

# Selective Deposition of Ru Nanoparticles on TiSi<sub>2</sub> Nanonet and Its Utilization for Li<sub>2</sub>O<sub>2</sub> Formation and Decomposition

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## **Experimental Section**

**TiSi<sub>2</sub> Nanonet Synthesis:** TiSi<sub>2</sub> nanonets were prepared by a chemical vapor deposition (CVD) method. A Ti mesh (Cleveland Wire Cloth) was placed in the reaction chamber and heated to 675 °C. SiH<sub>4</sub> (10% in He, Voltaix; at 50 standard cubic centimetres per minute, or sccm), TiCl<sub>4</sub> (98%, Sigma-Aldrich; 2 sccm), and H<sub>2</sub> (industrial grade, Airgas; 60 sccm) were introduced to the chamber concurrently. The growth lasted typically 10 to 120 min with the pressure maintained at 5 Torr.

**Atomic Layer Deposition of Ru:** Ru nanoparticles were deposited on as-grown TiSi<sub>2</sub> nanonets in an Arradiance (Gemstar) ALD system. The growth temperature was 290 °C, with bis(ethylcyclopentadienyl) ruthenium(II) (Ru(EtCp)<sub>2</sub>, heated to 110 °C) and compressed air (room temperature) as reaction precursors. Each cycle consisted of 4 repeated pulse/purge sub-cycles of Ru(EtCp)<sub>2</sub> for sufficient surface adsorption and 1 pulse/purge of O<sub>2</sub> to decompose Ru(EtCp)<sub>2</sub>. The purge gas was N<sub>2</sub>, and its flow rate was 90 sccm. The loading of Ru was quantified using inductively coupled plasma optical emission spectrometry (ICP-OES) at the MIT Center for Materials Science and Engineering (CMSE) using an ACTIVA S (Horiba) ICP-OES Spectrometer.

**Material Characterizations:** Samples were imaged using a transmission electron microscope (JEOL 2010F) operating at an acceleration voltage of 200 kV. Raman spectra were obtained in a customized air-tight sample holder using Horiba XploRA micro Raman system with excitation laser of 532 nm. The surface species and oxidation states were characterized by an X-ray photoelectron spectrometer (K-alpha XPS, Thermo Scientific, Al K $\alpha$ =1486.7eV).

**Electrochemical Characterizations:** 0.1M LiClO<sub>4</sub> in dimethoxyethane (DME) with water level lower than 10 ppm was used as purchased from Novolyte (BASF). Tetraethylene glycol dimethyl ether (TEGDME,  $\geq$  99%, Sigma-Aldrich) was first stored over freshly activated 4 Å molecular sieves and then distilled. The distilled TEGDME was stored over molecular sieves before usage. LiClO<sub>4</sub> (99.99%, Battery grade, Sigma-Aldrich) was further baked at 130 °C under vacuum in the heatable tray of a glove box (MBraun) and then dissolved into TEGDME to give a 1M solution. Customized Swagelok type cells were used as the electrochemistry study platform. Cells were assembled in the glove box (O<sub>2</sub> and H<sub>2</sub>O levels < 0.1 ppm) with Li foil as the anode, 2 Celgard 2500 film sheets as the separator, 0.1 M LiClO<sub>4</sub> in DME or 1 M LiClO<sub>4</sub> in TEGDME as the electrolyte. Ru-decorated TiSi<sub>2</sub> nanonets on Ti mesh (1 cm<sup>2</sup>) were used as the cathode directly without further treatment. No binder or carbon was added in our system. The mass loading of TiSi<sub>2</sub> on Ti mesh is 0.1mg/cm<sup>2</sup> and Ru loading on each cathode is approximately 0.1mg/cm<sup>2</sup>. The final weight ratio of Ru:TiSi<sub>2</sub> was 1:1. The loading quantity of each individual sample was measured by the mass gain after ALD growth using a microbalance and also confirmed by the ICP-OES.

For comparison, carbon black cathode was prepared by dispersing carbon black (Vulcan XC72) and Polytetrafluoroethylene (PTFE, 60wt% dispersion, Sigma-Aldrich) with weight ratio of 8:2 in Isopropanol (10mg carbon/mL) then drop coated on Ni foam with the loading density of 1mg/cm<sup>2</sup>. The cathode was further dried in the vacuum oven at 100 °C overnight. The Ru decoration was performed in the same fashion by ALD as described above after the preparation of the carbon electrode, and the result loading was around 5:1 for Carbon:Ru.

