Supporting Information

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Experimental Section:

**Materials synthesis:** The e-TAC support material was prepared using an effective strategy that consisted of NaOH solution leaching and surface modification. Briefly, 0.5 g of pristine Ti$_3$AlC$_2$ powder (Beijing Hutong Wangyi Commerce & Trade Co., Ltd., Beijing, China) was immersed in 500 mL of a NaOH solution (1 M) and stirred for 100 h at 80 °C to remove the surface Al atoms that incorporated between the special Ti$_3$C$_2$ layers of the bulk Ti$_3$AlC$_2$. Further removal of the exposed Al atoms and the installation of hydroxyl groups on the supporting material were accomplished by soaking the e-TAC in 100 mL of 1 M H$_2$SO$_4$ at 80 °C for 2 h. The material was then washed with ultrapure water and dried.

The Pt/e-TAC catalyst was synthesized using a previously reported ethylene glycol (EG) reduction method. Specifically, 170 mg of e-TAC was ultrasonically dispersed in EG solvent. Next, an already-prepared mixture composed of 180 mg of trisodium citrate dehydrate (TCD) and 3 mL of 40% mg mL$^{-1}$ chloroplatinic acid (H$_2$PtCl$_6$·6H$_2$O) was added. The obtained inky slurry was then stirred at room temperature for 48 h to achieve homogeneous adsorption of Pt ion precursors to the support and then refluxed at 160 °C for 4 h under an atmosphere of highly purified nitrogen. When the reaction was complete, the sample was cooled to 80 °C, and the black precipitate was collected by repeated centrifugation. The solid was washed with ethanol and ultrapure water before drying under vacuum at 80 °C overnight, which resulted in the formation of the Pt/e-TAC.

**Materials Characterization:** X-ray diffraction (XRD) patterns were recorded on a XRD-6000 using Cu KR radiation (λ=1.5418 Å) at a step rate of 2° s$^{-1}$. X-ray photoelectron spectra were obtained using a Cratos XSAM800 spectrometer equipped with a monochromatic Al X-ray source.
(Al Kα, 1.4866 keV), the vacuum in the analysis chamber was maintained at 10^{-7} \text{ Pa}, and the binding energy was calibrated by using 285 eV as the C 1s peak energy. Both low-resolution transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted on a FEI Tecnai G2 20S-TWIN instrument operating at 120 kV. The Pt loading on the support was determined by SEM-EDS. Electrical conductivity analysis was performed at room temperature using a home-made button cell by confining the sample between two smooth polished steel discs and measuring the electrical resistance of the sample by electric impedance spectroscopy. A Solartron SI 1287 Electrochemical Interface equipped with a Solartron SI 1260 Impedance/Gain-phase Analyzer coupling system was used.

**Electrochemical tests:** The electrochemical properties of the catalysts were characterized using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques. All the electrochemical experiments were performed in 0.1 M HClO\textsubscript{4} using a Princeton Parstst 4000 potentiostat, a platinum wire counter electrode and an Ag/AgCl (saturated KNO\textsubscript{3}) reference electrode. All potentials in this study, however, are given relative to the reversible hydrogen electrode (RHE). A rotating disk electrode (RDE) with a glassy carbon (0.19625 cm\textsuperscript{2}) was used as the working electrode. The catalyst ink was prepared by blending the catalyst powder (Pt/e-TAC or commercial catalysts from Johnson-Mathew Co., UK, Pt/C) with ethanol in an ultrasonic bath. For comparison of the electrochemical surface areas (ECSAs), cyclic voltammograms recorded in nitrogen were used to obtain the ECSA using the following relation:

$$\text{ECSA} = \frac{Q_{H}}{Q_{\text{ref}} m}$$

where \(Q_{H}(\text{mC})\) is the charge due to the hydrogen adsorption and desorption in the hydrogen region (0.05-0.40 V) of the CVs, \(Q_{\text{ref}} = 0.21\ \text{mC}\) is the electrical charge associated with a monolayer adsorption of hydrogen on Pt, and \(m\) is the loading of Pt on the working electrode.

Oxygen reduction reactions were conducted in a 0.1 M HClO\textsubscript{4} aqueous solution. The polarization curves were obtained by sweeping the potential from 1.0 to 0.2 V at a scan rate of 10 mV s\textsuperscript{-1} and a rotation rate of 1600 rpm. The current density was normalized in reference to the
ECSA of the catalyst. Based on the ORR polarization curves, the number of electrons transferred (n) during the course of the ORR was calculated from the slopes of Koutecky-Levich (K-L) plots using the following equation:

\[
\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_D} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}}
\]

\[
B = 0.62nFCD^{2/3}n^{1/6}
\]

where \( J \) is the measured current density, \( J_K \) and \( J_D \) are the kinetic and diffusion-limiting current densities, respectively, \( \omega \) is the angular velocity, \( n \) is the electron equivalence, \( F \) is Faraday’s constant, \( C \) is the bulk concentration of \( O_2 \), \( D \) is the diffusion coefficient of oxygen and \( \nu \) is the kinematic viscosity of the electrolyte.

