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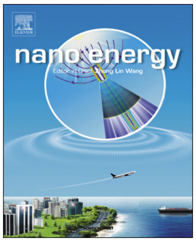

Coupling of piezoelectric effect with electrochemical processes

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Abstract
The coupling effect between piezoelectric polarization and electrochemical processes depicts the engineering of charge-carrier conduction characteristics at the heterojunction between a strained piezoelectric material and a chemical solution. It is a unique subcategory of piezotronics. This mini review paper introduces the fundamental principles of such coupling effects. Applications of this coupling effect are reviewed and discussed in several different aspects, including selective etching enabled by piezo(ferro)-electric polarization; selective (photo)electrochemical deposition directed by piezo(ferro)-electric potential; and the directly utilization of piezoelectric potential to drive electrochemical reactions (piezocatalysis). At the end, perspectives of this coupling effect are discussed as a new approach in the fields of corrosion management, nanomanufacturing and renewable energy conversion.

Introduction

Piezoelectrics are a class of materials that create an electric field in response to mechanical deformation. The origin of the electric field (i.e. piezoelectric field) is a break in the inversion symmetry which lead to electric dipoles within the material, the strength of which changes as the material is strained. The changing dipole field leads to a change in the electric field which permeates the material (Fig. 1). Piezoelectrics as a phenomenological description encompasses three subcategories of materials: ferroelectrics, pyroelectrics and piezoelectrics (Fig. 2) [1,2]. Piezoelectric materials that are non-ferroelectric and non-piezoelectric (e.g. SiO_4) have no electric dipoles when under no strain, but upon strain there is a separation between the positive and negative charge centers which results in an non-zero electric field. Pyroelectric materials that are non-ferroelectric (e.g. $LiTaO_3$) exhibit spontaneous polarization: even in the absence of mechanical deformation or an electric field, the positive and negative charge centers in each unit cell do not coincide, giving rise to a resultant electric dipole. Upon strain, the separation between charge centers changes and thus the electric field changes. Pyroelectric materials will also experience a change to their dipoles when subjected to a change in temperature. The polarization in piezoelectric materials that are not ferroelectric is not permanently changeable by applying an external electrical field. Ferroelectric materials (all of which are piezoelectric) also contains a spontaneous polarization in the absence of strain, as well as a

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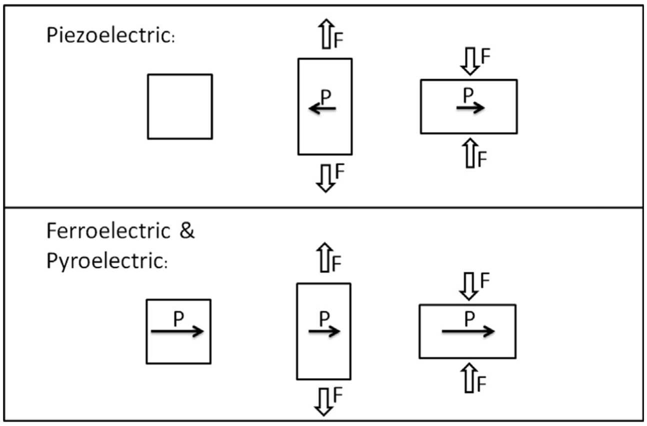

Fig. 1 (a) Piezoelectric materials that are non-ferroelectric and non-pyroelectric being with zero internal dipole. When these materials are strained, the lattice displacement creates dipole moments that create an electric field across the material. (b) Ferroelectric and pyroelectric materials have spontanious dipoles without strain. When these materials are strained, their dipoles change in strength, again changing the electric field saturating the material.

