**Supporting Information**

Cross-linked solid-liquid interfaces enable a fast proton transport in the aluminate heterostructure electrolyte

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**Supplementary Note 1**

The conductivity is calculated according to the equation (1):

(1)

where *L* represents the length, and *S* is the area, and the total resistance (*R*) is obtained by EIS.

The activation energy of the NAO/LAO composites can be calculated by plotting ln(*σT*) versus 1000/*T* according to the Arrhenius equation (2):

(2)

Here, A is a pre-exponential factor, *T* is the absolute temperature, Ea is the activation energy, and K is the Boltzmann constant.

**Supplementary Note 2**

The DRT analysis method improves the resolution of EIS data by transforming it from the frequency to the time domain via the following equation (3):

(3)

where *L*0 is an inductance, *R*0 is ohmic resistance, *j* is the complex unit, the characteristic time constant *τ* is the inverse of angular frequency: . *ϒ*(ln *τ*) is the distribution function of relaxation times for the electrochemical system studied on the logarithmic. The establishment of the DRT equation requires ensuring that *Z*(*ω*) converges at the limit ω→0. It should be noted that the research object in this work meets this condition, and the non-convergence of the spectrum at the low-frequency cut-off frequency (0.1 Hz) of EIS is due to limited working conditions. The distribution relaxation time reflects the time required for the fuel cell system to transit from one equilibrium to another under small disturbance, and the different chemical processes correspond to different relaxation time.

**Supplementary Note 3**



**Fig. S1** **a** XRD patterns of LiAlO2,NaAlO2 and NaAlO2-LiAlO2 samples, **b, c** structure parameters and schematic of the idealized structure of LiAlO2 and NaAlO2.

The XRD results of synthesized samples were characterized as shown in **Fig. S1a**, and the diffraction peaks can be indexed to the γ-LiAlO2 structure with tetragonal P41212 space group and β-NaAlO2 structure with orthorhombic Pna21 space group. The corresponding structural parameters of LAO and NAO were shown in Fig. 1b. Obviously, NAO and LAO have good stability and compatibility after high-temperature sintering at 800 °C. The Li and Na based aluminum oxides manifest a similar polymorphism, and the corresponding structural parameters were shown in **Fig. S1b**. The β and γ phase are identified as favorable structure at low temperature, which are based on the framework of corner-linked distorted tetrahedra as shown in **Fig. S1c**. For instance, the structure of β-NaAlO2 consists of Al and Na centered tetrahedral that form a three-dimensional network, in which each tetrahedron shares an edge with a different tetrahedron and each tetrahedron vertex is shared by two neighboring tetrahedral.



**Fig. S2** **a** *I-V* and *I-P* characteristics, **b** Nyquist curves and **c** DRT results of LAO electrolyte fuel cell operated in H2-air condition at various temperatures.

**Fig. S2****a** displays the *I-V* and *I-P* characteristics for the synthesized LAO devices in a configuration of Ni-NCAL/LAO/NCAL-Ni at various temperatures. The pristine LAO is typical insulation material, and the electronic transmission can be effectively avoided in the LAO fuel cell device. Hence, the OCV of device stay at 1.1 eV indicating that the ionic transference number is near unity, which is approach to the Nernst theoretical potential (1.23V). Meanwhile, the maximum power output of the fuel cells using LAO electrolytes reached 612 mW cm−2 at 550 °C. The corresponding EIS data of LAO electrolyte fuel cell is shown in **Fig. S2b**. The semi-circle diameters increase dramatically with the temperatures being reduced, indicating that the ionic conduction has been affected markedly by the operation temperature. To detect the further details of the ion conductive properties under fuel cell operation conditions, EIS spectra of LAO fuel cells were measured and analyzed by distribution of relaxation times (DRT) as shown in Fig. S2c. The intensity of DRT peaks exhibits an inverse temperature dependence, and the resistance of this stage increased with decreasing temperature. In addition, the obvious differentiation near the high-frequency arcs can be detected, which can be divided into three different electrochemical processes in Fig. S2c.



**Fig. S3** Porposed proton transport mechnism schematic of **a** SE(LAO) and **b** SE/LE (NAO-LAO) fuel cell.

To further investigate the electrochemical evolution process of the cell, and the ion transport models were shown inFig. S3, Nyquist plot is modeled by an equivalent circuit Rb,S(Rgb,SQgb,S)(RpQp) with bulk resistor (Rb,S), grain boundary resistance (Rgb,S), polarization resistance (Rp) and corresponding constant phase element (Qi, the definition of i changes with R).



**Fig. S4** The thermal expansion coefficient (a) and TEC values (b) of NAO-LAO.

The coefficient of thermal expansion (TEC) of NAO-LAO was characterized as shown in Fig. S4. The TEC values of NAO-LAO range from 3.0 to 6.5 × 10−6 K-1 with temperature ranging from 150 °C to 600 °C (Fig. S4a). The TEC values kept about 3~4 × 10−6 K-1 with the temperature increasing from 150 to 370 °C. Further increasing the temperature, the TEC values increase to about 4.5–5.5× 10−6 K-1 (Fig. S4b). This change is consistent with NAO-LAO SE/LE transition temperature.



**Fig. S5** Operational stability of the fuel cell running at 100 mA cm−2 and 550 °C with H2/air condition.

Attribute to the material compatibility and dense electrolyte, the SE/LE fuel cells possessed good long-term stability over 100 h in Fig. S5, and the slight fluctuation of voltage may be affected by flowing air into the chamber of electrode. Therefore, it is suggested that SE/LE is a highly promising electrolyte for PCFC, as verified by the demonstrated high cell performance, excellent cell cycling, and long-term durability.

**Table S1.** The EIS fitting parameters of the fuel cells using LAO-NAO and LAO electrolytes with the corresponding equivalent circuit model. R and Q have the unit of Ω and S secncm-2 respectively. (Rb,S, ohmic resistance of solid electrolyte; Rb,L, ohmic resistance of liquid electrolyte; RSL, resistance of the interface between solid and liquid phase; Rgb,S, grain boundary resistance; Rp, polarization resistance; Qi, corresponding constant phase element, the definition of i changes with R)

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| --- | --- | --- | --- | --- | --- | --- | --- |
| Fuel cell assembly | Ni-NCAL/NAO-LAO/NCAL-Ni | | | | Ni-NCAL/NAO/NCAL-Ni | | |
| Operation temperature  (℃) |  | | | |  | | |
| Rb,S | Rb,L | RS,L | Rp | Rb,S | Rgb,S | Rp |
| 550 | 0.15 | 0.01 | 0.12 | 0.15 | 0.32 | 0.28 | 0.18 |
| 520 | 0.16 | 0.04 | 0.14 | 0.25 | 0.59 | 0.24 | 0.46 |
| 490 | 0.18 | 0.08 | 0.11 | 0.47 | 0.86 | 0.81 | 0.85 |
| 460 | 0.20 | 0.10 | 0.11 | 0.63 | 1.21 | 2.80 | 2.74 |