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Title: Proton transport enabled by a field-induced metallic state in a semiconductor heterostructure

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Abstract: Tuning semiconductor to fast proton conductor is an emerging methodology to meet demands for rapidly growing proton ceramic fuel cells (PCFCs). The key challenge for PCFCs is the proton conducting electrolyte with sufficient proton conductivity > 0.1 Siemens per centimeter for low temperatures (300 to 600 Celsius). Herein we present a novel effective methodology to design super proton conductor via a semiconductor heterostructure of $\text{Na}_x\text{CoO}_2/\text{CeO}_2$, where a field-induced metallic state at the interface accelerates proton transportation. We have realized the ionic conductivity of 0.30 Siemens per centimeter and a demonstration for PCFC of 1 Watt per square centimeter at 520 Celsius. Our results bring a new insight into proton transport mechanism by a semiconductor heterostructure methodology, which can also benefit other relevant energy applications by ionic transportation.

One Sentence Summary: Semiconductor interface with a metallic state builds up a super proton transportation highway.

Main Text: The key challenge for new generation proton ceramic fuel cells (PCFCs) is to develop high proton conducting electrolytes (1-3). Goodenough proposed to develop oxide-ion conductors based on the structural design for solid oxide fuel cells (SOFCs) (4). This approach is to design new oxide-ion conductors by using lower valence cations' doping high ones to create oxygen vacancies for O^{2-} conductivity, e.g. Y^{3+} or Sm^{3+} replaced Zr^{4+} or Ce^{4+} in zirconia or ceria fluorite structures. However, it has not yet made alternatives for the conventional yttrium stabilized zirconia (YSZ) electrolyte. A functional triple charge conducting $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY) cathode has explored a new promising strategy to bring PCFC as a competitor to SOFC (5), but the conductivities of proton ceramic electrolytes (6-8) are still far below the desired value of 0.1 S cm^{-1} . Our target is to develop functional conductors with proton conductivity of $> 0.1 \text{ S cm}^{-1}$ at 500°C to meet the demand of advanced PCFCs. Interfacial ionic transport properties in semiconductor heterostructure and local electric field (LEF) effect have unique advantages, owing to their accessibility and tunability of creating extended functionalities (9, 10). Here we introduce p-type Na_xCoO_2 (NCO) materials (Table S1) to construct semiconductor heterostructure system with n-type CeO_2 (Fig. 1A). The LEF is built to form proton transporting channels at the NCO surface to effectively modulate charge transport property and confine fast ionic mobility in the NCO/ CeO_2 heterostructure interfaces. This methodology is in strong contrast to the traditional doping crystal structures.

To understand the origin of the emergent electronic state in the NCO/ CeO_2 heterostructure, the first-principles calculations based on Density Functional Theory (DFT) were performed on three systems: bulk NCO and CeO_2 (Fig. S1), surfaces of the NCO and CeO_2 , and an interface of the NCO/ CeO_2 (Fig. 1B). The partial density of states (Fig. S2) further discoveries that the interface across a CoO_2 layer of NCO and Ce-O layer of CeO_2 causes band-bending, with the d -orbital electrons dipping below the Fermi level, thereby forming the metallic state. Further the ionic migration energy (E) provides us a new understanding for designing the optimal paths of proton transportation. Though proton may transport through the lattice of CeO_2 or layered-structure NCO, E_i ($i=1, 2$ respectively for CeO_2 and NCO) is high due to the structural bonding energy. In contrast, the $H \cdots NCO$ could provide a highly conductive path in terms of out-of-plane doping control of the in-plane electronic charge (11). The diffusion barriers are 3.17 eV (E_1) for proton migration in CeO_2 , 3.89 eV (E_2) in $Na_{0.6}CoO_2$, and 0.15 eV (E_3) at the interface, respectively. The proton barrier energy at the interface is significantly reduced more than 20 times than those of bulk CeO_2 and NCO. The interface between the NCO and CeO_2 can provide a weak bonding situation, thus building proton transport highway with much lower migration energy (Fig. 1C).

