HFTO Postdoctoral Research Award

Protonic Ceramic Electrochemical Cells for Hydrogen Production and Electricity Generation

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Outline

Research motivation and approach

- Background of protonic ceramic electrochemical cells (PCEC)
- Our approach on hydrogen and fuel cell technologies

R&D status and major accomplishments

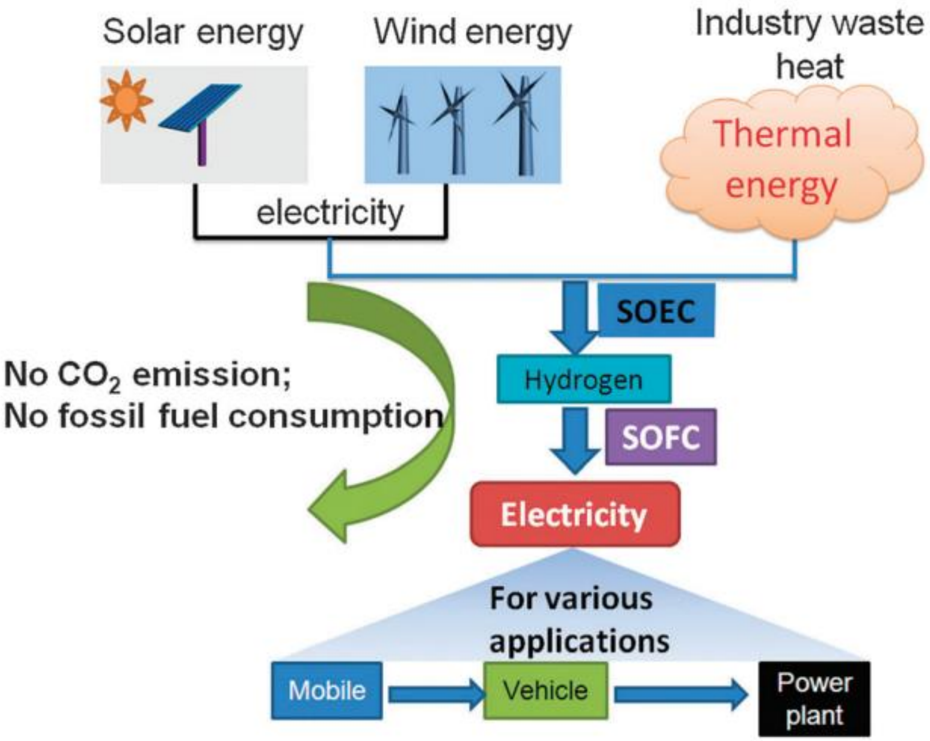
- Interfacial engineering
- Electrode microstructure improvement
- Cell component development

Future Plan

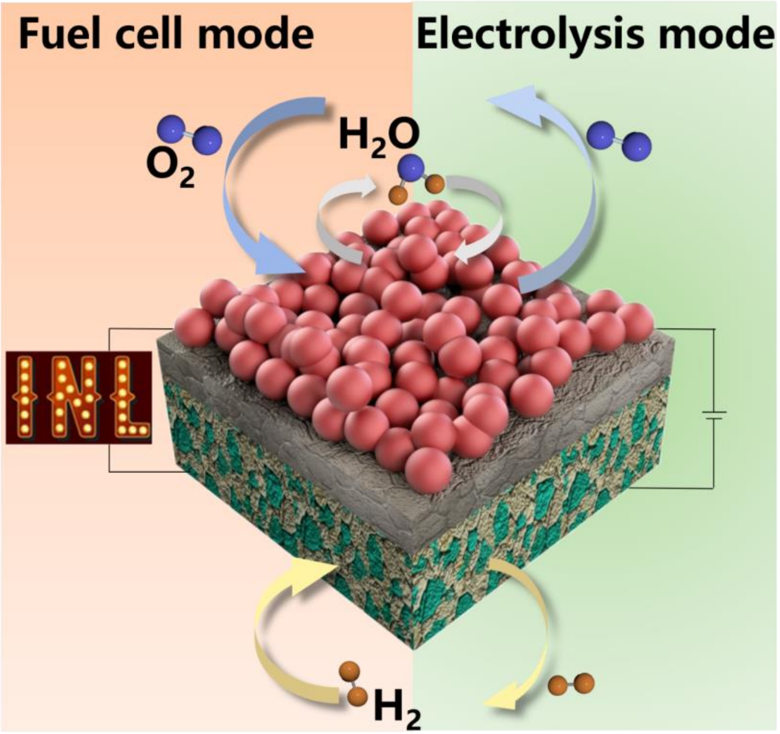
- PCEC in temperature ≤ 300 ^oC
- Large cell interfacial and component engineering
- CO_2 capture and natural gas upgrading

Research motivation and approach

- ❑ The **intermittency and variability** of renewable energies create challenges for operators to efficiently manage the grid.
- ❑ Solid oxide cells can act as an **energy storage/conversion device** to reduce the stress on peak shaving.



Concept diagram of applications of a sustainable energy system based on SOEC/SOFC technology.



Protonic ceramic electrochemical cells (PCECs) in fuel cell mode and electrolysis mode

PCEC advantages

- **Lower** operation temperature (400-600 ^{o}C)
- Relatively **lower** activation energy
- **No requirement** on gas separation
- **No partial oxidation** of the Ni-based electrode.