After cell assembly, oxygen (Ultrahigh purity, Airgas) was purged into the cell to replace Argon and the cell was then isolated from the gas line after reaching 780 Torr. Electrochemical characterizations were carried out on an electrochemical station (Biologic, VMP3).

**DFT Calculation:** The Vienna ab initio simulation package (VASP)<sup>1,2</sup> was used to perform periodic density functional theory calculations with planewave bases. The projector augmented wave (PAW) method was used to describe the interaction between electrons and the nuclei;<sup>3</sup> standard VASP-PAW potentials were used for Ti, Si, Pt, and Ru with a recommended kinetic energy cutoff of 245 eV. The Perdew-Burke-Ernzerhof form of the generalized gradient approximation was used for electron exchange and correlation.<sup>4</sup> Due to the large unit cell of the simulated systems, only  $\Gamma$ -point was used for the k-point sampling for structural optimization with a force convergence criterion of 0.025 eV/Å. The DFT optimized lattice parameters of the TiSi<sub>2</sub> C49 structure (a=3.54 Å, b=13.54 Å, c=3.58 Å) are in excellent agreement with the experiment (a=3.56 Å, b=13.61 Å, c=3.56 Å).<sup>5</sup> The metal nanoparticle was modeled as a 38-atom cluster. Both the TiSi<sub>2</sub> b plane [the (010) surface] and the c plane [the (010) surface] were modeled as a six-layer slab. The nanoparticle was placed on top of the surface; the bottom three layers of the surface were fixed at their bulk positions. The adsorption energy,  $E_{ad}$ , is defined as  $E_{ad} = E_{NP/TiSi_2} - E_{NP} - E_{TiSi_2}$ , where  $E_{NP/TiSi_2}$ ,  $E_{NP}$ , and  $E_{TiSi_2}$  are the energies of the adsorbed system, the isolated nanoparticle, and the clean TiSi<sub>2</sub> surface, respectively. So a negative  $E_{ad}$  indicates a favorable interaction.

**DEMS Detection:** For the Differential Electrochemical Mass Spec (DEMS) characterization, the cell was first discharged under 780 Torr pure O<sub>2</sub>. The cell was then evacuated for 3 hours to remove O<sub>2</sub> in the chamber prior to DEMS characterization. The gas content was analyzed using a customized mass spectrometer with quadrupole rods mass analyzer (Microvision 2, MKS).

The cell was further studied in two ways – *in situ* and accumulation modes. For *in situ* analysis, the cell was connected to the Mass Spectrometer under vacuum with a dry rotary pump (nXDS 10i, Edwards) as the primary pump and a turbo pump to power the Mass Spectrometer. The cell was wired to a potentiostat (609D, CH Instruments) for galvanostatic recharging. For a typical *in situ* test, a constant current (500 mA/g<sub>Ru</sub>) was applied to the cell and the gas generated was analyzed in real time to obtain the profile of gas content at the different stages of recharge. Every MS scan was collected from 28 to 44 amu within 2s to give both the desired time resolution and accuracy.

For the Faradic efficiency test (accumulation mode), the cell was treated in the same way to generate an evacuated discharged cell as described above. The cell was then sealed and recharged (200 mA/g<sub>Ru</sub>, 1000 mAh/g<sub>Ru</sub>) to the capacity which matches that of the discharge. At the end of recharge, all gases generated were introduced to the MS at once with the same set up as described above, and O<sub>2</sub> (m/Z=32) signal was acquired and integrated to obtain the peak area. Calibration was performed by introducing a known amount of oxygen into the cell and carrying out the same data acquisition and analysis. A linear relationship between the peak area and amount of O<sub>2</sub> in the cell was established. The final Faradic efficiency was calculated by dividing