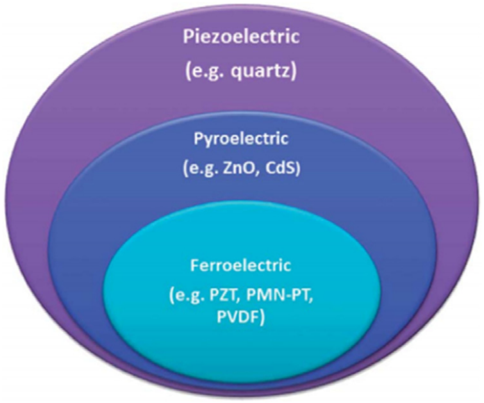

Fig. 2 Piezoelectric materials experience a change in internal dipole moment when mechanically deformed. Pyroelectrics are kind of piezoelectric material which have spontaneous dipoles in the absence of mechanical deformation. The dipoles cannot be made to permanently switch direction by applying an external electric field. The spontaneous dipoles of pyroelectric materials changes as a function of temperature. Ferroelectric materials are a special subclass of pyroelectrics. The spontaneous dipole in ferroelectric materials can be made to permanently change orientation by applying a strong enough external electric field.

temperature-sensitive polarization, but differ from the other classes of materials in that a ferroelectric material's spontaneous dipoles need not necessarily align from one unit cell to the next. Regions in which neighboring dipoles are aligned with one another are called domains. The direction of spontaneous polarization in a ferroelectric's unit cell can be changed if exposed to a sufficiently strong electric field.

The electric field exhibited by piezoelectric materials, whether strain induced, temperature induced, or spontaneously realized, can have a dramatic effect on the electronic properties both inside and outside of the material. Electric fields disrupt the energy of electronic states throughout the material (Fig. 3a) and can cause the rearrangement of free charge inside and outside of the material (Fig. 3b). This electronic rearrangement can dramatically affect charge-carrier conduction characteristics at the heterojunction between a piezoelectric material and another medium, because these characteristics depend sensitively upon the continuity of occupiable electronic states from one medium to the other and on the number of charges free to move between the mediums. This phenomenon is known as the piezotronics effect [3-5]. One such heterojunction that is particularly dynamic is that which exists between a piezoelectric material and a chemical solution [6,7]. Piezoelectric fields have been used to control the corrosion rate of materials exposed to etchant solutions [8-18], selectively control the energetics and spatial separation of adsorbed [19,20] and photo-deposition materials [21-28], and have even been used to directly drive electrochemical reactions across piezoelectric/solution interface [6,7,29-31].

Using piezoelectric fields to influence chemical reactions happening at the material's surface is closely related to electrochemical processes which typically take place at the surface of an electrode in contact with solution, influenced by an outside voltage source (Fig. 4). A chemically stable electrode material in contact with solution containing electroactive species will arrive at a steady state electrochemical equilibrium between the electrode and solution (Fig. 4a). Applying a voltage to a metal electrode can have one of two results: (1) the electrode potential rises above that of unoccupied states in solution, or (2) the electrode potential drops below that of occupied states in solution. In the first case it is now energetically favorable for there to be a net electron flow from occupied states in the electrode to unoccupied states of electroactive species in solution (i.e. cathodic current, Fig. 4b). In the second case it is energetically favorable for a net flow of electrons to come from occupied states of species in solution into the unoccupied states in the electrode (i.e. anodic current, Fig. 4c). In the case of an insulating piezoelectric material (Fig. 4d) the piezoelectric field, induced by mechanically deforming the piezoelectric material, exerts an energy shift on the occupied (valence band) and unoccupied (conduction band) states throughout the material. With sufficient shifts in the energies of these states, it is possible to drive the flow of electrons from the piezoelectric's surface to species in solution or from species in solution to the piezoelectric's surface (Fig. 4e) [7]. In pyroelectric and ferroelectric materials, the presence of a spontaneously dipole means an electric field, and its associated electronic distortion, is present throughout the material even in the absence of an applied strain. It is the presence of these spontaneous dipoles that allows pyroelectric and ferroelectric materials to exhibit useful corrosion, photochemical and electrochemical properties.

Applications of the piezopotential-electrochemistry coupling effect

Piezopotential used for material removal

The selective removal of a material can have disastrous effects, such as in the case of corrosion, or being used to craft useful, precisely engineered structures like undercut etching in microelectromechanical (MEM) or nanoelectromechanical (NEM) device fabrication [32-41]. Regardless whether the process is

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