論 文 の 内 容 の 要 旨

論文題目　Liquid-Crystal-Enhanced Electret Vibration Energy Harvester
(液晶により強化されたエレクトレット環境振動発電器)

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Low-frequency vibration-based electrostatic/electret energy harvester is an attractive candidate for powering low-power electronics in Internet-of-Things due to many reasons; such as, abundant energy source, compatibility with MEMS technology, and high output power at small volume compared to other energy harvesting methods. On the other hand, the current performance of such generator still cannot consistently meet the energy demand of wireless sensor nodes. Thus, it is called for further development to obtain higher output power at given conditions.

One way to enhance its output power is to introduce high permittivity fluid into its dielectric gap. However, parasitic capacitance (C_p) existing between 2 sets of electrode fingers has negative effect on its output power. Correlation model for C_p has illuminated the dependency of horizontal permittivity in dielectric gap (ε_x) and substrate permittivity (ε_s) while capacitance change ΔC is proportional to vertical permittivity in the gap (ε_y). In other word, if high isotropic permittivity ($\varepsilon_x = \varepsilon_y$) fluid is used, the increase of ε_x, i.e. C_p, will limit the potential enhancement of the generator.

This thesis aims to overcome this challenge by enhancing the output power through the increase ΔC while limiting the increase of C_p through the use of high anisotropic permittivity ($\varepsilon_x \neq \varepsilon_y$) fluid; especially the ones with $\varepsilon_y > \varepsilon_x$, which should greatly boost ΔC with its large ε_y while limit the increase of C_p with its smaller ε_x.

Nematic liquid crystal (LC) with anisotropic permittivity is an interesting material, which retain both crystalline order, like solid ,and fluid properties. It can align its molecular axis with electric field. The electrical characterization for LC is conducted using impedance analyzing technique. The axial $\varepsilon_{\|}$ and transverse $\varepsilon_{\perp}$ permittivities, resistivity and threshold voltage can be measured. Common nematic LCs, 5CB ($\varepsilon_{\|}$ =18 and $\varepsilon_{\perp}$=6) and BCH-5F.F.F ($\varepsilon_{\|}$ =13 and $\varepsilon_{\perp}$=4), are chosen for introductory testing. Preliminary output power generation experiment with electrostatic vibration energy harvester has been conducted. With 5CB and BCH-5F.F.F, the enhancements of output power are respectively 87 and 67 times higher compared to that conventional air-in-the-gap. C_p is measured and its ε_x is founded to be similar to isotropic permittivity of LC ($\varepsilon_{iso}=(\varepsilon_{\|}+2\varepsilon_{\perp})/3$).

On the other hand, it is widely known that the electret has poor surface charge stability with low resistivity fluid. With the characteristics of LC that resistivity is the inversely proportional to anisotropic permittivity ($\Delta\varepsilon=(\varepsilon_{\|}-\varepsilon_{\perp})$), it leads to the trade-off between generator's life time and its output power. To verify this, we choose the high resistivity LC, MLC-7030 ($\varepsilon_{\|}$=6 and $\varepsilon_{\perp}$=2.8), which has bulk resistivity of 10^{16} Ω·cm. On the other hand, LC is known to be easily contaminated by ionic impurity and absorption of water vapor. Impurity/humidity control, such as cleaning and isolation method, have been implemented. Preliminary experiment is performed. It is found that, with adequate impurity/humidity control of cleaning test cells in ultrasonic bath with IPA before use and sealed it with low-impurity epoxy, high resistivity of LC can be realized for a long time while only cleaning cannot retain high resistivity overtime and uncleaned cell results in very low resistivity. By cleaned generator and keeping relative humidity below 10%RH, LC-enhanced electret vibration energy harvester is realized for the first time. With MLC-7030, the maximum output power is 139 μW at 68 MΩ which is 7-times higher compared to that of air gap (19.8μW). High output power could be kept for over 40 hours. This also suggests that further impurity/humidity suppression is necessary for long-term performance of such generator.

