

Preface

Living bone is an electrically active tissue i.e. it is piezoelectric, pyroelectric and ferroelectric. In addition it is also an electret material. These electrical properties facilitate the growth of bone tissue as well as fracture healing. This is because, on external stimulation such as mechanical or electrical bone develops polarization charges and these charges further assists in various bone metabolisms for remodelling/reconstruction, growth and development of bone tissue. Therefore, development of electrically active materials having similar electrical characteristics with that of bone is clearly a need of hour. Hydroxyapatite (HA), a ceramic biomaterial has been recognized as a potential choice for the prosthetic orthopaedic implant due to its structural and chemical similarity with the bone apatite. However, synthetic HA possess poor electrical properties. Therefore, the present work attempts to enhance the electrical properties of HA by means of development of piezobiocomposite as well as functionally graded materials.

Secondly, it also needs to be emphasis here that the application of external electric field (E-field) is reported to enhance the osseointegration of the bone cells on the biomaterials substrate. In addition, E-field is also demonstrated to increase the functionality of living bone. Therefore, the study of the effect of E-field at the cellular level is necessary to overall predict the parameters of E-field which can have a fruitful effect on osseointegration as well as on bone functionality. Therefore, to begin with, this study analytically computed the coupling response of a single living cell with external electrical stimulation. For this purpose, four different electrical equivalent models of a living cell have been considered, based on the flow of ionic currents under an applied potential difference. In the first two models, only cell membrane has been considered to be a leaky dielectric while in the last two models, both, the cell and nuclear membranes were considered as leaky dielectrics. Thereafter, the time constants of these models were evaluated. Further, variation of time constant with various

cell parameters such as cell size, capacitance of cell and nuclear membrane, resistance of cell and nuclear membrane as well as cytoplasm and nucleoplasm was studied. To validate these models, intensity of E-field was evaluated for the well-known electroporation phenomenon using these models. These values are to be well within range of E-field values, generally used in electroporation experiments with a similar cell and E-field parameters. The E-field values were also evaluated for other duration of E-field pulses e.g., millisecond, microsecond and nanosecond pulses.

In the second part, to enhance the electrical properties of HA i.e. its polarizability, piezobiocomposite was developed using ferroelectric sodium potassium niobate ($\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$, NKN) which has been recognized as a prospective orthopaedic implant material. Therefore in this study compacts of HA, NKN and HA-25 vol% NKN (HA-25NKN) were developed via multi-stage spark plasma sintering (SPS) route (950°C , 5 min). Various characterizations such as phase analyses and microstructural analyses were carried out for these developed compacts. Electrical characterizations such as thermally stimulated depolarization current (TSDC) measurement, dielectric and ac conductivity behaviour was carried out for these compacts. For TSDC, compacts of HA and NKN polarized at various polarizing field (E_p ; 30, 50 and 90 kV/cm at 150°C for 1 h). While compact of HA-25 vol% NKN (HA-25NKN) composite was polarized at 90 kV/cm. The TSDC was measured at various heating rates (β) of 1, 5 and $10^\circ\text{C}/\text{min}$ upto 500°C . From the TSDC spectra it was revealed that the charge density in HA has increased from $1.12 \mu\text{C}/\text{cm}^2$ to $2.27 \mu\text{C}/\text{cm}^2$ with the increase in the polarizing field (E_p) from 30 to 90 kV/cm. To examine whether the bulk electrical properties are not altered under such a high E-field (90 kV/cm), dielectric and ac conductivity behaviour was investigated for polarized (90 kV/cm) and unpolarized HA. Thereafter, X-ray photoelectron spectroscopy (XPS) is also carried to inspect the alteration in the surface chemistry of HA under such high polarizing E-field (90 kV/cm).

In the TSDC spectra of NKN, the phase transition temperatures were shifted towards higher temperature region with the increase in polarizing field. In the case of HA-25NKN, the TSDC spectra revealed the charge density in the composite system was $6.4 \mu\text{C}/\text{cm}^2$ for polarization at 90 kV/cm. Therefore, there is a significant rise in polarization charge as compared with that of monolithic HA for similar parameters of E_p and heating rate (β). Similarly, to examine the alteration in the bulk electrical properties dielectric and ac conductivity behaviour of polarized (90 kV/cm) and unpolarized NKN and HA-25NKN was carried out. The dielectric constant values of HA-25NKN ($\epsilon \sim 62$) were significantly larger than that of pure HA ($\epsilon \sim 30$). Though, with the addition of NKN phase in the HA matrix, polarizability of HA-25NKN composite system has significantly increased but the excellent biocompatibility of HA has been sacrificed.

Therefore, functionally graded materials (FGMs) comprising of piezoelectric barium titanate (BaTiO_3 , BT) and non-piezoelectric calcium titanate (CaTiO_3 , CT) are developed. BT and CT are suggested to be prospective prosthetic implants for orthopaedic applications. Therefore, FGMs of HA-BT-HA and HA-CT-HA are developed via SPS (1100 °C, 10 min) route. To compensate the thermal mismatch between HA and BT/CT layers, buffer interlayers were inserted between HA and BT as well as in HA and CT layers. Microstructural analyses revealed no crack or delamination of the different layers in the FGMs. Electrical characterizations such as dielectric, ac conductivity behaviour and impedance spectroscopic analysis was carried out over wide range of temperature (35-500°C) and frequency (1 kHz to 1 MHz) for the developed FGMs. The dielectric constant values for the HA-BT-HA ($\epsilon \sim 29$) and HA-CT-HA ($\epsilon \sim 32$) at room temperature (35 °C) and 10 kHz of source frequency were almost double with that monolithic HA ($\epsilon \sim 16$). Overall, in the developed FGMs, the polarizability of HA was fairly enhanced without the alteration in the surface chemistry i.e., excellent biocompatibility.