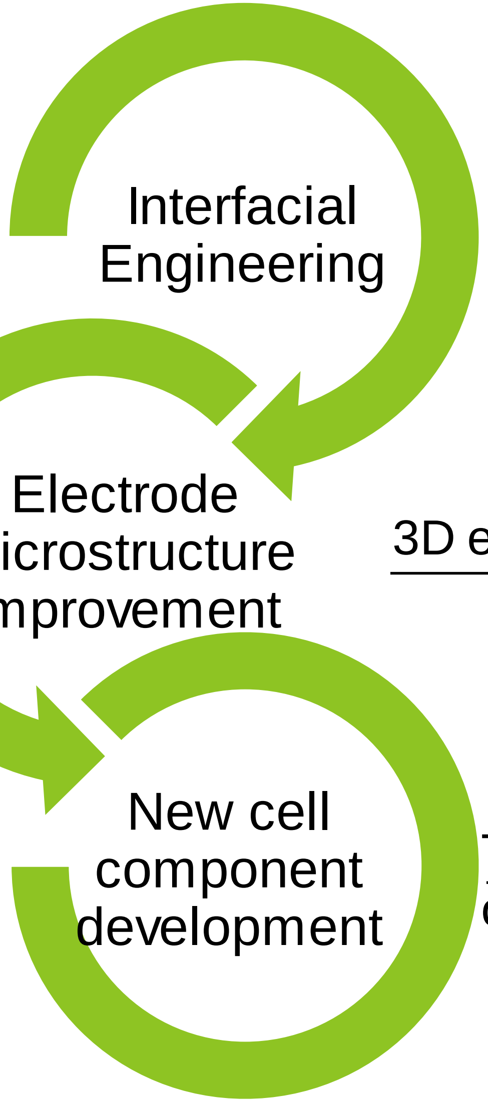
Bi, Lei, Samir Boulfrad, and Enrico Traversa. *Chemical Society Reviews* 43, no. 24 (2014): 8255-8270.
Journal of Materials Chemistry A 8, no. 29 (2020): 14600-14608.

Research motivation and approach

Issues in PCEC

- ❑ **Poor bonding** between oxygen electrode and electrolyte because of high sintering temperature of proton conductor.
- ❑ **Sluggish electrode kinetics** for oxygen reduction reaction and water oxidation reaction at reduced temperature.
- ❑ Unproven stability under extreme conditions.

Our approach



Acid etch →

3D engineering →

Triple conducting oxide →

Goal

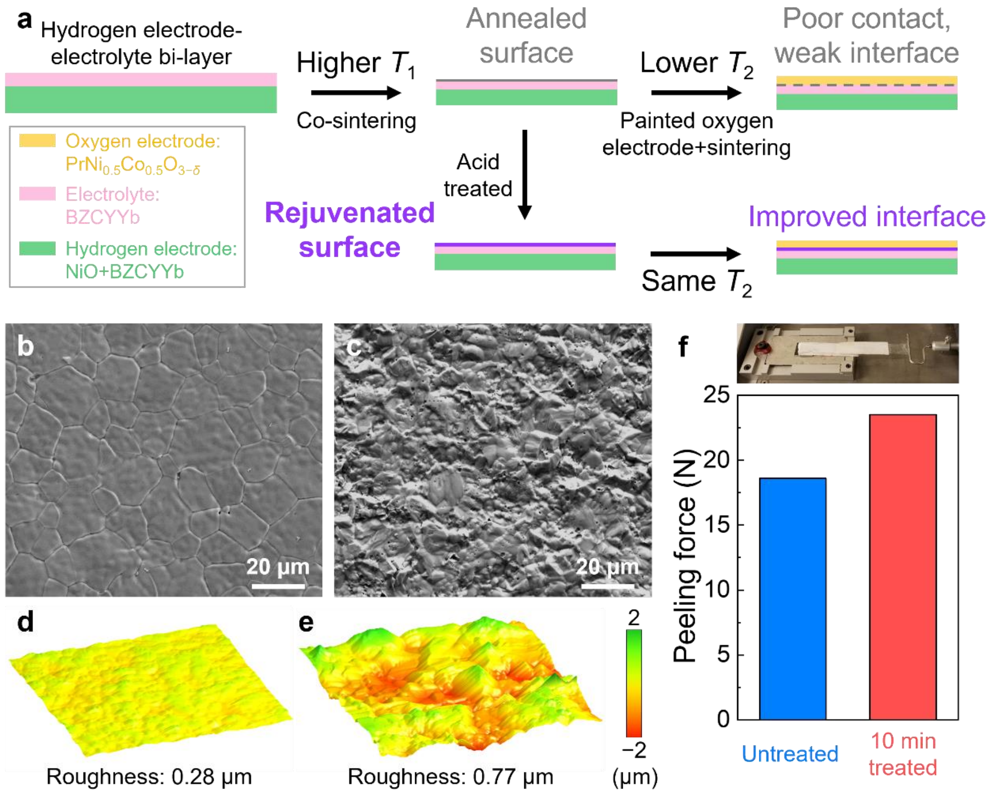
- Fully recover **intrinsic conductivity** of electrolyte
- Improved hydrogen production rate and power output
- High cell durability

- Mass and charge transfer **balance**
- High power output and improved hydrogen production rate

