# Supporting Information

## Robust non-Carbon $Ti_{0.7}Ru_{0.3}O_2$ Support with co-Catalytic Functionality for Pt: Enhances Catalytic Activity and Durability for Fuel Cells

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### 1. Experimental and material characterization

**1.1 Materials.** $RuCl_3.xH_2O$ (35-40% Ru), $TiCl_4$ (99.9%), $H_2PtCl_6.6H_2O$ (99.9%, 38-40% Pt), ethylene glycol (99.5%), $CH_3OH$ (99.99%) purchased from Acros were used in the experiments. $H_2SO_4$ (95-97%) was from Scharlau, and Vulcan XC-72R carbon black (particle size ~50 nm) was from Cabot corporation. Nafion 117 solution (5%) was obtained from Aldrich. The commercial catalysts, 20 wt% Pt/C (E-TEK), and 20 wt% Pt-10 wt% Ru/C (JM) were purchased from Alfa Aesar. Deionized water was used all through.

**1.2 Material characterization:** Powder X-ray diffraction (XRD) patterns of $Ti_{0.7}Ru_{0.3}O_2$, $Pt/Ti_{0.7}Ru_{0.3}O_2$, home-made Pt/Vulcan XC-72R nanocatalysts were obtained with a synchrotron radiation source (BL17A, NSRRC, Hsinchu, Taiwan) with an X-ray of wavelength 1.32633 Å (9.3 keV) and 1.5 mm × 0.5 mm beam size. The particle size of the prepared $Ti_{0.7}Ru_{0.3}O_2$ and $Pt/Ti_{0.7}Ru_{0.3}O_2$ nanoparticles was evaluated by transmission electron microscopy (TEM) and High resolution TEM (HRTEM) using an FEI-TEM-2000 microscope operated at an accelerating voltage of 3800 V. The average composition of the $Ti_{0.7}Ru_{0.3}O_2$ support and the elemental mapping of the $Pt/Ti_{0.7}Ru_{0.3}O_2$ catalyst were obtained using an energy-dispersive X-ray spectroscopic (EDX-JSM 6500F, JEOL) with an accelerating voltage of 15 KV. The BET surface area of the $Ti_{0.7}Ru_{0.3}O_2$ support was obtained from $N_2$ adsorption isotherms at 77 K (Porous Materials, BET-202A). The water content of the $Ti_{0.7}Ru_{0.3}O_2$ was determined by thermogravimetric analysis (Perkin-Elmer Instruments, Diamond TG/DTA). The proton dynamics of $Ti_{0.7}Ru_{0.3}O_2$ were studied using static $^1H$ NMR measurements performed on a Varian Infinity 400 MHz instrument equipped with commercial magic angle spinning (MAS) probes. Spin–lattice ($T_1$) relaxation time was measured by the conventional inversion recovery. X-ray absorption spectra (XAS) were recorded at the National Synchrotron Radiation Research Centre (NSRRC) of Taiwan, Beam Line 01 C, following the procedure described in detail elsewhere.[19] The control of parameters for EXAFS measurements, data collection modes, and the calculation of errors were all done as per the guidelines set by the International XAFS Society Standards and Criteria Committee.[19]

**1.3 Electrochemical Characterization:** A three-electrode cell connected to a Solartron 1480 potentiostat/galvanostat was used for electrochemical measurements. All potentials in this work are referred to normal hydrogen electrode (NHE). For the CO stripping studies, the electrochemical measurement was performed in a $N_2$-saturated 0.5 M $H_2SO_4$ by potential range 0.05 to 1.10 V at $v = 50$ mV $s^{-1}$. The electrochemical surface area (ECSA) was estimated from the integrated charge (after background correction) under the CO oxidation peak of the first scan, based on a monolayer CO adsorption charge of 420 μC $cm^{-2}$ on a smooth Pt surface. A solution of 10 v/v% $CH_3OH$ in aqueous $H_2SO_4$ (0.5 M) was used as the electrolyte in all the MOR studies. In cyclic voltammetry (CV), the potential was swept between 0.05 and 1.10 V at a scan rate ($v$) of 10 mV $s^{-1}$. Prior to the CV measurements, the electrode was activated in the same solution by potential cycling 30 times in the range 0.05 to 1.10 V at $v = 50$ mV $s^{-1}$. Steady-state polarization measurements of MOR were carried out from 0 to 1.1 V at $v = 1$ mV $s^{-1}$ with the electrode rotated at 1600 rpm. Chronoamperometry experiments were carried out at 0.6 V (NHE) in 10 v/v% $CH_3OH$ in aqueous $H_2SO_4$ (0.5 M) at room temperature for 1 hour. In all the above methanol oxidation studies, the electrolyte was deaerated with $N_2$ gas for 30 min before the current measurements, and the gas was passed above the solution level during the experiments. All the electrochemical experiments were carried out at (25±1) °C unless stated otherwise. Working electrodes of Nafion-impregnated commercial catalysts (Pt/C (E-TEK), PtRu/C (JM)) on Glassy Carbon Electrode (GC) were prepared following the same procedure as above to carry out the electrochemical measurements. Pt loading was maintained at 0.221 mg cm$^{-2}$ on all the catalyst electrodes in the electrochemical studies except for Membrane Electrode Assembly (MEA) for fuel cell performance studies.

