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Development of MnO_2 cathode inks for flexographically printed rechargeable zinc-based battery

Zuoqian Wang [a,*], Rich Winslow [b], Deepa Madan [b], Paul K. Wright [b], James W. Evans [c], Malcolm Keif [d], Xiaoying Rong [d]

[a] Applied Materials, Inc., Santa Clara, CA, USA
[b] Department of Mechanical Engineering, University of California, Berkeley, CA, USA
[c] Department of Materials Science and Engineering, University of California, Berkeley, CA, USA
[d] Graphic Communication Department, Cal Poly State University, San Luis Obispo, CA, USA

HIGHLIGHTS

- A flexographic printing method for battery fabrication was presented.
- Key criteria for developing functional flexographic inks were established.
- A variety of MnO_2 composite cathode inks were developed and analyzed.
- A PSBR based ink showed excellent printability and electrochemical performance.

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ABSTRACT

A novel roll-to-roll flexographic printing process for rechargeable zinc-based battery manufacturing was presented in this paper. Based on the fundamental operating mechanism of flexography, key criteria for developing functional flexographic printing inks were established, including composite ink rheology (steady-state viscosity and yield stress), ink wettability as well as ink dispersing qualities. A variety of MnO_2 cathode inks were developed and analyzed comprehensively based on these criteria. A novel type of aqueous cathode ink based on PSBR polymeric binder showed excellent flexographic printability as well as promising electrochemical performance.

1. Introduction

Long-life, energy dense, low-cost, flexible electrochemical energy storage systems have become a fast-emerging industry in recent decades, with potential applications from wireless sensor networks, [1–8] portable electronics, [9,10] electric vehicles [11–13] to grid energy storage [14–17], ranging from mW to MW scales. Both a fundamental breakthrough in battery chemistry and major innovations in fabrication methods are needed to significantly reduce battery cost, and to allow for easier integration with such a wide variety of applications.

Significant research efforts in the battery field have recently been made towards development of rechargeable zinc battery chemistries, motivated primarily by their high energy and power densities, inherent safety, low toxicity, relative ease in handling, and low cost. [18–21] Specifically, rechargeable nickel–zinc, [22,23] silver–zinc, [24] alkaline manganese dioxide (MnO_2)-zinc [25] and zinc-air [26,27] batteries have been studied. A printable zinc–manganese dioxide(MnO_2) microbattery was developed in previous research [21,28] for wireless sensor network applications, based on a novel ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM + Tf-) gel electrolyte. It has been shown by Ho [21] that MnO_2 appeared to be an reversible intercalation host for zinc ions, and served as a good cathode material in a zinc-metal oxide battery. The first microbattery prototype shows promising properties, with the cell exhibiting storage capacities of

* Corresponding author.
E-mail address: wangjoaking@gmail.com (Z. Wang).

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about 1 mAh cm^{-2} over more than 70 cycles. [21] A novel dispenser printing method was developed and utilized for additive manufacturing of the sandwich structured battery. The custom-built dispenser printer demonstrated great flexibility and precision in energy harvesting and energy storage device fabrication for prototyping. Research on electrochemical capacitors, [29,30] thermoelectric generators [6,31–38] as well as MEMS current sensors [39] have been also conducted using this versatile prototype dispenser printer. However, due to the limitations of this printer, only mm to cm scale batteries can be printed, even then at relatively low throughput rates, which is good for device prototyping but not for large-scale manufacturing.

A roll-to-roll printing process has therefore been proposed for the developed battery technology using commercially available flexographic printing presses, as shown in Fig. 1. Flexography is traditionally used for printing packages, newspapers and magazines. It was selected for scalable battery manufacturing because of its great advantages: it is a fully automatic process with high throughput rate; it is a mature wide web process – thus good for large-format device printing; it has flexible, soft plates thus it has great flexibility with the printing substrates including metal foils; it can print at resolution as low as 20 μm–30 μm, which is good enough for battery applications. Each of the four stations is designed to print or deposit the developed functional inks for the cathode, electrolyte, anode and current collector in series, respectively. Printing plates are designed to print the various components of custom-sized batteries in custom patterns, eventually forming a sandwich-structured battery. This roll-to-roll manufacturing technology is capable of fabricating batteries with capacities ranging from mA-hrs (microbatteries) to A-hrs (grid-scale batteries).