The electrochemical stability and performance of the Pt/e-TAC and commercial Pt/C catalysts were examined using an accelerated durability test (ADT) by continuously cycling the potential between 0 and 1.5 V in nitrogen-saturated 0.1 M HClO\(_4\) at a scan rate of 50 mV s\(^{-1}\) with periodic measurements of the ECSA in half-cell testing conditions. All electrochemical measurements were conducted 3 times to avoid any incidental error.

**Computational Section:**

A slab model approach was used to investigate the Pt on the Ti\(_3\)C\(_2\) surface of the e-TAC support and graphene with the DMo13 Package. The DFT semi-core pseudopots approximation was used to replace core electrons by a single effective potential, thereby reducing the computational cost. Double numerical plus polarization (DNP) basis sets were employed for the valance orbitals, which provided accuracy at increased computational cost. The exchange correlations have been treated using the generalized gradient approximation with the PW91 formulation. Full-geometry relaxations were performed for all models. For Ti\(_3\)C\(_2\), its unit cell parameters are \( a = b = 3.072\) Å, \( c = 17.832\) Å, \( \alpha = \beta = 90^\circ \), \( \gamma = 120^\circ \). We use graphene instead of carbon in the DFT calculation. The Pt\(_{13}\) cluster was chosen for a Pt nanoparticles according to “magic numbers” \( n \) \((n = 5, 7, 13)\) that provides a higher geometric of electronic stability than other clusters. The binding energy \( (E_{\text{bind}}) \) between the Pt\(_{13}\) cluster and Ti\(_3\)C\(_2\) and graphene are defined as
\[
E_{\text{bind}}(\text{Pt}_{13}) = - \left( E_{(\text{Pt}_{13}/\text{support})} - E_{\text{support}} - 13E_{\text{Pt}} \right) / 13
\]

where \( E_{(\text{Pt}_{13}/\text{support})} \), \( E_{\text{support}} \) and \( E_{\text{Pt}} \) are the energies of the Pt\(_{13}\)/support, the support and a single Pt atom, respectively.
**Figure S1.** XRD patterns of pristine Ti$_3$AlC$_2$, the e-TAC material and the prepared Pt/e-TAC catalyst.
Figure S2. TEM images of (a) - (c) pristine bulk Ti$_3$AlC$_2$ and (d)-(f) the e-TAC material.
Figure S3. SEM images of (a) pristine bulk Ti₃AlC₂ and (b) the e-TAC material.
In the present work, the novel e-TAC support is prepared by a well-design optimized hydrothermal etching method. Such an as-designed route leads to the selective etching of the Al layer from the 3D layered Ti$_3$AlC$_2$ and results in the formation of exfoliated and separated Ti$_3$C$_2$ nanolayers. However, Al layers that interleaved between the Ti$_3$C$_2$ structure could not be removed completely due to the poor etching ability of the NaOH solution. Thus, the cicada wing-like structure that pertinent to this work possibly a Ti$_3$C$_2$-(Al-Ti$_3$C$_2$)$_n$ sandwich structure with Ti$_3$C$_2$ layers terminate at the outermost surface and with a thickness raging from single layer and double layers to multiple layers. Therefore, Al signal can still be detected after the Al leaching process due to the residual Al in the layered structure. Whereas, the reaction products, aluminum oxides (AlO$_x$), can probably account for the most of Al signal seen in the XPS spectra of e-TAC material.
Fig. S5 (a) Nitrogen adsorption/desorption isotherms of the e-TAC material and pristine Ti$_3$AlC$_2$. (b) BJH pore size distribution of the e-TAC material and pristine Ti$_3$AlC$_2$. 
Figure S6. SEM-EDS analysis of the Pt/e-TAC catalyst.
Figure S7. Reproducibility of ORR response at (a) Pt/e-TAC and (b) Pt/C electrodes.
Figure S8. XPS surveys of (a) Pt/e-TAC and (b) Pt/C before and after 1,500 CV cycles.
### Table S1. Comparison of the surface elemental compositions of the Pt/C and Pt/e-TAC catalysts before and after 1500 CV cycles\(^a\)

<table>
<thead>
<tr>
<th>sample</th>
<th>Ti</th>
<th>Al</th>
<th>C</th>
<th>Pt</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Pt/C</td>
<td></td>
<td></td>
<td>88.31</td>
<td>1.66</td>
<td>10.04</td>
</tr>
<tr>
<td>Aged Pt/C</td>
<td></td>
<td></td>
<td>80.80</td>
<td>9.63</td>
<td>9.51</td>
</tr>
<tr>
<td>Fresh Pt/e-TAC</td>
<td>4.15</td>
<td>8.07</td>
<td>43.22</td>
<td>16.94</td>
<td>27.62</td>
</tr>
<tr>
<td>Aged Pt/e-TAC</td>
<td>4.46</td>
<td>8.83</td>
<td>40.01</td>
<td>17.45</td>
<td>29.25</td>
</tr>
</tbody>
</table>

\(^a\) All values in units of atoms %