The heterostructure exhibits a sphere-shape CeO_2 cluster epitaxially grown at NCO, forming uniform sphere-cluster-by-layer morphology with a top CeO_2 cluster and an NCO nanosheet (Fig. 2A). The high-resolution image in Fig. 2B demonstrates that (111) plane of cubic CeO_2 contacts well with (001) planes of NCO nanosheets. The crystal structure and component have also been characterized (Fig. S3). Especially, the oxygen K edge spectra (Fig. 2C) in different local chemical environments of NCO/ CeO_2 further displays an additional peak localized at 539 eV (peak 2) associated with the interface region. This additional peak is resulting from the unique electronic structure caused by the aggregation of oxygen in the interface region (12). Kelvin probe force microscope (KPFM) measurement is used to characterize the interface properties of CeO_2 and NCO (13-15). The topography spatial map and the corresponding surface potentials of NCO/ CeO_2 (Fig. 2D, E) reveal that there are notable changes between interfaces. In an illustrative line scan crossing the interface of NCO and CeO_2 (Fig. 2F), the surface potential difference between NCO and CeO_2 is about 15 mV , demonstrating the existence of LEF at the

NCO/CeO₂ interface, which is also verified by the NCO/CeO₂ heterostructure film device (**Fig. 2G**) with a clear rectifying effect.

The chemical and structural characterizations of the NCO/CeO₂ hydrogenation process were performed. The hydrogenation is only occurring in the NCO structure with a noticed H···O-Co bond formation (a new peak centered at 1071 cm⁻¹) confirmed by in-situ Raman measurement (**Fig. 2H**, **Fig. S4**) while no change observed in the CeO₂ structure (**Fig. 2I**). The ex-situ X-ray absorption near-edge spectroscopy (XANES) measurements of the cobalt *K*-edge and Ce *L3*-edge from a pristine and tested NCO/CeO₂ samples are shown in **Fig. S5**, confirming the hydrogenation process only taking place during the in-situ process.

The demonstration results of the designed NCO/CeO₂ heterostructure in PCFC device are presented in **Fig. 3**. The pristine NCO is an electron conductor (16, 17), does not show any performance in a fuel cell device (**Fig. 3A**). Pure CeO₂ electrolyte due to the existence of oxygen vacancies (**Fig. S6**), exhibits 300 mW cm⁻² power output at 520 °C. With the formation of the NCO/CeO₂ heterostructure interfaces, the device reaches 1000 mW cm⁻² at 520 °C corresponding to an OCV of 1.07 V (**Fig. 3B**) with a good reproducibility, see **Fig. S7**. Such great enhancement of the power output is attributed to the synergic effects of LEF at the interface and the metallic state of NCO surface, which accelerate the proton transport through the interface of NCO and CeO₂. The NCO/CeO₂ device can even run at 370 °C, and the power density output still maintains above 100 mW cm⁻² (**Fig. 3B**). The high OCV, e.g. 1.07 V at 520 °C is agreed to the Nernst theoretical potential, indicating that the ionic transference number is close to unity, so the electron conduction has been suppressed (18, 19). Moreover, we have also investigated fuel cells consisting of different Na_xCoO₂ composite samples in various Na contents ($x = 0.47, 0.55$ and 0.71) with the existence of metallic state (**Fig. S8**). These cells demonstrated high performances of more than 550 mW cm⁻² at 520 °C (**Fig. S9**), which further support the NCO/CeO₂ heterostructure electrolytic function.

The Nyquist plot of the Na_{0.6}CoO₂/CeO₂ (2:8) cell under OCV condition measured at 490 °C shown in **Fig. 3C**. The total ohmic area specific resistance (ASR) of this cell is remarkably low, 0.26 Ω cm² for the NCO/CeO₂ thickness of 400 μm, which is comparable with the target value (0.15 Ω cm²) for a 15 μm thick electrolyte used for high performance PCFCs. The Nyquist plot is modeled by an equivalent circuit with an ohm resistor (R_o) and serial elements each consisting with a resistor ($R_i, i=1, 2$), and a constant phase element ($CPE_i, i=1, 2$), as summarized in **Table S2**. These two semicircles (**Fig. 3C**) originate from the electrode polarization resistances. The corresponding ionic conductivity of NCO/CeO₂ measured at fuel-cell condition is presented in **Fig. 3D**, and compared with several other best oxygen-ion and proton conducting electrolyte materials (20-22). The NCO/CeO₂ exhibits the highest ionic conductivity, 0.30 S cm⁻¹ at 520 °C (0.24 S cm⁻¹ at 500 °C), also the lowest activation energy, 0.27 eV.