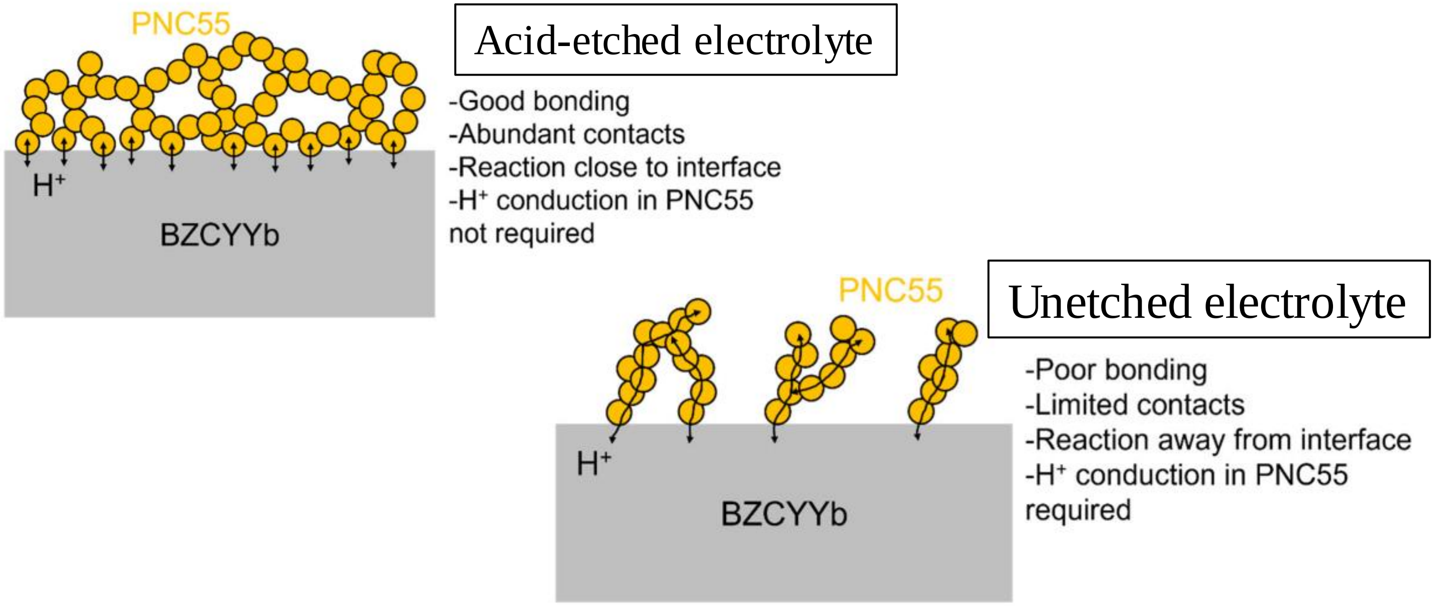
- Extend triple phase boundaries to electrode
- High chemical stability without alkaline metal doping

R&D status and major accomplishments

Schematic of acid etch process



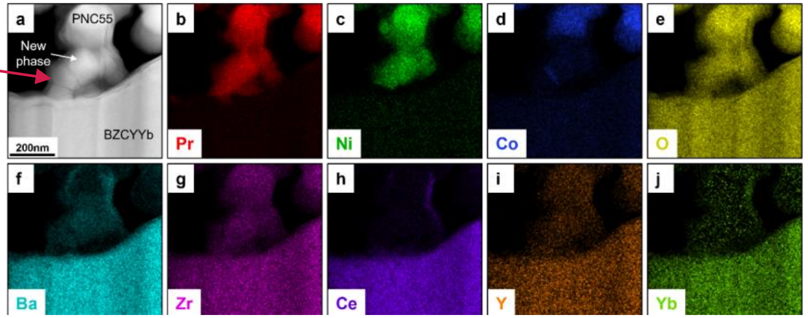
- Well-annealed electrolyte surface was **removed** by acid etch.
- The acid etch **creates a rough electrolyte surface**, with improved oxygen electrode/electrolyte connect area and bonding strength.
- **New phases was formed** between oxygen electrode and acid-treated electrolyte.
- The **segregated Y was removed** by acid etch, improving electrolyte conductivity.

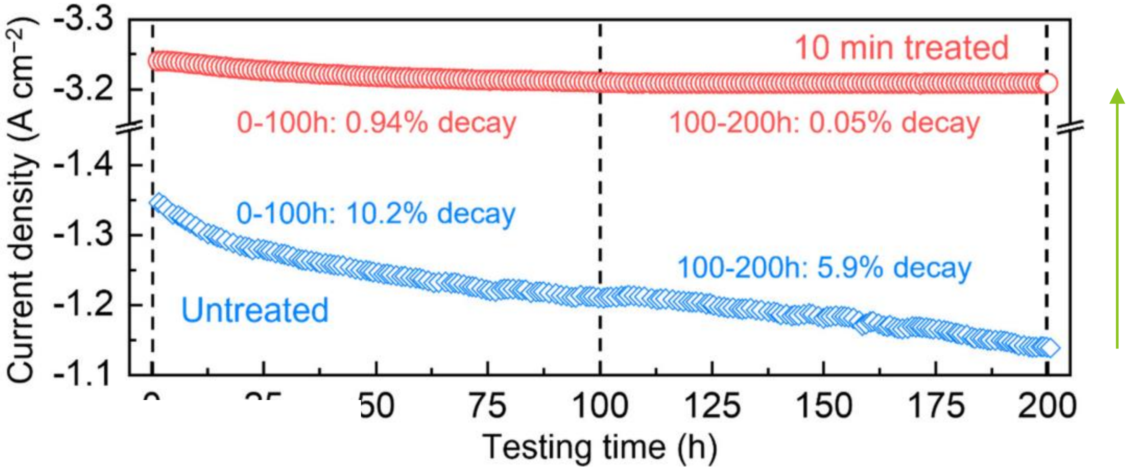


Bian, Wenjuan, Wei Wu, Dong Ding et al. ***Nature*** **604, no. 7906 (2022): 479-485**.

