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Theoretical underpinnings of a method of reduction of operating temperature of solid oxide fuel cells under resonant light irradiation

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ABSTRACT

This study examines potential benefits of adopting ultrashort optical pulses in fuel cell technology. General principles for jumping migration of protons in resonant laser fields have been elaborated. We find that, depending upon the frequency of phonon assistance, the effective activation energy for migration can be strongly diminished when excitation pulses are used. The obtained results indicate that at room temperature the picosecond-laser-induced proton transfer in rutile type oxides is much faster than that for thermal activation. Our estimates are in good agreement with time-resolved measurements for rutile samples excited by infrared light. The fundamentals of this transfer process are briefly analyzed in the light of structure diffusion and vibrational mode models. The most important conclusion to emerge from our work is that the use of the optical stimulation shows considerable promise as a means for decreasing the operating temperature of solid oxide fuel cells based on proton hopping transport.

Introduction

Solid oxide fuel cells (SOFCs) are good candidates for stationary power installations, but the well-known problems with materials stability and performance at high temperature need to be solved. On the basis of fuel cell constructions made to date it seems that a good superionic conductor (SIC) on its own, working at intermediate temperature, is an ultimate goal of related studies [1,2]. There continues to be strong interest in the reduction of the operating temperature (OT) of SOFC in which oxide ABO_3 crystals like doped $SrTiO_3$ or $BaCeO_3$ are used as proton-conducting materials. However, none of these oxides concurrently satisfies two of the principal requirements for SOFC application (high proton conductivity and chemical stability) [1,3,4]. In light of the above, it seems likely that the role of external stimulation in improving conduction properties will expand in future.

Do recent advances in the laser technology have anything to do with these problems? The study of proton transport processes in high-temperature proton conductors (HTPCs) is far from being completed, and a better microscopic understanding of proton transfer mechanisms might open new opportunities in the solution of the OT problem. The present paper is intended to illustrate scenarios in which an additional optical stimulation of a SIC may be advantageous in the stationary generation of energy. Essentially, at high temperatures

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the hydrogen (H) transfer in HTPCs involves the passage of protons from one oxygen ion to another. A further considerable reduction in OT results if an oxide-based device uses a special-purpose optical element to excite oxide lattices on resonance frequencies at the stretching region of O–H bonds [5,6]. This is a purely technological question, and principally there are no doubts that laser field can have a strong effect on behavior of the rate (τ^{-1}) of proton movement. Since the use of femtosecond pulses is a fresh approach to the study of fast processes in condensed media [7], one can reasonably imagine that such laser excitation can indeed be put to work in a highly efficient SOFC system as a trigger for some proton transfer reactions, like those involving phonons.

As we shall see, this might offer the direct possibility of exploiting the proton-phonon interaction to modulate such features of the transfer step as the activation energy E_a of hopping. This interaction can greatly improve the transport in H^+-ion conductors and gives direct insight into the way the OT can be optimized. With the proper combination of the strength of this interaction and laser radiation, we can arrive at a certain temperature below which the dominant physical channel of proton transfer is a classical looking phonon-assisted hopping. An intriguing result is that for rutile TiO_2, such specific temperature may, in some cases, be close to room temperature in view of natural causes [8]. This can be called the optimum temperature (denoted later as T_0) because the ratio between phonon-assisted and thermally activated rates is greatest at (or at least near) T_0. This latter is associated with some average phonon frequency, and this study presents a way to justify such relation.