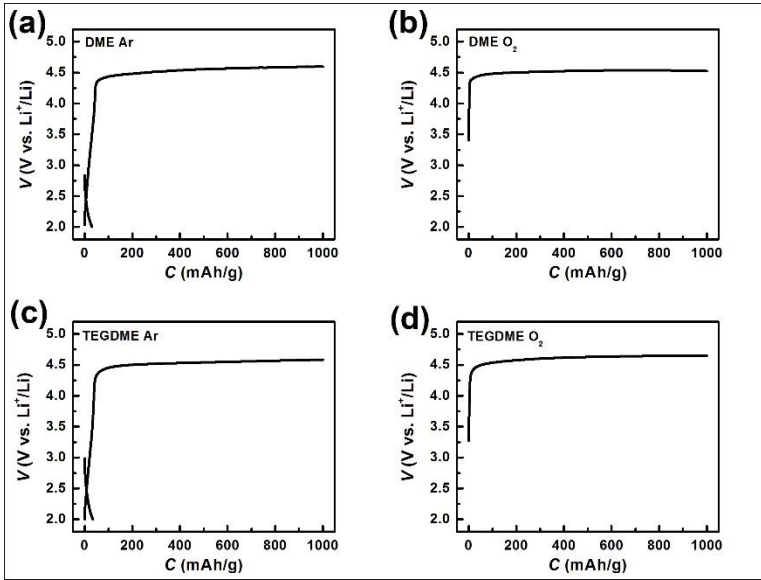
the amount of O<sub>2</sub> detected in the MS by the theoretical value calculated from the charges passed to the cell.

**Raman Characterization:** Raman spectra were acquired using a micro-Raman system (XploRA, Horiba) with a 532nm laser excitation. Discharged/charged cell was first disassembled in an O<sub>2</sub> tolerated Argon filled glove box (dew point -100 °C) and washed by pure anhydrous DME (Signal-Aldrich) three times. Then the cathode was assembled into a custom-made air-tight sample holder with a thin glass window. The discharged cathode was examined by Raman within the sample holder and no obvious peak of Li<sub>2</sub>O<sub>2</sub> or Li<sub>2</sub>CO<sub>3</sub> was detected. When the same sample was exposed to ambient air for several hours, significant Li<sub>2</sub>CO<sub>3</sub> signal was observed on the same piece of sample. The fact that no Li<sub>2</sub>O<sub>2</sub> signal was observed indicates that electrodeposited Li<sub>2</sub>O<sub>2</sub> may be of poor crystallinity to produce significant Raman response. Once exposed to H<sub>2</sub>O and CO<sub>2</sub> from ambient air, it was transformed to Li<sub>2</sub>CO<sub>3</sub> that was easier to be detected.

**XPS Characterization:** Surface analysis was carried out using a K-Alpha XPS (Thermo Scientific) with Al K-alpha micro-focused monochromator. The beam spot size was 400 μm. The sample was also washed by DME with the same procedure described above and mounted on the sample stage with minimal exposure to the ambient air before entering the load lock (on the order of minutes). The chamber was pumped down to 8×10<sup>-8</sup> mbar prior to tests. Data were fitted by CasaXPS after correction by setting the internal reference C1s peak to 248.8eV. Li 1s peak of Li<sub>2</sub>O<sub>2</sub> peak was assigned at 55.1 eV, that of LiOH was assigned at 54.3 eV, and that of Li<sub>2</sub>CO<sub>3</sub> was assigned at 55.7 eV. The absolute values of these peaks may vary from different reports, but the relative position remained constant.

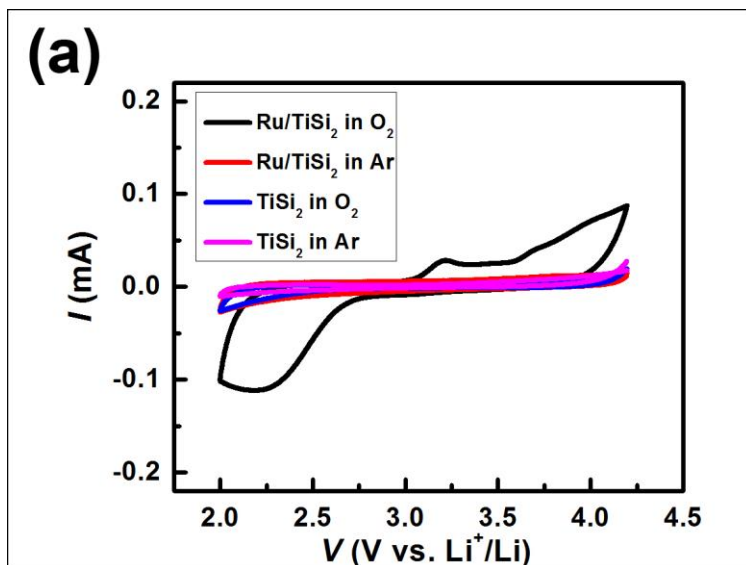
XPS was performed at the Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Infrastructure Network (NNIN), which is supported by the National Science Foundation under NSF award no. ECS-0335765. CNS is part of Harvard University.