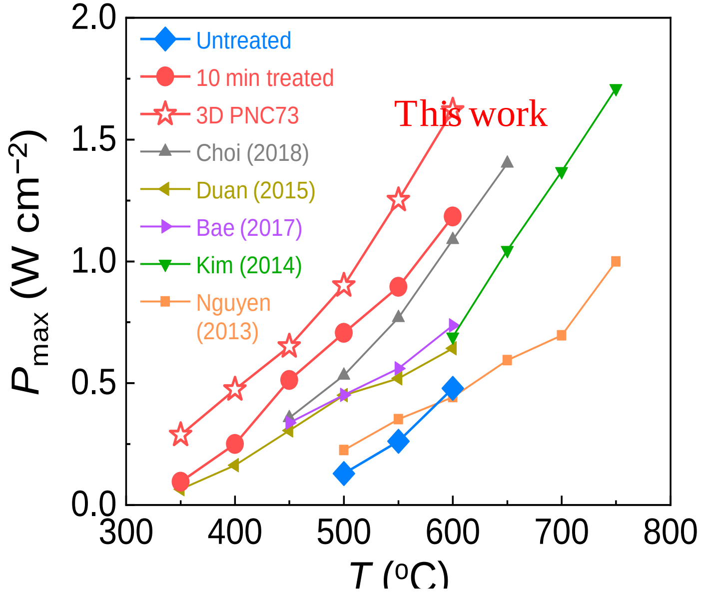
R&D status and major accomplishments

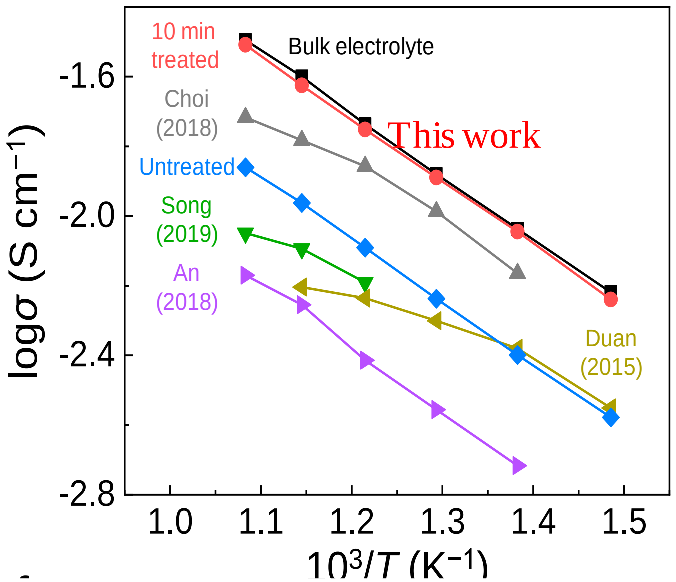
New phase





Top 1 output power in PCECs.





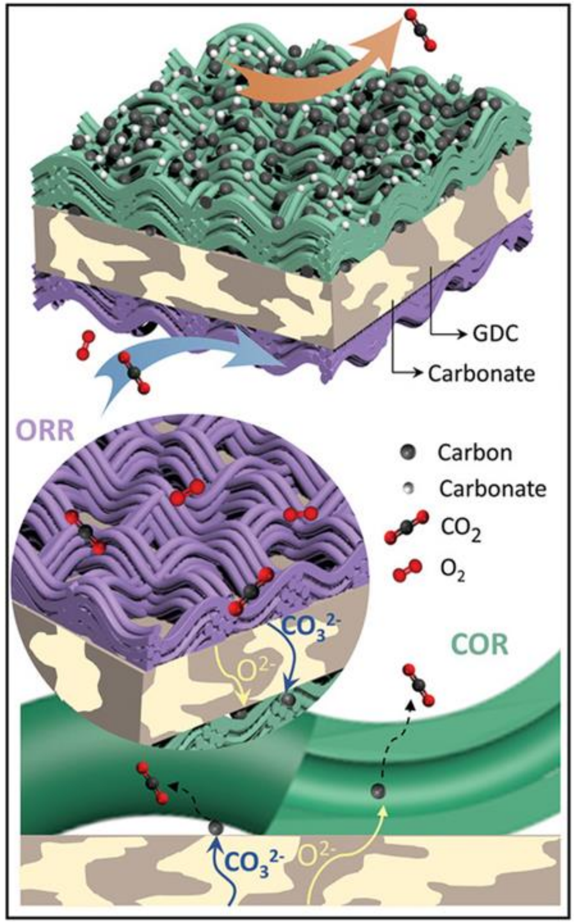
- ❑ Improved long-term durability at **30% steam concentration** and 600 ºC.
- ❑ **High current density** during long-term testing.

After etching, electrolyte was fully recovered and reached its **intrinsic, theoretical** value in bulk samples.

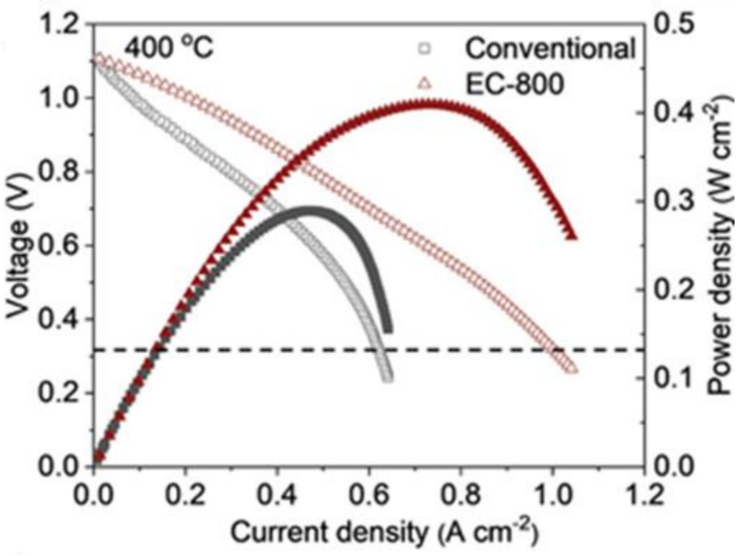
Operation temperature does down to **350 ºC**.

Bian, Wenjuan, Wei Wu, Dong Ding et al. ***Nature*** **604, no. 7906 (2022): 479-485**.