**1.4 MEA Fabrication and Single-Cell Test:** Fuel cell polarization performance with respect to Pt/$Ti_{0.7}Ru_{0.3}O_2$ and several commercial catalysts was evaluated using a single cell arrangement. The single cell was constructed using a MEA (5 cm$^2$ area) which had been fabricated by hot-pressing a Nafion® NRE-212 membrane (DuPont) between the anode and cathode at 132 °C under a pressure of 4 MPa for 3 min. The catalyst loading was 0.5 mg of Pt cm$^{-2}$ at the anode. The commercial 40 wt% Pt/C (E-TEK) with 0.5 mg of Pt cm$^{-2}$ was used as the cathode catalyst for all the measurements. Anodes were fabricated using catalyst inks which had been prepared by dispersing various Pt catalysts into a solution of the appropriate amount of 5 wt% Nafion and Ethylene Glycol (EG). On the anode, commercial-grade Carbon paper with 5 wt% PTFE-treated (SGL-10BA) was employed as the backing layer. The gas diffusion layers (GDLs) were fabricated on one side of the carbon cloth comprising Vulcan XC-72 carbon and 20 wt% PTFE content for the anode. The prepared anode inks were uniformly brushed on the GDL in 5 cm$^2$ area to give an approximate loading of 0.5 mg cm$^{-2}$. Finally, 0.5 mg cm$^{-2}$ of Nafion was uniformly over-coated on the anode and cathode layers and dried at 60 °C in an oven for 12 hrs. DMFC polarization performance curves were obtained at 60 °C by feeding humidified 2 M methanol at a flow rate of 1 mL min$^{-1}$ using a high-pressure piston pump and by purging humidified oxygen gas into the cathode at a flow rate of 150 mL min$^{-1}$. PEMFC polarizations were performed at 60 °C with fully humidified reactants (flow rates of both hydrogen and oxygen were 150 mL min$^{-1}$). Pt loading was controlled at 0.5 mg cm$^{-2}$ at anode and cathode sides. Performance curves were recorded under constant current with fuel cell test station Beam 100, Beam associate Co., Ltd, Taiwan.

**2. DFT simulation to model $Ti_{0.7}Ru_{0.3}O_2$ structure and its XRD pattern**: DFT simulation to model $Ti_{0.7}Ru_{0.3}O_2$ structure and its XRD pattern: DFT calculations were performed for $Ti_{0.7}Ru_{0.3}O_2$ structure evaluation using CASTEP software, which uses plane waves as basic functions, and the ultrasoft (PW91) method generalized gradient approximation (GGA).[26-29] Initially, the primitive unit cell of $Ti_{0.7}Ru_{0.3}O_2$ was constructed to consist of tetragonal anatase $TiO_2$ structure containing eight O atoms with one of the four Ti sites substituted by a Ru atom; the system was then allowed to reach its lowest energy configuration by a relaxation procedure. All the atomic positions of Ti in the unit cell were considered for substitution by Ru, and lowest energy configurations calculated. In addition to DFT modeling, the diffraction intensity profiles of $Ti_{0.7}Ru_{0.3}O_2$ were calculated based on the CASTEP simulated trajectories, by using the *Reflex/Powder Diffraction* modules of *Materials Studio* package: http://accelrys.com/products/materialsstudio/index.html, version 4.2., to compare with the experimental XRD pattern to confirm the most stable structure of $Ti_{0.7}Ru_{0.3}O_2$.