The proton conduction in NCO/CeO₂ was further verified from two experiment approaches. The first is to construct a fuel cell device with proton-conducting BaZr_{0.8}Y_{0.2}O_{3-δ} (BZY) filter (**Fig. S10**), where the NCO/CeO₂ electrolyte was sandwiched between two BZY ion-filter layers, only allowing protons passing through and determining H⁺ transport property (23). The device with BZY filters enables to achieve 890 mW cm⁻² at 520 °C (**Fig. 3E**), which is very close to the power output 1000 mW cm⁻² of the NCO/CeO₂ fuel cell. The difference is attributed to the ohmic losses caused by two additional BZY layers with limited proton conductivity that is significantly lower than that of the NCO/CeO₂, see **Fig. 3D**. In addition, polarization losses coming from additional contacting interfaces between the BZY and NCO/CeO₂ are also introduced. This result

clearly **proves** proton-dominating conduction in the NCO/CeO₂ heterostructure electrolyte. Another experiment is to measure the proton conduction isotopic effect, where conductivities of the NCO/CeO₂ were measured in 5% H₂-95% Ar and 5% D₂-95% Ar at various temperatures, respectively. The associated conductivities are significantly increased from 5% D₂ to 5% H₂, exhibiting a clear H/D isotope effect (**Fig. 3F**). This provides further a direct evidence of proton conduction in the designed material (24).

Compared with the best proton conducting BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O₃ thin film electrolyte fuel cell (500 mW cm⁻² at 500 °C), the NCO/CeO₂ device shows 800 mW cm⁻² at 500 °C and 1000 mW cm⁻² at 520 °C (**Fig. 3B**). In addition, NCO/CeO₂ as electrolytes in different molar ratios also show significant outputs (**Fig. S11**). The NCO/CeO₂ heterostructure has demonstrated promising advantages for PCFCs (25, 26). The durability of the NCO/CeO₂ device was tested under 100 mA cm⁻² during a 100 h period, of which the operation voltage was further improved from 0.9 V to around 1.0 V by introducing **an** anode buffer layer (ABL) (**Fig. S12**). The ABL can effectively enhance device performance and durability. This lab test can be further improved by exploring optimized electrode materials and device technology with more engineering efforts.

Theoretical calculations further reveal the proton conduction mechanism as illustrated in **Fig. 4**, where the charge density difference **distributions** of NCO/CeO₂ interface **are** presented in **Fig. 4A**. At NCO/CeO₂ interface, the unbalanced charge distribution between Ce-O and Co-O layers induces a LEF within the interface region; around oxygen vacancies of CeO₂ and sodium vacancies of NCO can further cause an in-plane LEF, where interfacial potential is verified by the KPFM (**Fig. 2F**) and the LEF through *I-V* curve of NCO/CeO₂ thin film device (**Fig. 2G**). Proton transporting states and paths are illustrated through **Fig. 4B-C**. Proton intercalation leads to a dramatic shift of spectra weight of Co 3*d* and Ce 4*f* bands towards higher energy. Correspondingly, distributed orbitals cover a wide range from E_F-3 eV to E_F+1 eV, indicating the proton transporting path with a lower barrier and resistance. Nudged elastic band (NEB) calculations were carried out to understand proton migration pathways, the energy diagram of diffusion of H at interface (**Fig. 4D**) reveals the lowest energy barrier between proton and NCO. This is the optimal migration pathway for proton moving from CeO₂ to NCO surface. During transporting process, the proton driven by the LEF could incorporate with lattice oxygen ion and hop through the oxygen vacancy of CeO₂ (i: Initial state) forming H-O-Ce bond (a bond length of 0.98 Å). Meanwhile, the LEF is confined within the heterostructure interface, which drives protons from the positively charged CeO₂ to the negatively charged NCO surface. (ii: Transition state) (**Fig. 4E**). Once proton is close to NCO, Na experiences a large distortion leading to a strong repulsive force to proton. This causes a deformation of H···O-Co (bond length 1.04 Å) to H···O-Ce bond (1.70 Å). In addition, the barrier is too high for protons to transport in the NCO and CeO₂ structure, so protons are confined in the NCO/CeO₂ interface. Finally, protons spontaneously flow along the superior proton channel resulted from the **LEF-induced metallic state** of NCO surface (iii: Final state), of which the active energy is 0.15 eV, being much lower than those of the bulk CeO₂ (3.17 eV) and NCO (3.89 eV). Such superior proton **conduction is** attributed to a synergic effect between LEF and metallic state of NCO surface to greatly accelerate proton transportation.