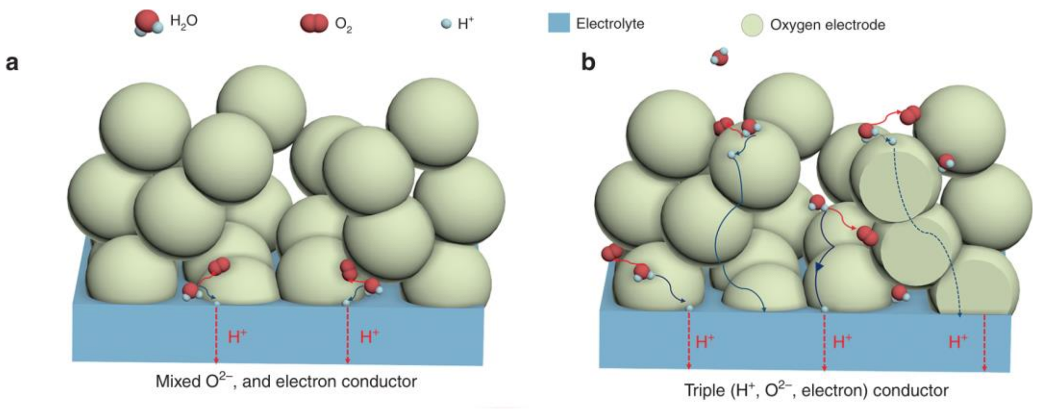
R&D status and major accomplishments



The **charge and mass transfer** were facilitated by a novel ultra-porous 3D ceramic textile (3DCT) in SOEC/SOFCs.



Compared with a cell using a conventional sponge-like cathode, **3D engineering improves** the cathode ORR by **41%** at **400 °C** with a peak power density of 0.410 W cm^{-2}.



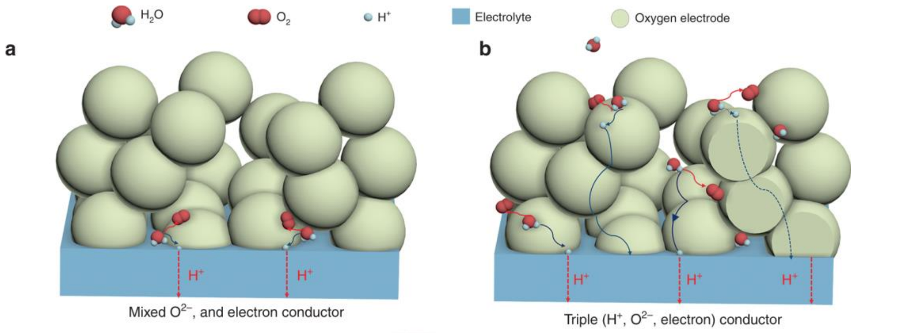
Triple conducting oxides **extend triple phase boundaries** from the electrolyte/electrode interface into the electrode bulk

Bian, Wenjuan et al. ***Advanced Functional Materials*** 31, no. 33 (2021): 2102907.
Bian, Wenjuan et al. ***Advanced Functional Materials*** 30, no. 19 (2020): 1910096.

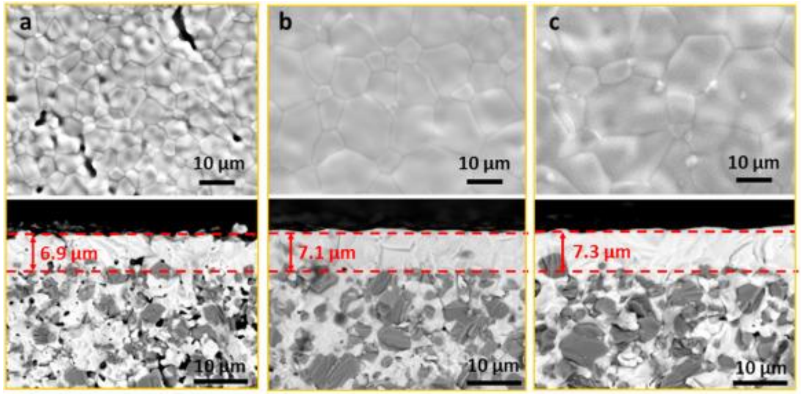
Ding, Hanping, Wei Wu, Chao Jiang, Yong Ding, **Wenjuan Bian**, et al. Nature communications 11, no. 1 (2020): 1-11.

R&D status and major accomplishments

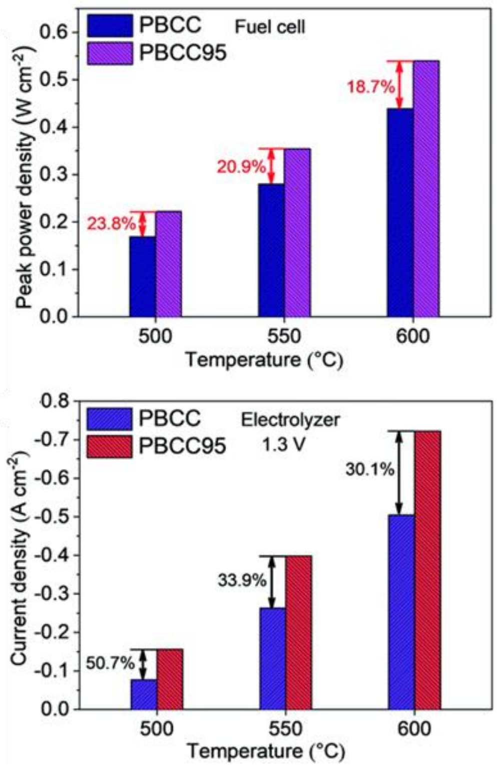
- We proposed **triple conducting oxides** PNC and A-deficient PBCC as oxygen electrodes in PCEC to.
- Electrolyte thickness of PCEC was decreased to **~7μm** by wet powder spraying.
- A protonic ceramic membrane reactor was proposed to direct convert ethane to hydrogen and ethylene.



(a) Mixed O^{2-} and electron conducting electrode.
(b) Triple (H^+, O^{2-}, and electron) conducting electrode.