There are previous studies, including multiple patents from Bjorksten [40], Story [41] and Bergum [42], on printable batteries as well as electrode ink formulations. However, as far as the authors know, there are no fundamental and systematic studies on the composite electrode ink development, especially for flexographic printing method. Different flexographic manufacturing process parameters, such as alignment, printing speed, drying techniques, intensity and time should be strictly designed at each printing station depending on the formulations of the functional ink to provide optimized printing quality and battery performance. What turns out to be most critical is to develop functional inks with suitable fluidic properties for this unique high-speed ink transfer process in order to achieve excellent printing quality. Large volumes of inks (in liters) are typically needed to fill the ink reservoir for a cost effective process, so the inks need to maintain high dispersing qualities and have minimal aging effect. Because the inks need to be transferred effectively at high speed from the ink reservoir to the substrate through multiple rollers and media, including rubber fountain rollers, ceramic anilox rollers as well as photopolymer plates, the viscosity and wetting properties must be well adjusted so that a high ink transfer rate and accuracy are achieved. Once the inks are transferred to a variety of substrates, both a compressive force from the impression cylinder as well as a shear force due to the relative motion of the substrates and plates are applied to the inks, so the inks need also to have proper structural properties to form desired pattern with high accuracy.

Because flexographic printing presses are designed for large volume manufacturing, aqueous-based inks are highly desired due to environmental, safety and cost concerns, compared to traditional organic solvent based formulations for battery chemistry and have therefore been the main subject of this investigation. In the previous work, a cathode slurry was developed based on traditional Poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) binding material, which requires volatile n-methyl-2-pyrrolidone (NMP) as the solvent. [43] Water-soluble binder systems such as sodium salt of carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) have been recently introduced in the manufacturing of lithium ion battery electrodes. [44–47] This work explores the application of various water-based CMC/SBR binder formulations as well as water-based single modified SBR (PSBR) binding solution, in the zinc-based battery chemistry and electrode fabrication using flexographic printing technology.

Inks developed previously for the custom dispenser printer show various poor printing qualities on flexographic printing press. Among them, poor wetting shown in Fig. 2(b) was typically due to the high surface tension of the inks relative to the low surface energy of the foil substrate, especially for some aqueous-based composite inks; Non-uniformity as shown in Fig. 2(c) happened frequently with low viscosity NMP-based inks with poor structural properties. Active particles in the cathode slurry were easily squeezed to the edge of the square on the stainless steel substrate instead of spreading uniformly. Comparing to what we obtained from using commercial graphic black inks (inks used for printing newspapers etc) in Fig. 2(a), it was concluded that substantial ink fluidic property analysis and improvements, beyond inks developed for dispenser printing, are necessary to achieve high quality functional thick films from flexographic printing. In the following sections, the rheology and wettability as well as dispersion analysis focused on a variety of synthesized cathode inks will be discussed. Physical characterizations of the dried cathode films were performed and correlated to the ink formulations and properties. With good battery cathode films flexographically printed, electrochemical characterizations were then conducted for further optimization of the battery chemistry.

2. Experimental

2.1. Composite ink development and preparations

2.1.1. Commercial flexographic graphic inks (Performa Ink System) were directly ordered from Actega WIT, Inc. The specific graphic ink used for this work is water-based black ink.

2.1.2. A type of composite ink based on commercial extender solution was developed with active cathode powders. The formulation includes 90 wt% activated MnO_2 powder with particle sizes <5 μm (Sigma–Aldrich), 6 wt% acetylene black (AB) conductive

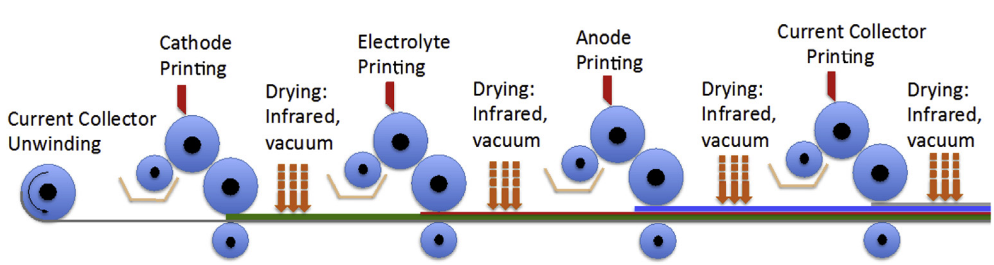

Fig. 1. Proposed multi-station flexographic printing process for large-scale battery production.