We have presented a new approach to design and develop super proton transport with accelerating channels **through** a unique **field-induced metallic state** in the NCO/CeO₂ semiconductor heterostructure. The ever-high proton conductivity, 0.1-0.3 S cm⁻¹ (at 370-520 °C) has been realized in this system. The NCO/CeO₂ fuel cell has exhibited a remarkable

power density of 1000 mW cm⁻² at 520 °C. It presents a general methodology based on unique interfacial structure and property to develop new functional semiconductor heterostructures. More broadly, this work lays the theoretical and experimental foundations for designing and exploiting novel materials in energy applications.

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Authors contributions: Y.W., H.B.S. and B.Z. conceived the idea, designed the experiments and analyzed the data. L. L. and Q.S. carried out most of the characterizations and device optimizations. M.H. performed the theoretical simulations and analyzed the results. Y.W., M.H., C.C, L.L. Q.S., J.S.K., H-B.S. and B.Z. participated in the device optimization and data analysis. J.W. and J.F.L. carried out Raman characterizations and analyzed the results. L.R.Z. carried out XANES characterizations and analyzed the results. M.A. verified fuel cell results. Y.W., H-B.S. and B.Z. wrote the paper; all the authors commented on the manuscript.

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Supplementary Materials:

Materials and Methods

Supplementary Text

Figs. S1-S12

Tables S1-S3

References (27-37)

Fig. 1. Design of the NCO/CeO₂ heterostructure functionalities for fast proton migration. **A**, Schematic of the NCO/CeO₂ fuel cell and its operation mechanism (Local electric field built at the NCO/CeO₂ interface from CeO₂ to NCO side confines proton along NCO surface). **B**, total density of states (DOS) of surface of CeO₂, NCO and Na_xCO₂ ($x=0.60$)/CeO₂ interface. **C**, CeO₂ lattice with (111) plane, interface of the NCO/CeO₂ heterostructure, and NCO layer with (001) plane with different proton migration activation energies, ϵ_1 , ϵ_2 , ϵ_3 , respectively.

Fig. 2. Characterizations of NCO/CeO₂. **A**, Transmission electron microscopy (TEM) image. **B**, High resolution TEM image. **C**, Oxygen *K* edge spectra in different local chemical environments. **D**, Atomic force microscopy image and **E** scanning Kelvin probe force microscopy (KPFM) image of NCO/CeO₂. The scanning area is $2.5\ \mu\text{m} \times 2.5\ \mu\text{m}$. **F**, Contact potential difference along the solid white line drawn in (**E**) and (**F**). **g**, *I-V* curve of NCO/CeO₂ heterostructure deposited on ITO/glass substrate with Au electrodes. In-situ and ex-situ Raman spectra of NCO (**H**) and CeO₂ (**I**) under air and H₂ atmospheres.

Fig. 3. A, *I-V* and *I-P* characteristics of NCO, CeO₂, NCO/CeO₂ device operated at 520 °C. **B**, *I-V* and *I-P* characteristics of the NCO/CeO₂ device operated at various temperatures. **C**, Nyquist plot obtained under OCV condition at 490 °C for a Ni/NCAL/ NCO/CeO₂/NCAL/Ni cell. **D**, The ionic conductivity of NCO/CeO₂ compared with the best oxygen-ion-conducting electrolytes (dashed lines) and proton conductor (solid lines). **E**, *I-V* and *I-P* characteristics of the NCO/CeO₂ (2:8) device operated at various temperatures with proton filters. **F**, Temperature dependence of conductivities in NCO/CeO₂ (2:8) device operated in 5% H₂-95% Ar and 5% D₂-95% Ar at various temperatures.

Fig. 4. Proton transporting path. **A**, charge density differences of NCO/CeO₂ interface. **B**, **C**, **D**, the energy diagram of diffusion of H at NCO-CeO₂ interface. **E**, the corresponding charge transfer behavior in NCO/CeO₂ interface area. **i**), initial state, **ii**), transition state, and **iii**), final state of H absorption in NCO/CeO₂ interface with Na vacancy.

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