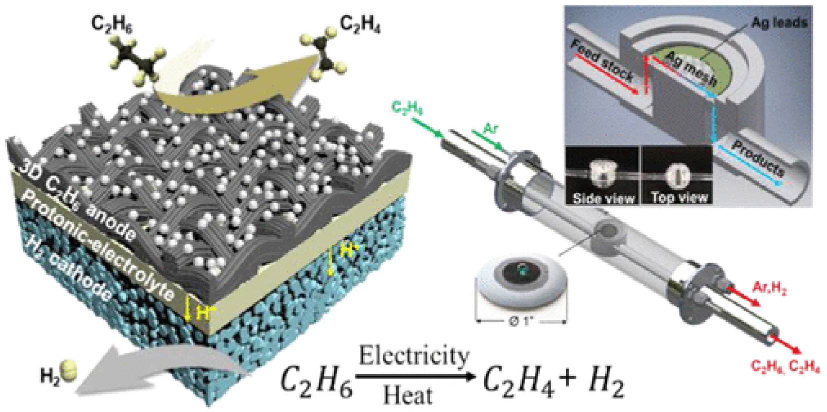


Proton conducting thin electrolyte fabricated by wet powder spraying.



Peak power density and electrolysis current density comparison of A-deficient PBCC and PBCC.

PNC: $PrNi_{0.5}Co_{0.5}O_{3-\delta}$
PBCC: $PrBa_{0.8}Ca_{0.2}Co_2O_{6-\delta}$



1. Nature communications 11, no. 1 (2020): 1-11.
2. ACS Catalysis 11, no. 19 (2021): 12194-12202.
3. Journal of Power Sources Advances 11 (2021): 100067.
4. Journal of Materials Chemistry A 8, no. 29 (2020): 14600-14608.

Future and aspirations

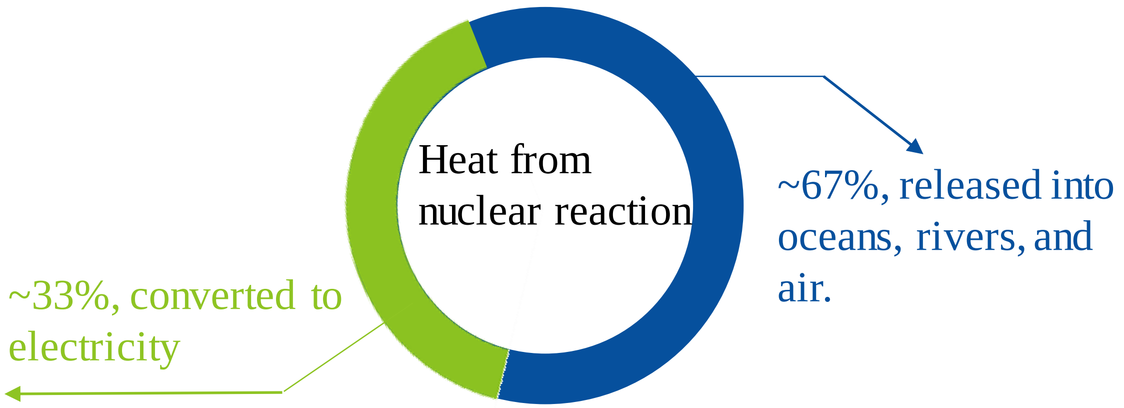
Further Lower operation temperature

Improve CO_2 capture efficiency and realize natural gas upgrading

Advanced manufacture

Push PCEC to work at lower temperature ≤ 300 °C

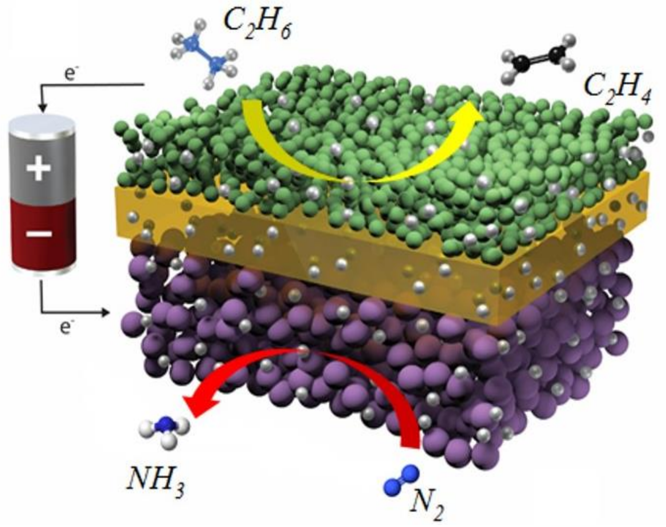
1. Realize the utilization of the nuclear heat waste.
2. Match industrial process.
3. Consume less heat.
4. Improve cell stability.



Thermal energy produced in nuclear reactions.

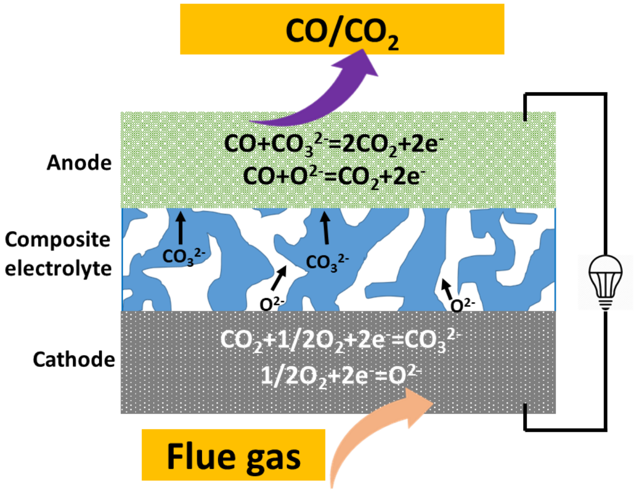
Future and aspirations

Apply the interfacial and component engineering on **natural gas upgrading** and **electrochemical CO_2 capture**.
Integrate interfacial engineering and optimized component to large cell for **high output power**.



$$C_2H_6 \longrightarrow C_2H_4 + 2H^+ + 2e^-$$

As an electrode in ethane side, high porosity **triple conducting oxides** will promote the catalytic process.

