Co-Extrusion Printing for Low Cost and High Performance Energy Devices

Eric Shrader and Corie L. Cobb

Palo Alto Research Center
3333 Coyote Hill Rd. Palo Alto CA 94304
Shrader@parc.com, Corie.Cobb@parc.com

ABSTRACT

The method of co-extrusion of dissimilar materials has been developed at PARC, a Xerox Company, to successfully produce high aspect ratio structures for solar cell gridlines and battery electrode structures. In the solar application, the process is stable and repeatable, and a fully integrated tool has been developed that is now being demonstrated at a customer site. The co-extrusion process is capable of non-contact, direct deposition of features as small as 1 – 10 um with aspect ratios in the range of 1:1 to 30:1. Alternating fluids are co-extruded to form a fine vertically interdigitated lamina structure. The relative thickness, width, and length of the deposited features can be varied by altering the printhead geometry, fluid properties, and printing process conditions.

Keywords: extrusion, electrode, battery, deposition

1 INTRODUCTION

1.1 Non-contact printing

Printing of metallization is a key enabling technology for many different energy generation and storage devices. Subtractive methods starting with a blanket coat of metal and etching away features, are commonly used in electronic circuit fabrication but are often too costly for use in energy devices. Additive methods including aerosol jet[1], ink jet [2-4] and screen printing are used for energy devices. In addition to the relative immaturity of aerosol jet and ink jet, these methods may be challenged to deposit the large quantities of material needed for thick film deposition at a low cost. compared to screen printing.

Screen printing is commonly used for energy devices and is the industry-standard process for metalizing crystalline Si solar cells. However, in this application wafer breakage is a challenging issue due to yield loss and due to the machine downtime caused when broken wafer shards and ink residues need to be removed from a screen printer. Thus, non-contact metallization printing would be very useful, because it can reduce wafer breakage, thereby increasing manufacturing yields, particularly as silicon wafers increase in surface area larger and become thinner.

Aside from better handling of fragile substrates, non-contact printing also offers advantages for printing features on flexible and non-uniform substrates.

1.2 High aspect ratio printing

Another important goal of screen printing alternatives for front contact solar cells is to improve the gridline electrical resistance while reducing the optical shading loss due to the gridlines. Thus, for the amount of conductive paste necessary to achieve the desired gridline resistance, it is preferable to increase the height and decrease the width of the lines. Extensive practice has shown that the aspect ratio of fired screen prints is limited to an aspect ratio of about 1:6 Height:Width, with typical lines about 20 µm tall and 120 µm wide on average [3]. Naturally, for front contact cells, this is less than optimal because the gridlines shade about 5% of the solar cell surface.

High aspect ratio printing is valuable in another application, Li battery electrode deposition. In electrode deposition, similar highly viscous, particle containing pastes are deposited at fairly high speeds onto a thin substrate that becomes the current collector. These pastes are typically slot coated in a uniform layer, leaving particle size and composition as the only varialbes available for performance tuning.

Traditional dispense methods are similarly limited to low aspect ratio structures (~1:5 Height:Width) because the low viscosities cause slumping of the dispensed material. Recently, some screen printing vendors have introduced double printing methods to improve the aspect ratio of the print. Because screen printing does not permit wet-on-wet printing, the double printing approach involves printing a first set of gridlines on the substrate, drying them in an oven, and then registering a second screen print onto the dried print. Although double printing may not reduce shading, it can add metal to reduce series resistance. Double printing however not only involves more processing equipment, but also places tight demands on the registration control of the printer. Issues like screen stretching and warping become critical factors when attempting to register double prints.

Methods such as ink jet and aerosol jet printing produce inherently lower aspect ratio prints than screen printing. As with double screen printing, multiple registered jet prints can increase the film thickness, at the expense of either throughput or machine simplicity (i.e. many independent jet nozzles). The viscosity of ink jet inks is typically in the 1 to 10 centipoise range which is about 10,000 times thinner than screen printing inks. Low viscosity liquids carry a lower material load and slump more than viscous pastes. Use of ink jet or aerosol jet printing for solar cell metallization may therefore require making multiple depositions either at elevated temperatures or with intervening drying steps. Another approach to producing taller gridlines via ink jet or aerosol jet printing is to follow the printing step with an additional plating step. Unfortunately, plating introduces higher costs by adding an additional wet process step using chemicals that are not always environmentally friendly. Yield and throughput can be an important consideration for plating.