For further development of LC-enhanced electret vibration generator, accurate output power model is necessary. This calls for the detailed investigation of molecule alignment inside LC-enhanced electret generator. 2 measurements are performed; static molecule alignment and dynamic molecule alignment. For static molecule alignment, Fourier-transform infrared spectrometer (FT-IR) with narrow-band detector and spatial resolution of 9×9 μm^2 is used. The molecule alignment can be captured by sensing the characteristic absorption of axial bonds. Test cell is fabricated from CaF_2 substrate with patterned ITO electrode and coated with rubbed polyimide alignment layer for initial planar alignment. BCH-5F.F.F is chosen for this investigation due to its noticeable characteristic bonds. From the preliminary test, relation between IR absorbance and permittivity is established. It is founded that the LC molecules gradually change their alignment over the interdigital gap from horizontal alignment (i.e., $\varepsilon_{\perp}$) at grounded electrode to vertical alignment (i.e., $\varepsilon_{\|}$) at electrode with strong electric field from applied voltage. The misalignment at interdigital gap is caused by the fringe electric field between high-voltage electrode and other grounded electrodes. Estimation of about 100 μm from electrode edge has been affected from the misalignment during idle state. The effect is progressively lessened until no change in alignment is observed under both grounded and charged electrodes. Hence, the overall alignment, i.e. average ε_y, under each region does not significantly affected by the misalignment.

Dynamic molecule alignment data is captured using polarized optical microscopy (POM) equipped with high-speed camera. By utilizing the cross-polarizer, alignment of LC can be determined. Electret vibration generator with ITO electrodes is fabricated with Al_2O_3 as insulation layer and CYTOP-EGG as electret. Electret is charged to -1kV with soft x-ray charging technique. An environmental chamber is employed to isolate generator from outside humidity. MLC-7030 is chosen for this measurement due to its high resistivity. From preliminary test, POM images can be interpreted into ε_x, ε_y and, alignment angle θ. Output power generation experiment is performed and POM images is captured at optimal resistance. Real-time in-situ alignment change of LC inside the generator has been observed for the first time. It reveals that the alignment at interdigital gap is periodically changing and mostly affected by high electric field from charged electret. Consequently, time-averaged C_p is slightly larger compared to the correlation model. At low $\Delta\varepsilon$ but large ε_s, the effect of dynamic alignment at interdigital gap may be small. But, with large $\Delta\varepsilon$ and ε_s, the effect could be more noticeable. Similar to results from FT-IR, the alignment at charged electret region maintains constant vertical alignment due to high electric field strength of electret. On the other hand, LC molecules align quite horizontally in grounded area due to Al_2O_3 acts as horizontal alignment layer. Furthermore, it should also be noted that effects of oscillating flow and unsteady electric field are negligible due to high electric field strength of electret.

Based on LC characteristics and information on molecule alignment, this study develops 1-D electrostatic model with field-dependent permittivity and dynamic C_p. The present model agrees well with the experimental results. The performance of LC-enhanced electret vibration energy harvester is predicted using the proposed 1-D model by comparing its electrostatic damping force and viscous damping force, which represents output power and viscous loss, respectively. Due to the limit of $\Delta\varepsilon$ for high resistivity is 5, the upper limit of output power enhancement is 12. Viscous energy loss by LC is approximated using rotational electret energy harvester model. It is found to be dependent on rotational speed rather than $\Delta\varepsilon$, i.e. viscosity, of LC. With MLC-7030, viscous energy loss is estimated to be about 1/9 of electrical output power. Figure of Merit (FoM) for comparing the output power enhancement effects of different fluids is defined. Comparing to isotropic liquids, both power enhancement and FoM of MLC-7030 with $\Delta\varepsilon$=3.2 are much higher at about 17 and 14.4, respectively.