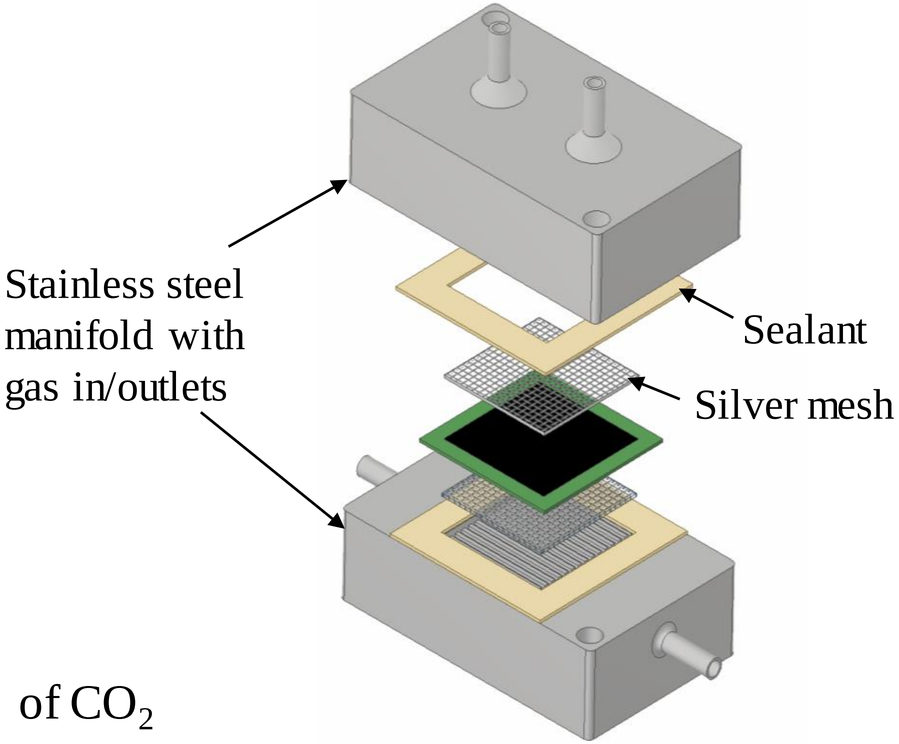


$$U^{meas}_{CO_2} = \frac{x^{in}_{CO_2} - x^{out}_{CO_2}\left(x^{in}_{N_2}/x^{out}_{N_2}\right)}{x^{in}_{CO_2}}$$

Utilization of CO_2

$$t_{CO_3^=} \approx \frac{U^{meas}_{CO_2}}{U^{ideal}_{CO_2}}$$

Steady state CO_2 transference number.



Large scale cell testing

Energy & Environmental Science, 11(7), 1710-1716.

Publication

1. 9 peer-reviewed publications as **first author** in ***Nature*** (IF=49.96), ***Advanced Functional Materials*** *(IF=18.81)*, ***ACS Nano*** (IF=15.88), ***Applied Materials Today*** (IF=10), and so on.
2. 25 total publication and 1 patent