In this paper, we introduce a printing method conceived to meet all of the goals of contactless mask-less printing with high aspect ratio and stable pitch. We call this method co-extrusion printing.

2 CO-EXTRUSION PRINTING METHOD

High pressure extrusion, injection and dispense of viscoelastic materials appear in many practical applications such as food processing and polymer injection molding. However for extruding micron scale features, especially with higly loaded metal pastes required for energy devices, it is impractical to use traditional dispense needles because the operating pressure needed to force paste down a long narrow tube at useful printing speeds is not feasible in a high-production envrionment.

PARC has developed a single pass, high speed micro-extrsion print head technology which consists of a modular non-bonded fluidic stack of nozzles and supply channels (Figure 2). As shown in Fig. 1 and in exploded form in Fig. 2, a co-extrusion printhead assembly typically includes a layered nozzle structure sandwich between two plate structures. One plate guides extrusion material from an inlet port to the layered nozzle structure. The basic building block of each extrusion nozzle structure in our print head is a converging structure that minimizes the pressure drop throughout all of the upstream portions of the ink delivery system. The concept of hydrodynamic focusing [1] is used to minimize the pressure drop while narrowing the extruded line feaures. Each of the nozzles in our printheads, for example, has a wide feed at its proximal end and one narrow exit at its distal end. In the convergent section, the stripe of target material is squeezed laterally into a tall and narrow structure before it exits. During dispensing, the extruded material is then directed towards a substrate surface. The flow velocity at the exit nozzles has been tested nominally at 100mm/s but speeds greater than 100mm/s can be realized. The high viscosity of the material ensures that the flows are laminar and largely retain the shape formed in the nozzle orifice during extrusion.

Depending on the application at hand, the fluidic stack of nozzles can easily be exchanged for a multitude of designs in order to achieve the necessary extruded line dimensions and pitch. In the remainder of this paper, we highlight two applications of PARC's co-extrusion technology: (1) extrusion of high aspect ratio conductive gridlines for solar cells and (2) extrusion of interdigitated high aspect ratio battery electrodes.

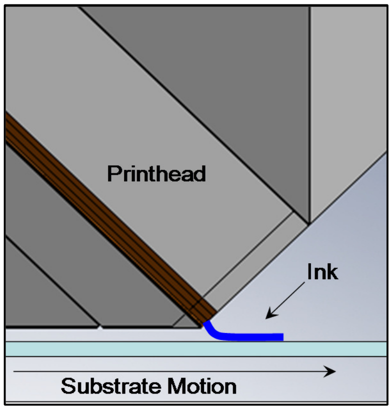

Figure 1: Side view schematic of dispense printing onto a moving substrate.

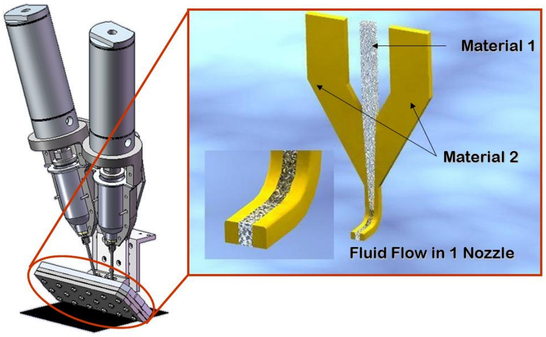

Figure 2: Exemplary image of micro-extrusion system

3 INK CONSIDERATIONS

The inks used for co-extrusion printing are similar to screen printing inks. They are very high viscosity pastes in the 100,000 Cp regime that use low vapor pressure solvents as a base for the organic matrix that suspends the active particles. We have used the same printhead for experiments for weeks at a time without the nozzles clogging due to ink drying. Although commercial screen print inks or battery pastes do not flow reliably through the micro-fluidic portions of our print heads, we have formulated application-specific inks for both solar gridlines and battery electrodes that are designed to have the required flow characteristics during printing and function properly during the subsequent processing steps.

4 SOLAR APPLICATION

For extrusion printing lines of conductive ink onto a solar cell, there are special considerations. The basic concept involves forcing a heavily filled viscous paste (silver particles suspended in an organic matrix) out through the printhead nozzles and onto a substrate surface, much like toothpaste. The target dimensions for solar applications are of course, much smaller, about 50-100µm instead of ≥1 mm as for typical industrial extruders.