**3. Calculation the number of unfilled d states ($h_{Ts}$)**: The number of unfilled d states ($h_{Ts}$) was calculated following these steps [19]: Briefly, in the first step, the fractional change in the total number of unfilled d-band states of the sample compared to the reference platinum foil ($f_d$) was calculated using eqn. [1].

$$f_d = \frac{\sigma_3 \Delta A_3 + (1.11\sigma_2 \Delta A_2)}{\sigma_3 A_{3r} + (1.11\sigma_2 A_{2r})} \qquad [1]$$

Here, $A_{3r}$ and $A_{2r}$ are the areas corresponding to electronic transitions to unfilled d-states in the XANES spectra for the reference Pt foil for $L_{III}$- and $L_{II}$- edges, respectively. $\Delta A_3$ and $\Delta A_2$ are the areas corresponding to electronic transitions to unfilled d-states in the XANES spectra between samples and the reference foil for $L_{III}$- and $L_{II}$- edges, respectively. $\Delta A_3$ and $\Delta A_2$ were calculated by subtracting the reference platinum foil data from the catalyst data and then numerically integrating the resulting curves between –10 and +14 eV for $L_{III}$- and $L_{II}$- edges. All the areas ($\Delta A_3$, $\Delta A_2$, $A_{3r}$, $A_{2r}$) were normalized by multiplying with the X-ray absorption cross section ($\sigma$) at the respective edge jump. Values of 117.1 and 54.2 cm$^2$ g$^{-1}$ were used for the $\sigma$ at the Pt $L_{III}$- and $L_{II}$- edges, respectively. Once the $f_d$ value was evaluated, $h_{Ts}$ was able to be calculated from eqn [2],

$$h_{Ts} = (1 + f_d)\, h_{Tr} \qquad [2]$$

where $h_{Tr}$ is the number of unfilled d states in the Pt foil reference sample, which is a known quantity equal to 1.6.

## 4. Supporting Figures and Table

**Table S1.** Characteristics of different fuel cells support materials.

| Material | Specific surface area ($m^2 g^{-1}$) | Particle size (nm) | Ref. |
|---|---|---|---|
| $Ti_{0.7}Ru_{0.3}O_2$ | 275.6 | 8-10 | this work |
| Vulcan XC-72 R | 241.0 | 50 | 2a |
| $W_2C$ | 176 | ~12 | 4c |
| $RuO_2 . xH_2O$ | - | 20 | 10 |
| Ti-doped $WO_3$ | - | - | 11 |
| In-doped $SnO_2$ | 9.7 | 26 | 12 |
| $TiO_2$ nanotube | - | 100* | 13 |
| W-doped $TiO_2$ | - | 50 | 14 |
| Ebonex, $Ti_4O_7$ | 1-3 | ~70 | 30,31 |
| $WO_3$ nanorod | - | 200* | 32 |
| Sn-$In_2O_3$ | - | 38 | 33 |

*diameter

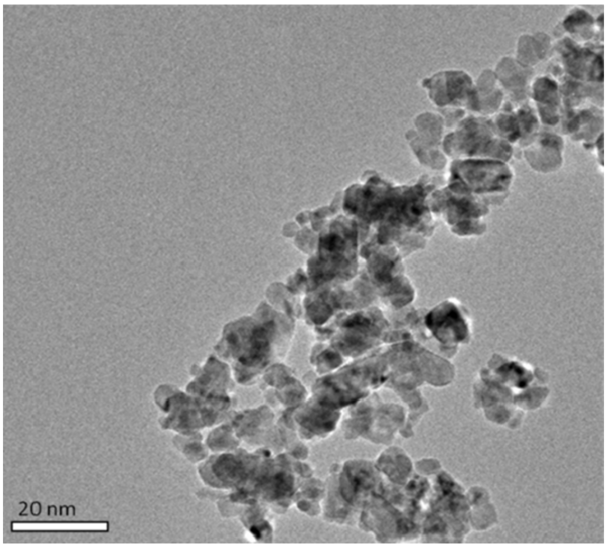
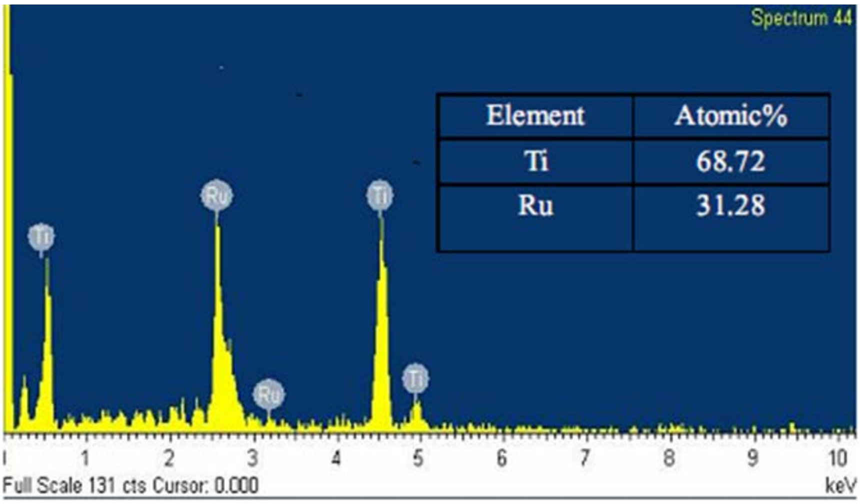