For laser pulses of 1 ps duration, we will report here some relationships between kinetic characteristics, such as τ^{-1}, and dynamic parameters of oxide lattices needed to describe the proton-phonon interaction. There are basically two types of proton-related coupling constants known respectively as a proton-phonon coupling parameter u^2 capable of modulating the barrier height (E_a) and a coupling A by which some effect of the interaction is absorbed in the preexponential factor [5,6]. We will show how the experimental evidence for the optically stimulated proton transport in TiO_2 single crystals having quasi-one-dimensional c-channels for easy diffusion might be interpreted in the light of the concept of the phonon assistance of a frequency Ω, a notion introduced in Ref. [8] in order to describe a unique mode to which the unstable O–H oscillator of a high frequency ω is to be coupled. For TiO_2 lattice saturated with H_2 or D_2, one is concerned mostly with localized vibrational modes of the O–H stretch ($\omega = 3287\ cm^{-1}$) or O-D stretch ($\omega = 2445\ cm^{-1}$) types [5] (here D refers to deuterium). It is known also that for solids, the transfer of vibrational energy typically proceeds toward low-frequency degrees of freedom [9]. The perhaps simplest realistic scenario of resonant activation of protons is that in which these two basic oscillator frequencies differ by a factor of 10 (i.e., the most likely condition for two phonon oscillators involved is $\omega/\Omega \sim 10$). So, in the framework of our theory, the mentioned necessary condition for Ω to attain a moderate value is simply a generalization of experimental facts.

At favorable conditions, the low-temperature over-the-barrier proton motion can occur in laser fields with a giant value of τ^{-1}, as revealed by time-domain pump-probe techniques [5]. In general, these latter become very important for both understanding the nature of the superionic (superprotonic, in our case) state at the ionic level in HTPCs and SOFC application. In the context of our problem, the pump-probe experiment permits both making an O–H vibrational mode decay (which offers an alternative to the thermal H-bond breaking process characteristic of the diffusion at high temperatures) and lifetime observation. This time-resolved knowledge is helpful in defining the course of the overall relaxation process, which, with this method, should be uniquely determined as a sort of hopping motion. However, the exact nature of this vibrational relaxation channel can only be inferred, since it has not been observed directly (it requires further research for clarification). By purely mathematical reasoning it is possible to establish a claim that such relaxation can manifest itself as a proton hopping transfer, such that the newly forming effective barrier to be surmounted is an (u, Ω)-depending function. Here, this barrier is designated as $E_a^{(d)}$ in contrast to E_a in a conventional SIC operated at high temperatures, which is static. Correspondingly, pump-beam-induced proton flow and diffusion (the former is assigned to the dissociation of O–H bonds which involves transferring proton, and the latter is identified with further relaxation) are to be related to a newly appearing reaction coordinate q correlated to the phonon assistance direction. To be more specific, in the pioneering experimental study [5] the OH lifetime T_1 was perfectly fitted by our lattice-assisted proton hopping (LAPH) model with a specified $E_a^{(d)}$, put forward originally [10] to account for some features of HTPC behavior, and all standard possible explanations (e.g., pure tunneling) do not explain it. The term "proton hopping rate" refers now to the rate at which the proton breaks its bond with the host and moves to form a bond with a different nearby oxygen [11]. As we have recently noted [6], this fitting, while correct, is not as rigorous as is required for a justified interpretation of the observed relaxational behavior. The point is that in Ref. [10] attention focuses on a formal possibility of mathematical description of the proton diffusive motion in HTPCs in terms of the polaron behavior. A new opportunity afforded by laser excitation of oxide samples is the increased probability of the direct interaction between the excited oscillator and a local phonon mode of quite arbitrary nature from the environmental lattice. Ultrafast spectroscopy analysis is growing in importance for identifying this phonon assistance (hypothetical currently) with an actual accepting mode. The present theoretical underpinnings are intended for correct analysis of T_1 (and hence τ^{-1}) in terms of phonon assistance.

The latter relates specifically to a THz transfer rate associated with a very short $T_1 \sim 1.5$ ps, both observed and produced by pump-probe technique in TiO_2 using laser pulse widths of the same order [5,11] (this is, probably, the most recent innovation of a fundamental rather than technical nature associated with a potential new generation of energy-converting devices using lasers). This classical looking (but quantum in nature [6]) room-temperature transport mechanism, unconventional in modern theory [3] of SOFC, may be useful for the laboratory fuel cell based on a traditional perovskite-related oxide system excited by picosecond optical pulses.