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Inks for Li-ion battery anodes printed by rotogravure

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Short abstract

Inks for Li-ion battery anodes were formulated for printing with the rotogravure printing process. Graphite with different particle sizes were used as conductive materials along with nanoparticle carbon fillers. As polymer binders, polyvinylidenefluoride PVDF (commercial names Kureha 9100, Kureha 9300, Solef 5130) and polyvinyl pyrrolidone (PVP) were tested. Inks were printed using proprietary gravure engraving. Ink solid content of 30–70 % was examined. At 70 % solids, ink layers were 25–27 µm thick with mass loading of 2.1–2.5 mg/cm^2. Half cells were made using print with 1 000 µm holes or they were bar coated. Half cells were charged and discharged in order to measure irreversible capacity loss (ICL). Inks with mixed binders Kureha/PVP were performing better than sole polymers. Half-cell testing revealed that PVP should be mixed with PVDF for improved performance. ICL was lower when mixed PVDF/PVP binder was employed.

Keywords: printed batteries, anodes, rotogravure, ink formulation, half-cell, capacity, irreversible capacity loss

1. Introduction and background

Due to the increasing impact of oil pollution on the environment (CO_2 production and liquid spills), more automobile and many other industries have turned to electric item manufacturing. Therefore, the production of more energy-efficient and environmentally friendly batteries has become a hot topic at the moment. The traditional lead-acid battery is bulky and heavy, but the printed battery can print much thinner and lighter batteries through the printing process to provide power for wearable devices, flexible displays, smart labels among others (Costa, Gonçalves and Lanceros-Méndez, 2020; Khan, Lorenzelli and Dahiya, 2015). With the advent of printed electronics, flexible batteries have undergone rapid development in the past ten years. Currently, many researchers are focusing on screen printing of battery electrodes. This printing technology can use semi-liquid inks for printing, which allows them to have good coverage on substrates of different materials, such as paper, plastic, or foil, which are suitable for printing lithium metal battery electrodes (Khan, Lorenzelli and Dahiya, 2015). Based on the size required to print battery electrodes, the number of active materials, the roughness of the electrode layer, and the thickness of each layer of the battery can be modified. There have been many studies using printing methods such as gravure printing, flexographic printing, screen printing, extrusion printing, and inkjet printing to explore battery electrodes production (Søndergaard, Hösel and Krebs, 2013; Huebner, et al., 2015). Lithium metal powder-based inks, which include lithium metal powder, polymer binders, and other conductive materials, can be used in anode printing. In general, the advantages of printed batteries are based on mature printing technology, and the fact that they are light, flexible, low cost, can be mass-produced, customizable, and more environmentally friendly.

Research in the printed batteries based on gravure printing showed that the quality of the gravure printing layer mainly depends on several physical parameters such as ink, substrate, and process. To enable the mass production of batteries through gravure printing, the study was done using carbon coated $Zn_{0.9}Fe_{0.1}O$ (encapsulated in a thin film of carbon) as a reference alloying material (Bresser, et al., 2013). With the water based electrode inks, 2-propanol can be used as a cosolvent to reduce the excessive surface tension of water-based inks, in combination with corona pretreatment of the substrate, for increased surface energy and thus ink adhesion (Biscay, Ghoufi and Malfreyt, 2011). Using the gravure printing process, multiple layers can be deposited, and the multilayer method applied is able to obtain the required mass loading (about 1.7 mg/cm^2) to achieve high homogeneity of the gravure printing layer, and its highly reproducible electrochemical performance up to 400 life cycles (Montanino, et al., 2021).

Printing inks for anode and cathode inks include active materials such as graphite, silicon, or active fillers such as nanocarbons, and resins or binders which were selected based on ink chemistry whether ink was solvent, or water based. Resins can include among others itigated polyacrylic acid, or polyvinylidene fluoride of different degree of polymerization. Printed layers should be thick, preferably up to 100 µm and therefore screen-printing is the process of choice (Rassek, et al., 2019). In this work, the aim was to formulate rotogravure printing inks for anodes and evaluate their printability in terms of print uniformity, thickness of the layers and ultimately, half-cell battery performance.