**Figure S1.** TEM of $Ti_{0.7}Ru_{0.3}O_2$ support material.



| Element | Atomic% |
|---|---|
| Ti | 68.72 |
| Ru | 31.28 |

**Figure S2.** EDX spectrum of $Ti_{0.7}Ru_{0.3}O_2$ support material.

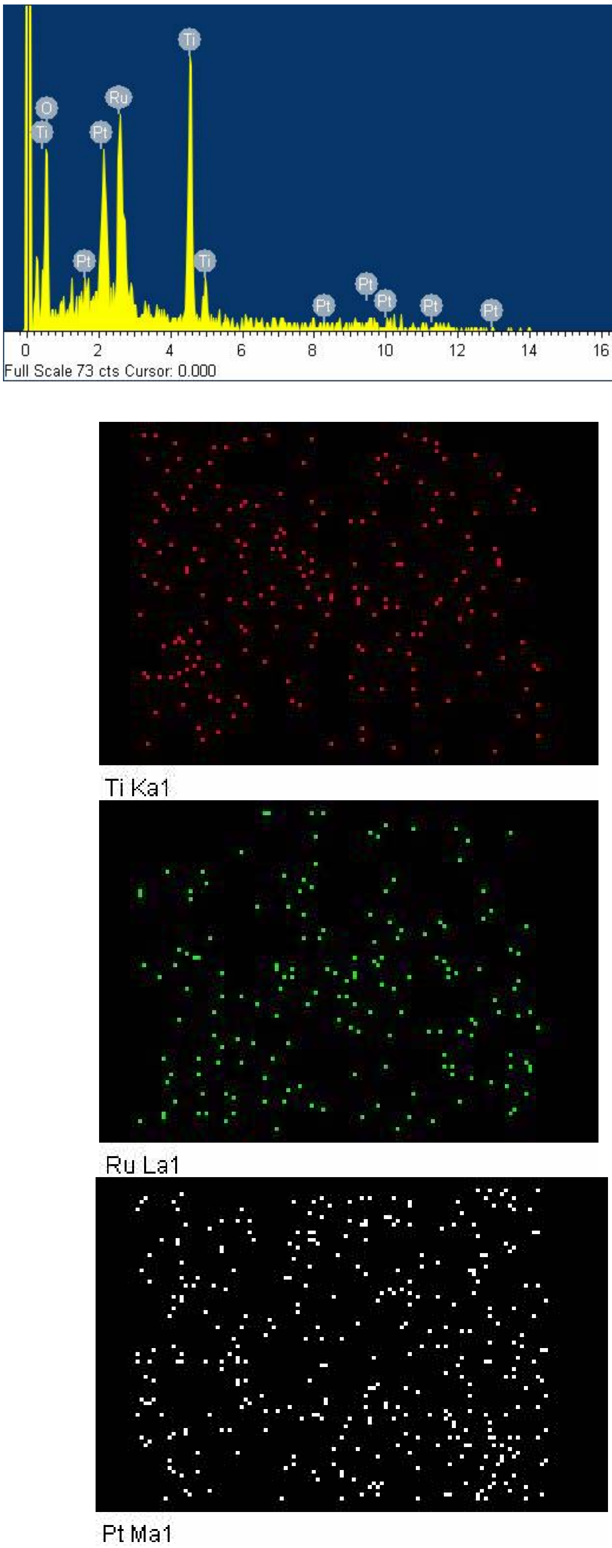


**Figure S3.** EDX spectrum and elemental mapping of Pt/$Ti_{0.7}Ru_{0.3}O_2$ catalyst.

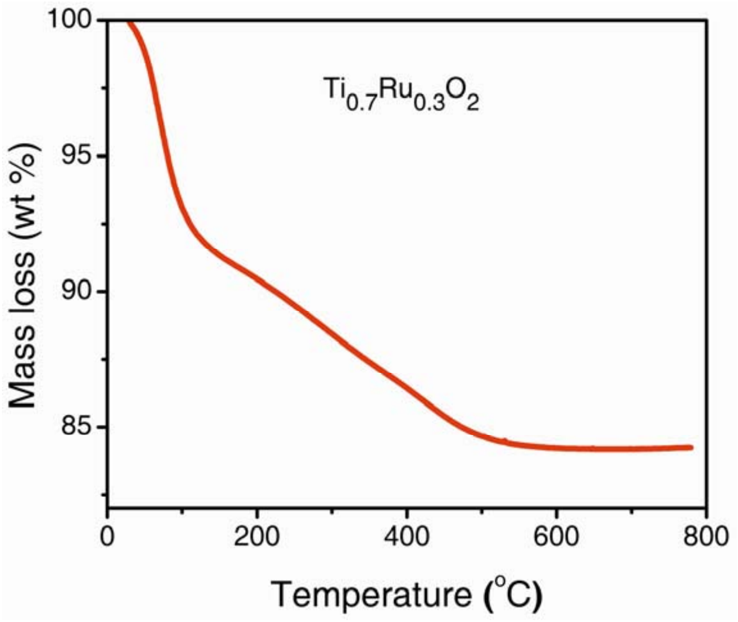


**Figure S4.** TGA curve of $Ti_{0.7}Ru_{0.3}O_2$ support material. The material was measured under flowing Ar for the $Ti_{0.7}Ru_{0.3}O_2$ support and the residual mass at 500 °C was compared with that at 120 °C to determine the water content in the crystalline structure, $Ti_{0.7}Ru_{0.3}O_2.xH_2O$.