1. **Wenjuan Bian**, Wei Wu, Ding Ding et al. Revitalizing interface in protonic ceramic cells by acid etch, ***Nature***, 604(7906), 2022, 479-485.
2. **Wenjuan Bian**, Wei Wu, Dong Ding et al. Regulation of Cathode Mass and Charge Transfer by Structural 3D Engineering for Protonic Ceramic Fuel Cell at 400 °C, ***Adv. Funct. Mater.*** 2021, 2102907.
3. **Wenjuan Bian**, Wei Wu, Dong Ding, Dual 3D Ceramic Textile Electrodes: Fast Kinetics for Carbon Oxidation Reaction and Oxygen Reduction Reaction in Direct Carbon Fuel Cell at Reduced Temperatures, ***Adv. Funct. Mater***. 2020, 30, 1910096.
4. Hanping Ding, Wei Wu, Chao Jiang, Yong Ding, **Wenjuan Bian**, Dong Ding, Self-sustainable protonic ceramic electrochemical cells using a triple conducting electrode for hydrogen and power production, ***Nat. Commun.*** 2020, 11, 1.
5. **Wenjuan Bian**, Yue Lin, Ting Wang, et al. Direct Identification of Surface Defects and their Influence on the Optical Characteristics of Upconversion Nanoparticles, ***ACS Nano*** 2018, 12, 3623.
6. **Wenjuan Bian**, Meng Zhou, Gen Chen, Xue Yu, Madhab Pokhrel, Yuanbing Mao, Hongmei Luo, Upconversion Luminescence of Ytterbium and Erbium co-doped Gadolinium Oxysulfate Hollow Nanoparticles, ***Applied Materials Today*** 2018, 13, 381.
7. Wei Wu, Lu-Cun Wang, Hongqiang Hu, **Wenjuan Bian**, Dong Ding et al. Electrochemically Engineered, Highly Energy Efficient Conversion of Ethane to Ethylene and Hydrogen below 550 °C in a Protonic Ceramic Electrochemical Cell, ***ACS Catal.*** 2021, 11, 12194-12202.
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9. **Wenjuan Bian**, Yushuang Qi, Wei Lu, et al. Controllable Synergistic Effect of Yb3+, Er3+ Co-Doped KLu2F7 with the Assistant of Defect State, CrystEngComm 2016, 18, 2642.
10. **Wenjuan Bian**, Wei Lu, Yushuang Qi, et al. Effect of Defect State on Photon Synergistic Process in KLu2F7:Yb3+, Er3+ Nanoparticles, J. Solid State Chem. 2016, 242, 222.
11. **Wenjuan Bian**, Yushuang Qi, Xuhui Xu et al. Effect of Defect States on the Upconversion Emission Properties in KLu2F7 Nanocrystalline, ECS J. Solid State Sci. Technol. 2016, 5, R137.
12. Wuxiang Feng, Wei Wu, Congrui Jin, Meng Zhou, **Wenjuan Bian**, Dong Ding et al. Exploring the structural uniformity and integrity of protonic ceramic thin film electrolyte using wet powder spraying, ***J. Power Sources Adv.*** 2021, 11, 100067. 3 4.
13. Jiangyan Cao, Qiuhong Min, **Wenjuan Bian**, Liuli Yang, Jing Lei, Mingyu Zhang, Hongqing Ma, Jianbei Qiu, Xuhui Xu, Xue Yu, Highly Sensitive Detection of Amaranth Realized with Upconversion Nanoparticles-Based Solid Sensor, J. Electrochem. Soc. 2020, 167, 127511.
14. Wei Tang, Jie Jian, Gen Chen, **Wenjuan Bian**, Jiuling Yu, Haiyan Wang, Meng Zhou, Dong Ding, Hongmei Luo, Carbon-nanotube Supported Amorphous MoS2 via Microwave-Heating Synthesis for Hydrogen Evolution Reaction, Energy Mater. Advances, ENERGYMATADV-D-20-00001.
15. Zhichao Liu, Hongqing Ma, Lei Zhao, **Wenjuan Bian**, Xuhui Xu, Xiaotong Fan, Xiuxia Yang, Shuyu Tian, Jianbei Qiu, Luminescence quenching properties of Sr2Ga2GeO7:Pr3+ with and without traps participation, J. Solid State Chem. 2019, 271, 23.
16. Zhichao Liu, Lei Zhao, Wenbo Chen, Shuangyu Xin, Xiaotong Fan, **Wenjuan Bian**, Xue Yu, Jianbei Qiu, Xuhui Xu, Effects of the Deep Traps on the Thermal-Stability Property of CaAl2O4: Eu2+ Phosphor, J. Am. Chem. Soc. 2018, 101, 3480.
17.Qiuhong Min, **Wenjuan Bian**, Yushuang. Qi, Wei Lu, Xue Yu, Xuhui Xu, Dacheng Zhou, Jianbei Qiu, Temperature Sensing Based on the Up-Conversion Emission of Tm3+ in a Single KLuF4Microcrystal, J. Alloy Compd. 2017, 728, 1037.
18.Yushuang Qi, Lei Zhao, **Wenjuan Bian**, Xue Yu, Xuhui Xu, Jianbei Qiu, Energy Transfer Between Ce3+ and Sm3+ in Zn2GeO4 Phosphor with the Native Defects for Light-Emitting Diodes, Chin. Opt. 4Lett. 2017, 15, 081601.

Publication

19. Yushuang Qi, **Wenjuan Bian**, Xue Yu, Xuhui Xu, Jianbei Qiu, Near-IR Emission Enhancement of K_2LuF_5: Yb^{3+}/Er^{3+} via the Cross-Relaxation Processes with the Assistance of Ce^{3+} Ions, ECS J. Solid State Sci. Technol. 2016, 5, R199.
20.Ting Wang, **Wenjuan Bian**, Dacheng Zhou, Jianbei Qiu, Xue Yu, Xuhui Xu, Red Long Lasting Phosphorescence in $Ca_2Ge_7O_{16}$:Sm^{3+} via Persistent Energy Transfer from the Host to Sm^{3+}, Mater. Res. Bull. 2016, 74, 151.
21.Xuhui Xu, Yumei Wu, **Wenjuan Bian**, Xue Yu, Buhao Zhang, Qianyue Li, Jianbei Qiu, Bitao Liu, Improved Near-Infrared Up-Conversion Emission of Tm^{3+} Sensitized by Yb^{3+} and Ho^{3+} in LuF_3 Nanocrystals, J Nanosci. Nanotechno. 2016, 16, 3664.
22.Xuhui Xu, Xue Yu, Ting Wang, **Wenjuan. Bian**, Jianbei Qiu, Rewritable LPL in Sm^{3+}-Doped Borate Glass with the Assistance of Defects Induced by Femtosecond Laser, Opt. Mater. Express 2016, 6, 402.
23.**Wenjuan Bian**, Ting Wang, Yanmei Guo, Xue Yu, Xuhui Xu, Jianbei Qiu, Visible and Near-Infrared Upconversion Photoluminescence in Lanthanide-Doped KLu_3F_{10} Nanoparticles, CrystEngComm 2015, 17, 7332.
24.Ting Wang, **Wenjuan Bian**, Dacheng Zhou, Jianbei Qiu, Xue Yu, Xuhui Xu, Tunable LLP via Energy Transfer between $Na_{2-y}(Zn_{1-x}Ga_x)GeO_4$ Sosoloid Host and Emission Centers with the Assistance of Zn Vacancies, J. Phys. Chem. C 2015, 119, 14047.
25. Xue Yu, **Wenjuan Bian**, Ting Wang, Dacheng Zhou, Jianbei Qiu, Xuhui Xu, Up-Conversion Luminescence Properties of Lanthanide-Doped LuF_3 with Different Morphologies Synthesized via a Facile Ionothermal Process, CrystEngComm 2015, 17, 2147

Patent

Dong Ding, **Wenjuan Bian**, Wei Wu. Facile methods to rejuvenate electrolyte surface for high-performing protonic ceramic electrochemical cells. ***US Patent Provisional Application*** (63/298,084), 2022.

Acknowledgement

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Thank you!