2. Materials and methods

A Thinky Mixer AR 100 (THINKY Co., Tokyo Japan) was used for mixing the inks. As the conductive graphite Philips 5 µm, 10 µm, 15 µm (Philips 66, Houston, Texas) and Mage 3 graphite (Hitachi Chemical, Sakuragawa, Japan), and conductive nanoparticle carbon filler (CB 4400 or C45) were used. Polyvinylidenefluoride (PVDF) (by Sigma Aldrich) with different degrees of polymerization and commercial names Kureha 9100, Kureha 9300 (Kureha Co., Japan) or Solef 5130 (Solvay Co.), with various molecular weights of 1×10^6 to 2.8×10^5 was dissolved in N-methyl-2-pyrrolidone (NMP) solvent and used as the vehicle. In some inks, a polyvinylidene/polyvinylpyrrolidone mix of binders (PVDF-PVP) was employed. Printing was done on Cu foil.

Rotogravure plate for RK gravure K-proofer was engraved in WRE /ColorTech (Greensboro, NC, USA) with proprietary engraving at 75 LPI. A plate was engraved with 1 000, 500, 250 and 125 µm hole shaped nonimage areas. Detail of 500 µm nonimage area is shown in Figure 1 and white light interferometry detail is shown at Figure 2, showing depth of cells at 75 µm and cell opening in one direction at 1 194 µm. Engraving was done by hybrid process of laser ablation and chemical etching.

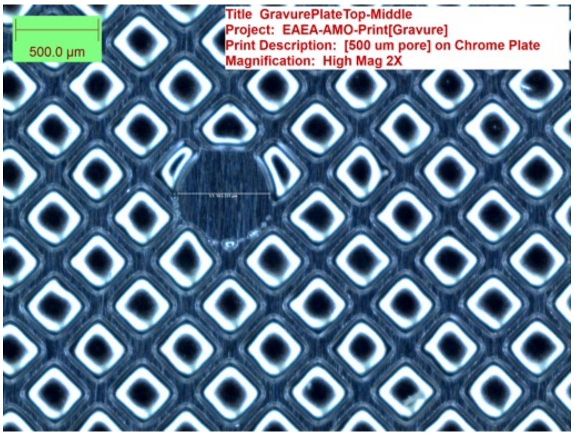

Figure 1: Detail of new gravure engraved plate (by WRE Color/Tech, Greensboro, NC, USA) with 500 µm nonimage area (round hole)

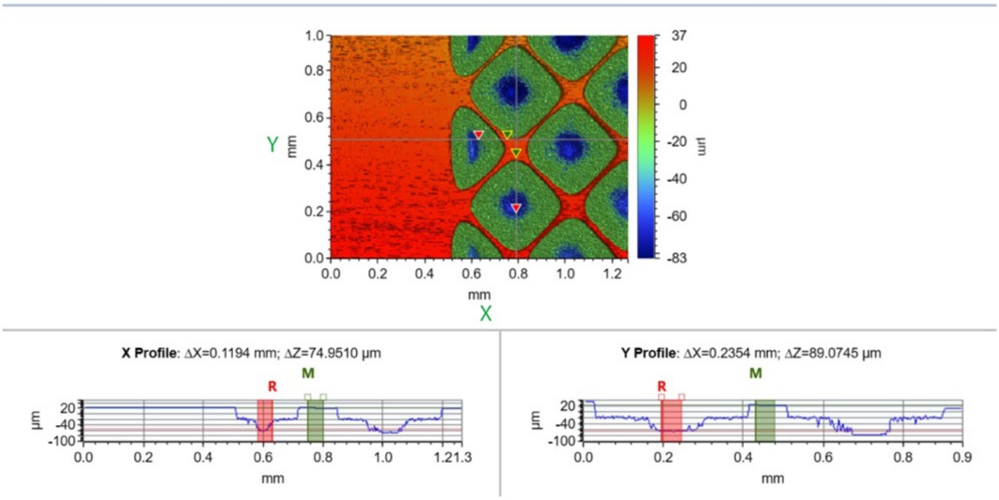

Figure 2: White light interferometry of gravure engraved plate

The profile of the plate and ink films was done on a Bruker white light interferometry instrument. Image analysis of printed ink films was done using Pax it 2 software.