With co-extrusion, closely spaced high aspect ratio gridline structures are fabricated on a substrate surface. The gridlines are co-extruded with a sacrificial material on either side which helps compress and shape the gridlines. Looking at Fig. 2, Material 1 in this application is the silver gridline while Material 2 is the sacrifical material which helps form and shape the dimensions of Material 1.

Figure 3 below displays parallel gridlines formed on a glass substrate by the aforementioned printhead construction. The lines have a pitch of 2.5mm and the gridlines themselves have an aspect ratio of ~3:1.

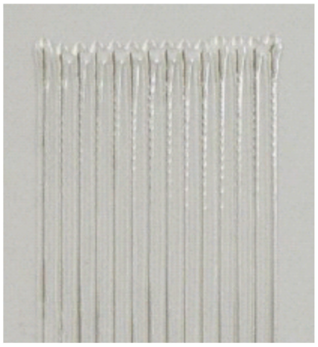

Figure 3: Image of gridline dispense on glass substrate

5 BATTERY ELECTRODE APPLICATION

By utlizing the layered printhead design dicussed in section 2 and reducing the pitch between nozzles to zero, we can extrude interdigitated, high aspect ratio structures for battery electrodes. Alternating pastes are co-extruded side by side to form a fine vertically interdigitated layer structure. The relative thicknesses, widths, and lengths of the deposited features can be varied by altering the paste parameters, printhead geometry, and process parameters. The vertical stripes can be tuned for improved power or energy giving the electrode designer more freedom to optimize the overall cell.

The foundation of the co-extrusion performance gain is to geometrically structure the electrodes to include specific regions of optimized ionic and electronic conductivities for charge transport, together with other regions of increased energy-storing lithium densities, Through proper design of these respective regions, the effective current path can be shortened while at the same time increasing the lithium storage density (see Fig. 4). The conductive regions also allow the electrode layers to be 2 to 3 times thicker than the typical 100µm without increasing internal losses, resulting in a larger fraction of Li compared to current-collector and separator overhead materials which further increases energy density. The result is a significant net increase in battery energy density and power.

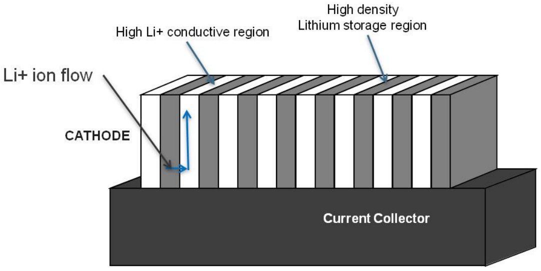

Figure 4: Schematic of Li Ion flow

Modeling and proof-of-principle demonstration for $LiCoO_2$ battery half-cells show that structured electrodes can increase power and energy density by 20% (or alternately, reduce cell cost by 20% for equivalent energy). Figure 5 presents electrochemical modeling results for different $LiCoO_2$ cathode geometries using the multiphysics package, Comsol [5]. The results show comparisons between a conventional monolithic electrode and expected performance limits of a structured electrode. Figure 6 demonstrates how the structured electrode increases Li utilization by shortening conduction paths which in turn increases the utlization of Li at high C-rates.

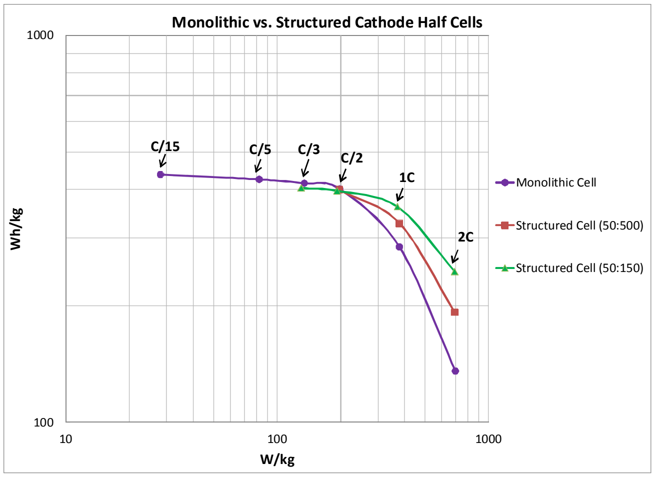

Figure 5: Modeling energy density results for interdigiated $LiCoO_2$ half cell batteries.

