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The co-casting process: A new manufacturing process for ceramic multilayer devices☆

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ABSTRACT

In this work we present a simplified process chain of the conventional multilayer ceramic technology and offer a comfortable method for precise multilayer manufacturing without complex equipment. To circumvent the usual stacking and laminating of single ceramic green tapes to get multilayer devices, a *Magnetically Assisted Stencil Printing* (MASP) technique was developed. It enables a subsequent casting of ceramic layers and printing of electrode layers. How the co-casting process can be performed either by the use of a modified tape caster at the lab scale or by use of a precision squeegee is described in this paper. Both variants are suited for manufacturing multilayer ceramics with layer thicknesses less than 25 μm. We successfully manufactured pentalayers without cracks or de-laminations from a soft- and also a hard-PZT powder. In a previous work, we investigated sintering additives for PZT. By the use of a PZT-based low-temperature sintering powder composition, cost-effective silver inner electrodes could be realized inside the multilayer ceramics. Piezoelectric low-cost multilayer bending transducers are of particular interest for the use as generators in vibration energy harvesting systems. The proposed triplelayer beam harvests 20 μW (3.2 V) at 71 Hz and an input acceleration of 17.8 m/s^2.

1. Introduction

Vibration Energy Harvesting (VEH) represents an effective method of acquiring energy from our ambient surroundings and converting it into usable electrical energy. The harvested energy is sufficient to power electronic devices as ubiquitous sensor networks of wireless sensors and communication nodes. In particular, piezoelectric VEH has the potential to create a large market and significantly impact society in view of the "Internet of Things" since it offers high power density compared to other scavenging methods [1–3]. Most of the *Piezoelectric Energy Harvesters* (PEHs) are in form of beam-shaped cantilevers and consist of one or two piezoelectric layers [4]. A variety of unimorph [5–8] and bimorph [9–11] PEHs were presented in recent times. Their geometries have been varied to increase their output voltages by matching their resonance frequencies to the low frequencies of available mankind vibration sources like machinable and human-motional. Admittedly, piezoelectric materials typically generate high voltages and small currents, in contrast to standard electronic circuits that require high currents at low voltages. Therefore, it is desirable to reduce the output voltage but simultaneously increase the output current of PEHs [12–14].

Multilayer Piezoelectric Energy Harvesters (MPEHs) have been reported to be a feasible option for reducing the output voltage while increasing the output current [9,12,14,15]. Although, an MPEH delivers not more power output than a corresponding singlelayer device of the same geometrical dimensions, its overall capacitance is much higher and so its internal impedance is reduced significantly.

On this account, an N–layer MPEH generates an N times lower output voltage but concurrently an N times higher output current [14]. This larger current can for example shorten the charging time when the harvested energy is stored in batteries or supercapacitors for sensor node operation. Most electronic devices have only several hundred ohms of resistance. Therefore, MPEHs are significantly more suitable to match the individual operating conditions of self-powered wireless sensor networks than unimorph or bimorph structured PEHs.

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There are different approaches to fabricate *Multilayer Ceramics* (MCs). The easiest approach is to stick several already sintered singlelayer ceramics together [16]. However, adhesive bonding cannot offer the required mechanical stability and additionally, deteriorates the electrical performance of the devices. Commercial piezoelectric MCs are usually fabricated as stack actuators and typically made out of soft PZT, since ferroelectrically soft piezo ceramic materials can be polarized at relatively low field strengths due to their small coercitive field strengths [17]. In 2013 Xu et al. and in 2014 Gül et al. successfully tested commercial MCs as PEHs [18,19]. Generally, power acoustic applications used in dynamic long-term operations, as MPEHs, benefit from the properties of hard piezoelectric materials. Due to their higher mechanical quality factors, their electrical properties hardly change under high mechanical loads and they can be subjected to high mechanical and electrical stresses. To be able to resonate, bending transducers need to be thin enough. For high aspect ratios low layer thicknesses are required. In case, the extensive facilities for a conventional MCs production are available, MPEHs can also be fabricated by the regular route of the multilayer ceramics technology (MCT).

However, this implies access to a tape casting unit, a screen printing stage, sheeting and stacking machines, and a heatable isostatic press with corresponding pressing tools. Unlike the industrial route for the complete manufacturing process, at most research facilities all these opportunities are not given. Stamos et al. developed a screen printable PZT paste for simplified manufacturing of MCs through screen printing for both, metal layers (that act as inner electrodes) as well as for the ceramic layers [20]. However, for screen printing MCs a substrate is needed and additionally, it has to be coated with a dielectric layer. The mismatch of the thermal expansion coefficients of the different materials can cause the dielectric film to crack and the majority of devices to short-circuit during poling. At the end, only devices with single active layers could be realized by this method. In this paper, a new co-casting process is presented. The method is fairly simple and can be easily copied for manufacturing of MCs, up to ten layers. The basic idea was to integrate screen printing into the tape casting process to circumvent stacking and laminating of single green tapes. Precise stacking requires full automation of green tape processing, and to this end we developed a *Magnetically Assisted Stencil Printing* (MASP) method. Using MASP, this integration could be realized in a very simple, cost-effective and reliable co-casting process. Here, we explain the details of preparing a pourable slurry and metal paste for performing co-casting of ceramics green tapes and printing electrodes using the MASP method.