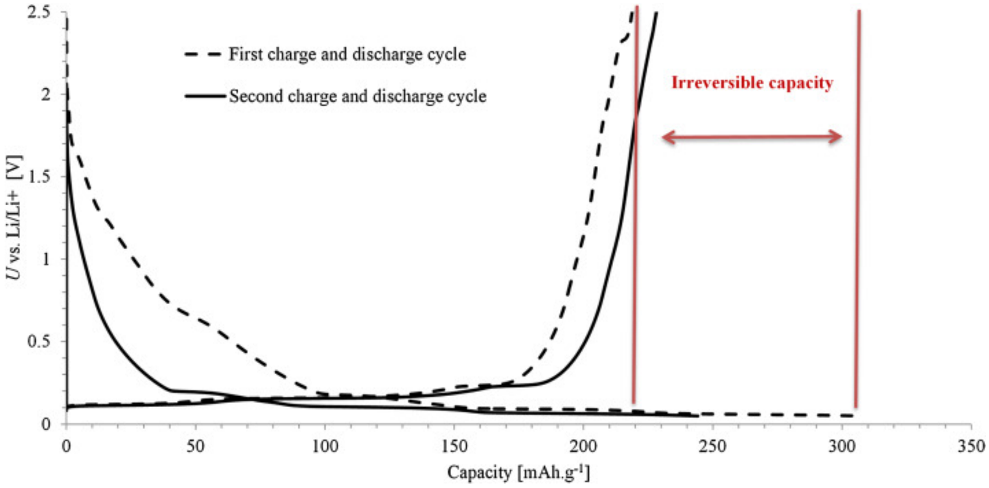

Figure 3: Illustration of irreversible capacity loss determination (Libich, et al., 2017)

Reversible/irreversible capacity and stability of the electrode can be obtained from the galvanostatic cycling technique (Figure 3). The galvanostatic cycling technique provides information about reversible/irreversible capacity and stability of the electrode. In order to test irreversible capacity loss of anodes, half coin cells were constructed (Figure 4).

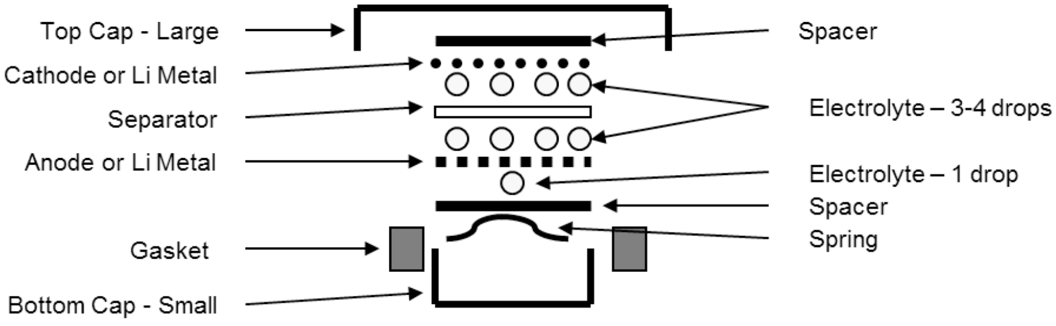

Figure 4: Schematic of half coin cell (Jansen, et al., 2018)

3. Results and discussion

A plate for rotogravure printing of anodes was engraved with 1 000, 500, 250 and 125 μm nonimage areas. Detail of engraving along with 500 μm nonimage area is shown in Figure 1 and white light interferometry detail of engraved plate is shown at Figure 2, showing depth of cells at 75 μm and cell opening in one direction 1 194 μm. Holes (non-image areas) in the electrode design are meant to improve access of electrolyte to electrodes in assembled battery. Anodes were printed with long chain polyvinylidenefluoride polymer inks such as Kureha 9300 or Solef 5130. As a solvent, with N-methylpyrrolidone (NMP) was employed. Inks were filled with graphite of different particle sizes. Gravure printing of these inks did not result in successful substrate coverage (data not shown). Because of ink's high viscosity, it most likely could not enter and exit gravure cells.

A new resin polyvinylpyrrolidone (PVP) at 10 000 molecular weight was used to disperse graphite and nanocarbon active materials. Inks with 30−72 % solids were made. Inks were formulated with Graphite from Philips (P5) with size of 5 microns, and conductive filler CB 4400 with the ratio of ingredients: Philips P5/CB 4400/PVP (80:5:15). As a solvent, ethanol or NMP were used. Ethanol was evaporating too fast, thus N-methylpyrrolidone (NMP) was chosen as a more suitable solvent. The average surface tension of NMP ink with 70 % solids was 39.4 mN/m and average contact angle with copper surface was 40.8° (data not shown). At 70 % solids, ink layers were 25−27 μm thick with mass loading of 2.1−2.5 mg/cm^2 (data not shown). Half cells were made using print with 1 000 μm holes or they were bar coated. Gravure prints with N-methylpyrrolidone (NMP) as a solvent were easier to work with than using inks with water or ethanol as a solvent. Designed holes with diameter 1 000 μm were resulting in printed 846 ± 20 μm in diameter, while 500 μm holes were printed with 219 ± 11 μm diameter (data not shown).