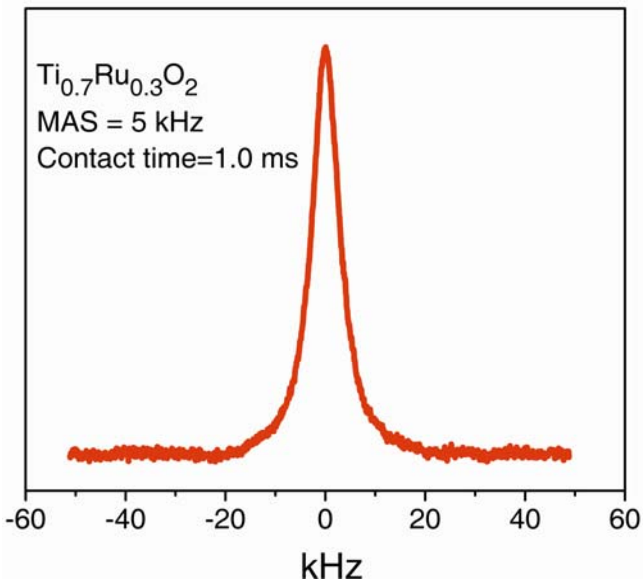


**Figure S5.** Wide-line $^1H$ NMR spectrum of $Ti_{0.7}Ru_{0.3}O_2$ support material.

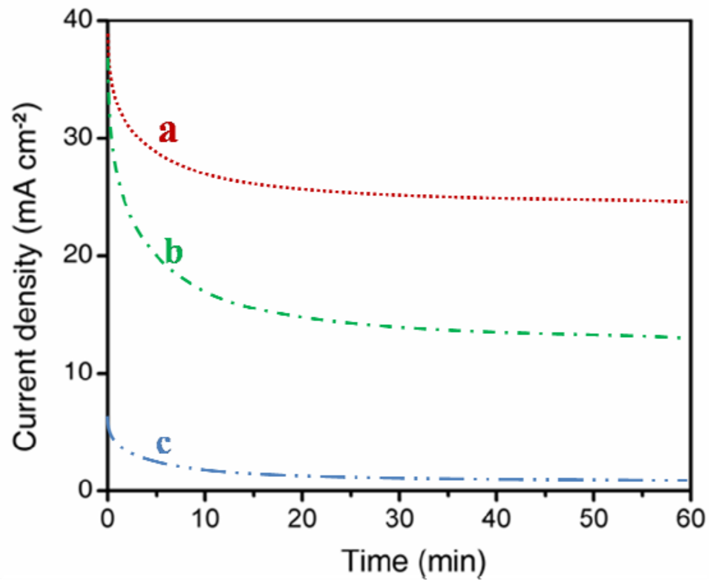


**Figure S6.** Chronoamperometry curves of (a) the 20 wt% Pt/$Ti_{0.7}Ru_{0.3}O_2$ and (b) commercial 20 wt% Pt-10 wt% Ru/C (JM) and (c) 20 wt% Pt/C (E-TEK) catalysts in 10 v/v% $CH_3OH$ in 0.5 M $H_2SO_4$ solution at 25 °C for 1 hr. The oxidation potential was kept at 0.6 V vs. NHE.

## References

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