In regards to impurity/humidity control for LC, this thesis proposes the use of ferroelectric material for impurity control in LC-enhanced electret generator. By utilizing its local electric field from remnant polarization of ferroelectric materials, ionic impurity could be permanently trapped; leading to the realization of long-term high resistivity in LC. $BaTiO_3$ and $LiTiO_3$ are chosen to verify long-tern resistivity retention property of ferroelectric/LC mixtures. For the verification, LC doped with metal oxide particles, TiO_2 and ZnO, are also examined to validate the effect of ferroelectricity and chemisorption effect on impurity control. With 0.1wt% of $BaTiO_3$ particles, MLC-7030 can keep its high resistivity of 10^{16} Ω·cm for over 1000 hours. On the other hand, at least 0.5wt% of metal oxide particles is needed to reach similar results. This proves that ferroelectricity is more beneficial in impurity control than chemisorption effect. Despite its promising potential, This method is found to be incompatible for charged electret because of the particle accumulation on electret surface.

In the present study, $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin film fabricated by atomic-layer-deposition (ALD) is proposed as ferroelectric film for impurity control. Thermal ALD and plasma-enhanced ALD process are investigated. Based on x-ray diffractometry (XRD) and piezoresponse force microscopy (PFM), post-deposited annealing with deposition temperature of 250˚C and annealing temperature of more than 400˚C, i.e. relatively high thermal budget, is found to be essential in realizing high remnant polarization and multiphases in the HZO films. By using thermal ALD HZO film with deposition and annealing temperature of 250˚C and 600˚C, the high resistivity of 5μm-thick and 100μm-thick MLC-7030 can be kept over 10^{16} Ω·cm for more than 1000 hours and 800 hours respectively.

In conclusions, the present thesis proposes a method to enhance the output power through boost of ΔC while limit the increase of C_p using nematic LC with anisotropic permittivity. Enhancement of up to 90 times has been achieved with electrostatic vibration energy harvester and common LCs. Low resistivity of permittivity fluids is found to be the common trait for electret discharge. By keeping resistivity of nematic LC over 10^{16} Ω·cm with proper impurity/humidity control, LC-enhanced electret vibration generator has been realized for the first time with MCL-7030 ($\Delta\varepsilon$=3.2); 7-times higher output power compared to conventional air gap is kept for over 40 hours. Based on the characterization of LC molecule alignment inside the generator using FT-IR and POM, 1-D electrostatic output power model with field-dependent permittivity and dynamic C_p has been developed. The model agrees well with experimental data. Performance of LC-enhanced electret vibration generator is predicted. The upper limit of enhancement is found to be 12 due to the maximum anisotropic permittivity for high resistivity over 10^{16} Ω·cm is $\Delta\varepsilon$=5. Viscous energy loss is estimated and found to be strongly dependent on velocity and surface potential. For MLC-7030, the enhancement ratio and FoM are 17 and 14.4, respectively, which are much higher than any other isotropic permittivity liquids. Impurity control using ferroelectric materials for LC-enhanced electret vibration energy harvester has been proposed; ferroelectric particles and thin films. In preliminary experiment, ferroelectricity is found to be more beneficial in impurity control than chemisorption effect. By adding 0.1wt% $BaTiO_3$, high resistivity over 10^{16} Ω·cm of MLC-7030 is maintained for over 1000 hours; though, it is found to be unsuitable for the generator due to particles agglomeration; leading to electret discharge. Instead, ALD-deposited HZO thin film is proposed for impurity control because of its stationary structure and low thermal budget compared to common ferroelectric thin films such as PZT. Based on XRD and PFM characterization for phase/polarization direction, it is found that relatively-high thermal budget is necessary to realize multiphases and high remnant polarization in HZO thin film which serves as impurity trapping site. By using thermal ALD film with deposition and annealing temperatures of 250˚C and 600˚C, resistivity of 100μm-thick MLC-7030 can be kept high over 10^{16} Ω·cm for more than 800 hours.