### Stability of DME and TEGDME electrolyte



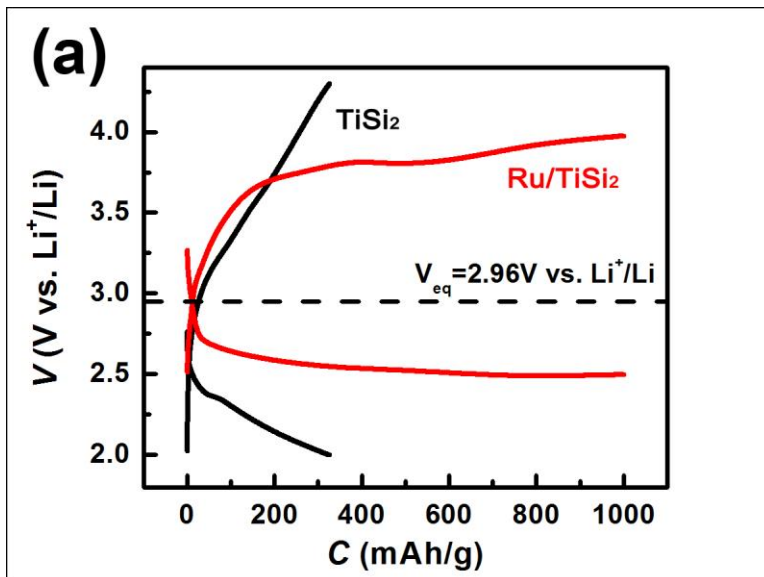
**Figure S1:** Stability of DME and TEGDME electrolyte. (a) Ru/TiSi<sub>2</sub> discharged and then recharged in DME, without O<sub>2</sub> (Ar environment); (b) Ru/TiSi<sub>2</sub> charged directly without discharge in DME O<sub>2</sub> environment; (c) Ru/TiSi<sub>2</sub> discharged and then recharged in TEGDME Ar environment; (d) Ru/TiSi<sub>2</sub> charged directly without discharge in TEGDME O<sub>2</sub> environment. Current density: 100mA/g<sub>Ru</sub>. Negligible capacity was measured at potentials below 4.2 V, which is the condition used for the characterization of Ru/TiSi<sub>2</sub> system in the main text, supporting that electrolyte decomposition should contribute little to the reported performance.

### Cyclic Voltammetry of $\text{TiSi}_2$ and $\text{Ru/TiSi}_2$ in Electrolyte



**Figure S2:** Cyclic Voltammetry of  $\text{TiSi}_2$  and  $\text{Ru/TiSi}_2$  in DME Electrolyte. Black and red curves are  $\text{Ru/TiSi}_2$  in  $\text{O}_2$  and Ar, respectively. Blue and purple curves are bare  $\text{TiSi}_2$  in  $\text{O}_2$  and Ar, respectively. It is observed from this set of data that  $\text{TiSi}_2$  does not exhibit reactivity toward ORR or OER, while  $\text{Ru/TiSi}_2$  are active toward both ORR and OER. We also see from this set of data that  $\text{Ru/TiSi}_2$  does not induce measurable redox reactions in the absence of  $\text{O}_2$ .

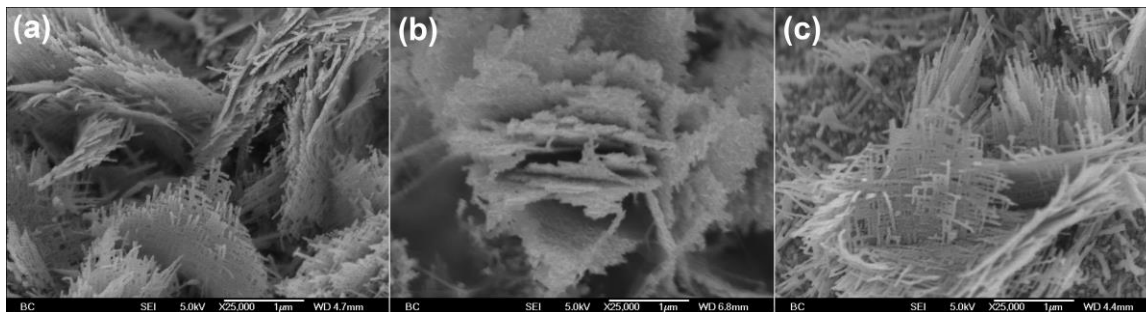
### Electrochemical characterization of bare $\text{TiSi}_2$



