by Imerys Graphite & Carbon Switzerland AS. Chitosan, low molecular weight (product no. 448869), DL-lactic acid (product no. 69785), and the electrolyte, 1,3-ethylmethylimidazolium ethanesulfate (EMIM-ES, product no. 51682), were purchased from Merck. The hot-melt film used to form the modulit laminate and to shape the cell compartments and inlet channels, Platilon[®] HU2 30 g/m², with polyethylene liner on both sides, was kindly provided by Covestro AG. Dreamweaver TitaniumTM 30 films kindly provided by Dreamweaver International Inc., were used as separators.

3.2. Electrode ink

The printable electrode composition was prepared by first dissolving chitosan in water and lactic acid, then mixing in CB and AC, and lastly homogenizing the ink in a rotor-stator high shear mixer for 30 min to provide the following composition (wt%) AC (12.3), CB (3.4), chitosan (2.5), water (77.7) and lactic acid (4.1).

3.3. Printing

Screen printing was done using a DEK Horizon 03iX printer and thermal drying was done in a Natgraph Air Force Combination UV Dryer. Screen printing webs were purchased from Coated Screens Scandinavia AB. Three materials were screen printed using four screen printing webs. The layout of the printed layers is shown in Supplementary Fig. S3. The web meshes are stated as (threads per cm – thread diameter in μm). The silver ink was printed through a (120–34) web mesh. The protective carbon ink was printed through a (120–34) web mesh to form the layer protecting the collector, and through a (77–48) web mesh to form the shunt resistors. The electrode ink was printed through a (77–48) web mesh. The resistor screen printing pattern was defined by a photopatterned Foteco 1711 + 20 μm Topaz capillary film. The other screen printing patterns were defined by a photopatterned Foteco 1068 WR film. DuPont 5000 was dried at 130 °C for 4 min. DuPont 7102 was dried 120 °C for 4 min and was printed twice when forming the collector protecting layer, to minimize pin-holes. The electrode ink was dried at 100 °C for 4 min and was printed twice to improve the electrode capacity. The electrode was 1.3 mg/cm², corresponding to a grammage of the active substance (AC) of 0.88 mg/cm².

Download English Version:

<https://daneshyari.com/en/article/7540047>

Download Persian Version:

<https://daneshyari.com/article/7540047>

[Daneshyari.com](https://daneshyari.com)