2. The entire process chain

The established process chain of the conventional MCT was modified to avoid any handling of single green tapes. Since for manufacturing, MCs with layer thicknesses below 50 μm the green tapes have to be in the range of 100 μm thickness. However, such thin green tapes are mechanically not form-stable enough to be handled properly without wrinkling them.

Using the novel co-casting technique that is shown in Fig. 1, the ceramic and the metal layers are subsequently cast on top of each other with intermittent drying steps. By means of the new MASP method that enables patterning the internal electrode layers with a high edge definition an alternating layer build-up can be realized.

3. Preparation

3.1. Ceramic slurry

First, PZT powder was mixed with sintering additives and organic vehicles to form a pourable slurry. In this work we used two different commercial lead zirconate titanate (PZT) powders from PI Ceramic in Germany as an example for functional oxide ceramics. The first PZT modification has hard piezoelectric characteristics (PIC 181, $Q_m = 2200$, $d_{31} = -120$ pC/N, $d_{33} = 265$ pC/N) while the other PZT powder with a higher piezoelectric strain constant but significantly lower mechanical quality factor (PIC 252, $Q_m = 80$, $d_{31} = -180$ pC/N, $d_{33} = 400$ pC/N) is a soft PZT variant. The sintering additives consists of the ternary metal oxide system Li_2CO_3, Bi_2O_3, and CuO (LBCu, 1 wt.%, all from Carl Roth, Germany) that has been found during previous work to be the most effective additive to lower the sintering temperature of PZT from about 1200 °C to 900 °C [21]. The particle size distribution of the PZT powders were determined by laser diffraction (Coulter LS 230, Beckman Coulter) to $d_{50} = 1.42$ μm ($d_{90} = 2.62$ μm) for PIC 181 and $d_{50} = 0.96$ μm ($d_{90} = 1.42$ μm) for PIC 252. To achieve very low layer thicknesses of about 20 μm in the co-fired MCs, the d_{90} value should be considered to be below 3 μm. Since the raw materials of the sintering additives reveal partially larger particle sizes, they were preliminarily ball-milled in anhydrous ethanol. As a result, the mean particle sizes of these sintering additives could be set below 1 μm.

An azeotropic mixture of ethanol (abs., 1% MEK, VWR) and toluene (abs., VWR) as its solvent formed the main components of the organic additives. 3,6,9-Trioxadecanoic acid (>90%, Clariant) was added as a dispersant agent to reduce particle agglomeration. As for the temporary binder, we used polyvinyl butyral (PVB, Kuraray Europe GmbH) with a high molecular chain length. Using size exclusion chromatography (PSS WinGPC Unity), the molecular mass of the B60 H binder type was found to be 2.74×10^4 g/mol $\left(\bar{M}_n\right)$ and 5.67×10^4 g/mol $\left(\bar{M}_w\right)$, respectively. It was observed that the higher the molecular weight of the polymeric binder is, the more solvent or plasticizer is needed to set the slurry viscosity in an optimum range of about 7 Pa s at 20 °C [21]. Higher solvent amounts entail a higher drying shrinkage and significantly longer drying periods of the cast green tapes. This is why the slurry was diluted with an increased amount of plasticizer. We used a combination of polyethylene glycol (PEG-400, Carl Roth) and dibutyl phthalate (DBP, VWR) in a ratio of 1:3 as plasticizer. This led to very short drying time periods (maximum 15 min depending on layer thickness) which in-turn is crucial for a time-efficient co-casting process. A binder amount of 8 wt.-% was found to be sufficient, since no free-standing green tapes are processed in contrast to the regular MCT. The green multilayer remained form-stable and could be manually handled easily without causing defects.

All components of the slurry were ball-mixed in a Yttrium-stabilized zirconia jar for 24 h with 200 rpm using a planetary mill (Retsch, PM 400). Before casting the slurry, it was degased in an ultrasonic bath for 15 min to avoid defects in the green tapes arising due to air bubbles.

3.2. Electrode paste

A highly viscous commercial conductive paste for co-firing (Sigma-Aldrich) consisting of silver particles and (−)-alpha-terpineol was used for the intermediate electrodes. When larger areas were metallized (>1 cm^2), micro-cracks were observed in the dried electrode layers. For this reason, also PVB binder and the same solvent used for the ceramic slurry, was added to reduce the paste's viscosity (to 10 Pa s). Thereby, cracks in the electrode layers could be prevented. A PVB binder type with a middle molecular mass (B45 H) is sufficient for this purpose. We measured 1.75×10^4 g/mol $\left(\bar{M}_n\right)$ and 4.34×10^4 g/mol $\left(\overline{M}_w\right)$ as mean molecular masses for this binder type.