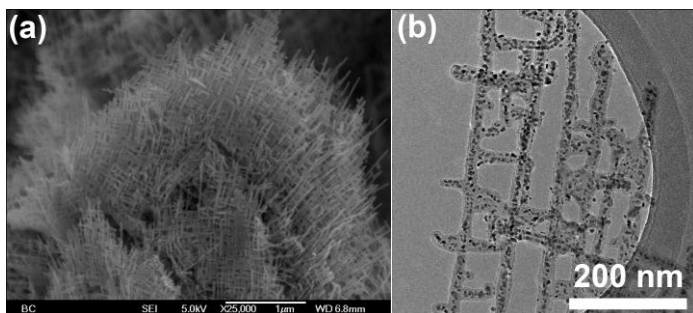
**Figure S3:** Electrochemical characterization of  $\text{TiSi}_2$  cathode with and without Ru catalyst. Current density:  $100\text{mA}/\text{g}_{\text{TiSi}_2}$  and  $100\text{mA}/\text{g}_{\text{Ru}}$  respectively. It can be seen that Ru as a catalyst is indispensable to the measured performance.



### Structural Characterization (SEM and TEM)

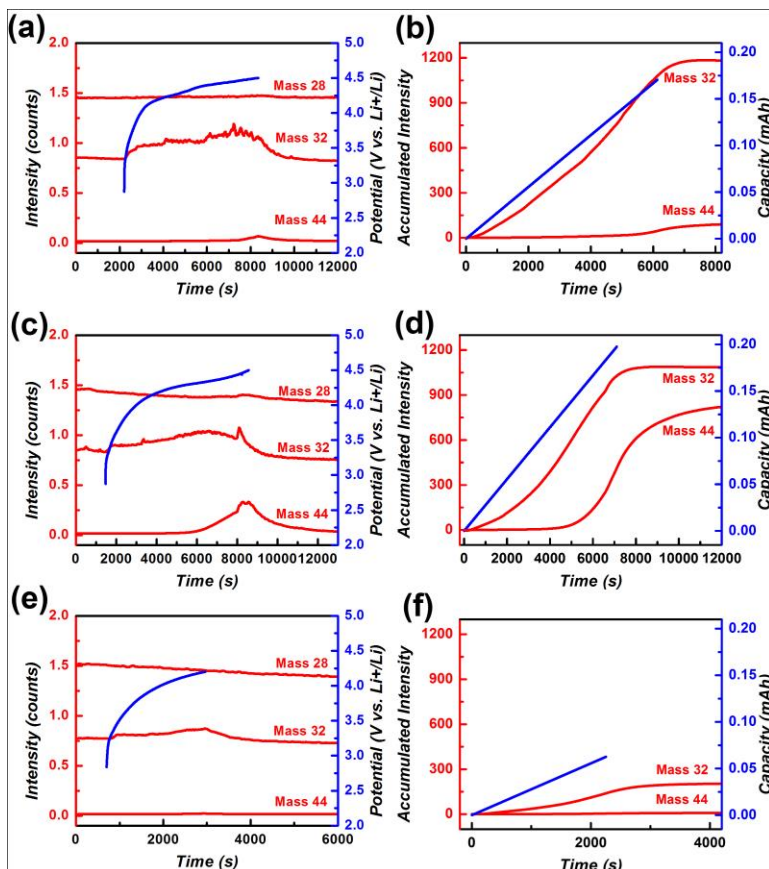


**Figure S4:** Structures of Ru/TiSi<sub>2</sub> heteronanostructures. (a) As-prepared Ru/TiSi<sub>2</sub>; (b) Ru/TiSi<sub>2</sub> discharged for the 1<sup>st</sup> cycle; (c) Ru/TiSi<sub>2</sub> recharged for the 1<sup>st</sup> cycle