These structural optimization gains in Li utilization have been demonstrated in this system but are applicable across different battery chemistries as well.

To date, PARC has experimented with $LiCoO_2$ sintered half-cells, structuring cathodes with high density Li regions and low density conduction regions as illustrated in Fig. 7.

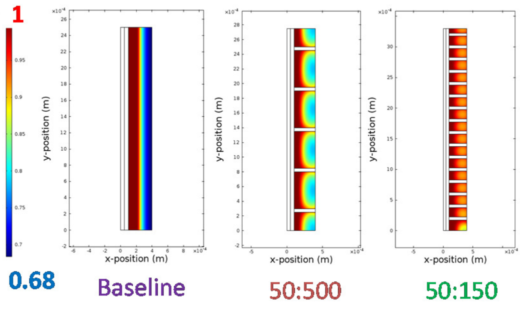

Figure 6: Normalized Li unilizationat the end of a 1C discharge.The structured cells have 50um wide and 300um tall regions of pure electrolyte which enable better active material utilization at higher C-rates.

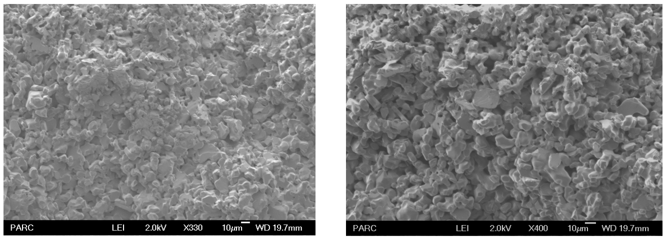

Figure 7: Photomicrographs of dense (left) and porous (right) region differences in $LiCoO_2$

PARC's half cells have demonstrated up to 75% improvement in gravinometric energy density at some discharge rates relative to the same monolithic cathode material, as illustrated by recent test results shown in Fig. 8.

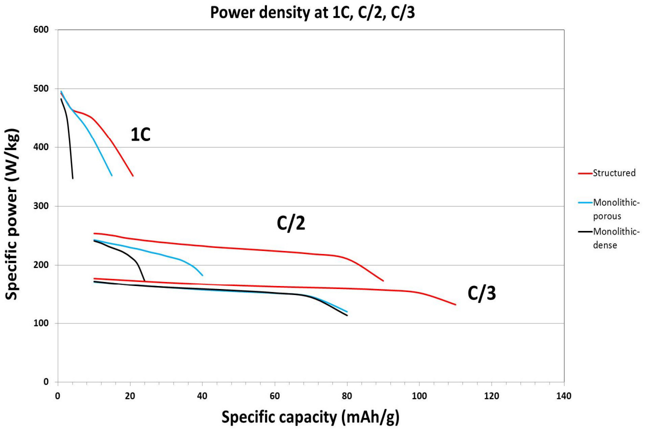

Figure 8: Power densiy at different discharge rates

6 OTHER CO-EXTRUSION APPLICATIONS

PARC has developed co-extrusion applications in solar and batteries, but the coextrusion technology may also be applicable to other applications that require surface area control in a packed media. For example, flow in a filter media could be preferentially directed by using alternating regions of different densities. Ultracapacitors, electrostatic energy storage devices, can also benefit from having structured porous electrodes. Structured electrodes made via co-extrusion would offer a higher usable electrode surface area which in theory can increase the energy density of the ultracapacitor by increasing the amount of charge stored on each electrode.

7 CONCLUSIONS

This work demonstrates the feasibility of co-extrusion printing for solar cell metallization and battery electrode fabrication. Advantages over other methods include:

- No physical contact with the substrate
- High aspect ratio features
- Improved dimensional stability
- High speed operation
- Proven efficiency gain in both solar and battery applications

Furthermore, in contrast to other proposed alternatives to screen printing for solar, our extrusion printing process requires only a single process versus separate seed-printing and plating steps. We believe that these advantages compare favorably not only with screen printing but also with emerging alternatives to screen printing for many solar cell applications. For battery aplications, co-extrusion allows structural improvements to electrodes that are not available to batteries designed with conventional coating methods.

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