Printed ink films on copper foil were used to construct half coin cells according to Figure 4. Half cells were used to assess reversible/irreversible capacity and stability of printed anodes. Irreversible capacity loss of half coin cells made with PVP inks was too high and half cells did not have sufficient electrical performance. Thus, in the next step PVP was mixed with PVDF – Kureha 9100 or Kureha 9300 and half cells were made again. First attempts showed that mixing Kureha and PVP resins is possible, so far 2:1 ratio was tested, and inks exhibited uniform prints. Their performance in terms of irreversible capacity loss (ICL) was tested again (Figure 5). Inks were bar coated, not gravure printed to ensure higher thickness of layers than what was possible to achieve with gravure printing.

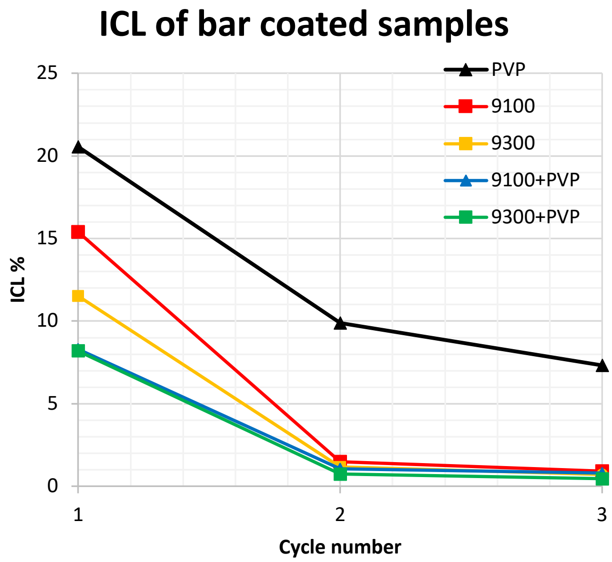

Figure 5: Comparison of half-cell battery performance (as ICL) with resins: sole PVP, sole PVDF or combination PVP/PVDF

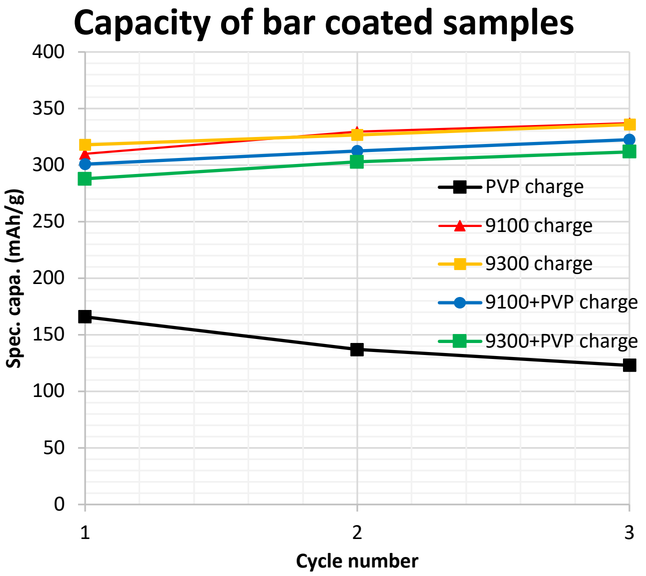

Figure 6: Capacity of bar coated samples; test conditions: formation: 0.01–1.5 V; +/– 0.1 C

From Figures 5 and 6 it can be seen that performance of mixed PVP/PVDF inks was greatly improved, and mixed PVP/PVDF achieved actually slightly better performance and suffered from less ICL than inks made with sole Kureha 9100 or 9300.

4. Conclusions

Gravure inks for battery anodes were formulated and printed on a laboratory K-proofer with proprietary engraving. It was found that polyvinylpyrrolidone (PVP) inks showed good printability but poor battery performance. Using mixed PVP/PVDF 9300 or PVP/PVDF 9100 binder combination could effectively improve battery performance without significantly sacrificing the printability. From several graphites having particle sizes between 5 µm to 15 µm, graphite with 5 µm particle size was the most suitable for gravure printing. Polyvinylidenefluoride (PVDF) inks under commercial name Kureha 9100 or 9300 with N-methylpyrrolidone (NMP) solvent showed best specific capacity during three charging/discharging cycles, and irreversible capacity loss was even lower when these PVDF polymers were mixed with polyvinylpyrrolidone.

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