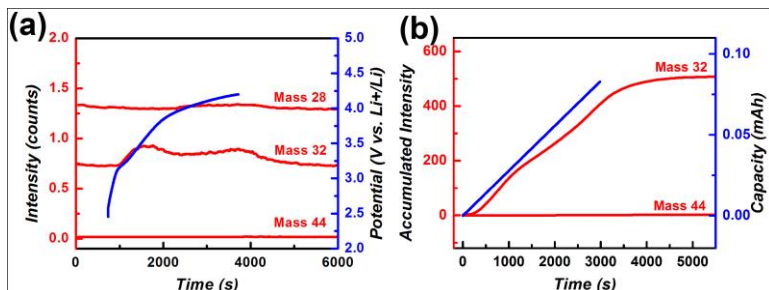


**Figure S5:** Structures of Ru/TiSi<sub>2</sub> heteronanostructures after 100 cycles. (a) SEM characterization; (b) TEM characterization. It can be seen that there was no observable erosion of the cathode material.

## DEMS Detection

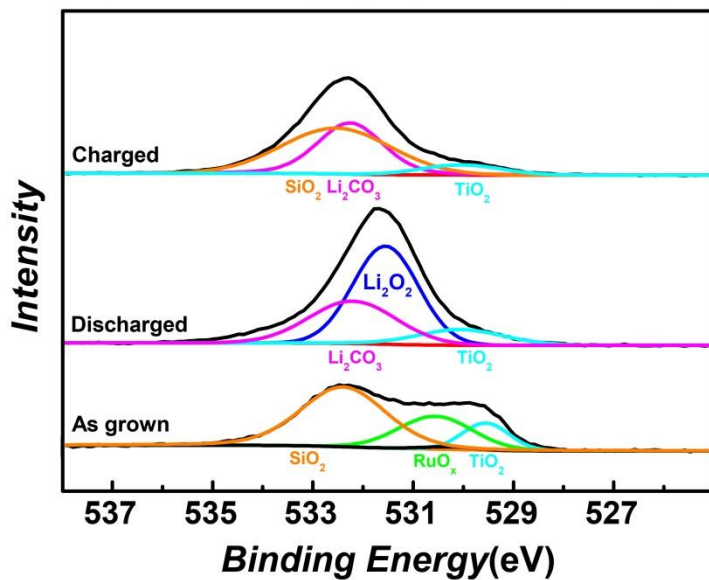


**Figure S6:** (a), (c), and (e) in-situ MS detection of gas generation at a fast 500mA/g charge rate for Carbon Black (up to 4.5 V vs. Li<sup>+</sup>/Li), Ru/Carbon Black (up to 4.5 V vs. Li<sup>+</sup>/Li), and Ru/Carbon Black (up to 4.2 V vs. Li<sup>+</sup>/Li); (b), (d), and (f) accumulated counts of mass 32 and mass 44 species for above samples. Unless the upper cut-off voltage is set below 4.2 V, CO<sub>2</sub> formation is significant. This set of data supports that carbon support participates in the carbonate formation significantly.

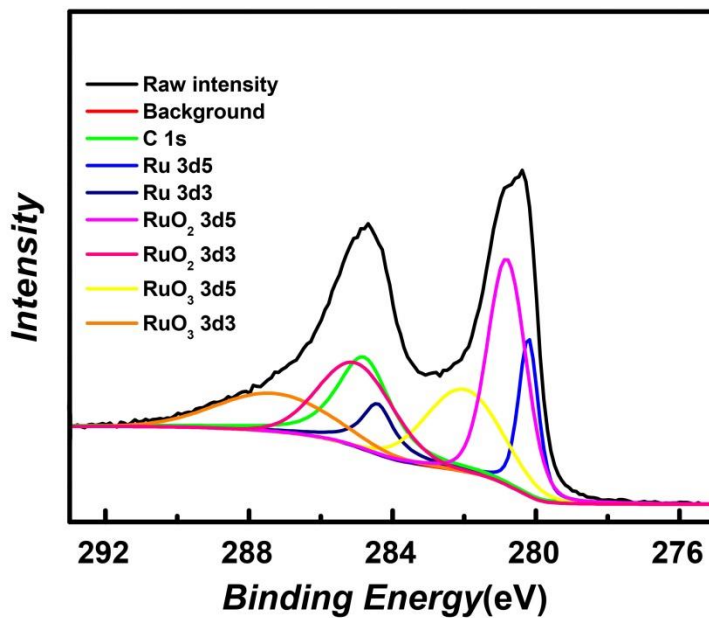


**Figure S7:** (a) in-situ MS detection of gas generation at a fast 500mA/g charging rate for Ru/TiSi<sub>2</sub> (up to 4.2 V vs. Li<sup>+</sup>/Li, after 5 cycles); (b) accumulated counts of mass 32 and mass 44 species. After 5 cycles of repeated discharge/recharge, no significant CO<sub>2</sub> formation is measured.

## XPS Characterization

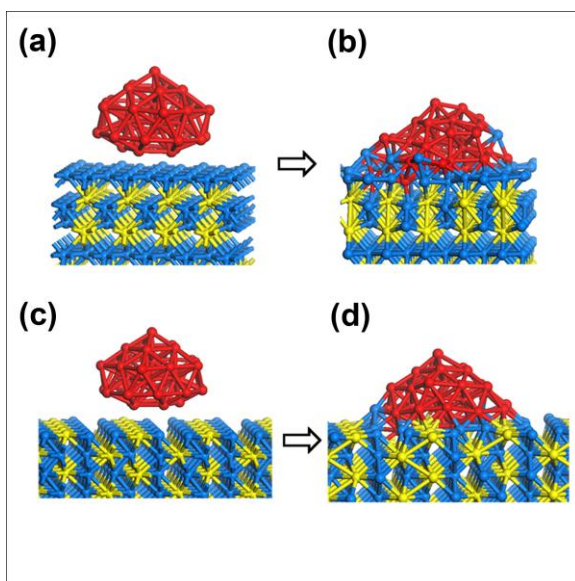


**Figure S8:** O 1s peak spectra of as grown, discharged and charged cathodes. The results are consistent with the Li 1s data as shown in the main text.

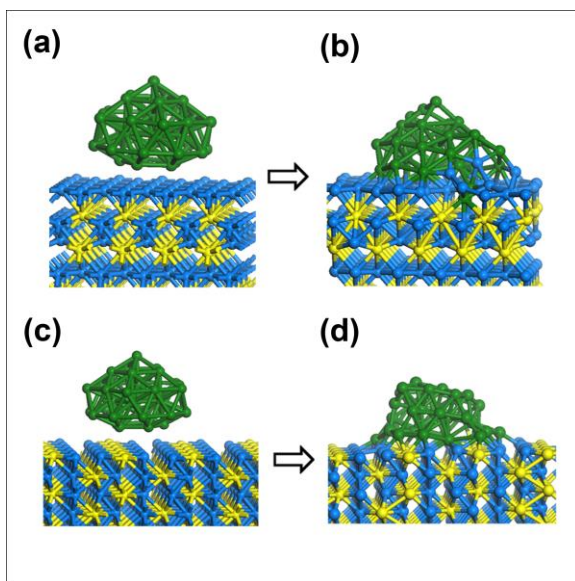


**Figure S9:** C 1s and Ru 3d spectra of as grown cathode.

### DFT Results (Ru on TiSi<sub>2</sub> and Pt on TiSi<sub>2</sub>)

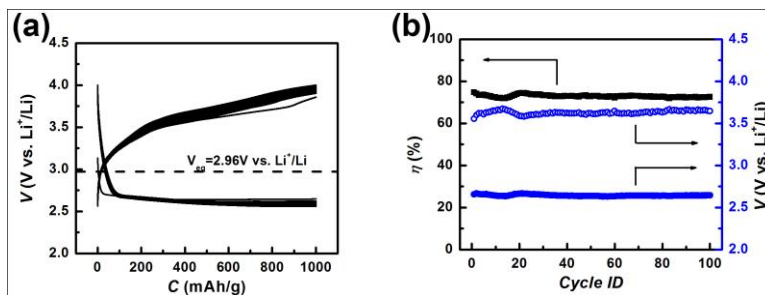


**Figure S10:** Initial (a) and final (b) states of the Ru<sub>38</sub> nanoparticle on the b-plane of the TiSi<sub>2</sub> C49 structure; initial (c) and final (d) states of the Ru<sub>38</sub> nanoparticle on the c-plane of the TiSi<sub>2</sub> C49 structure. Ru, red; Si, blue; Ti, yellow. The adsorption energy of the nanoparticle on the two TiSi<sub>2</sub> surfaces: -54 eV on the b-plane and -38 eV on the c-plane.

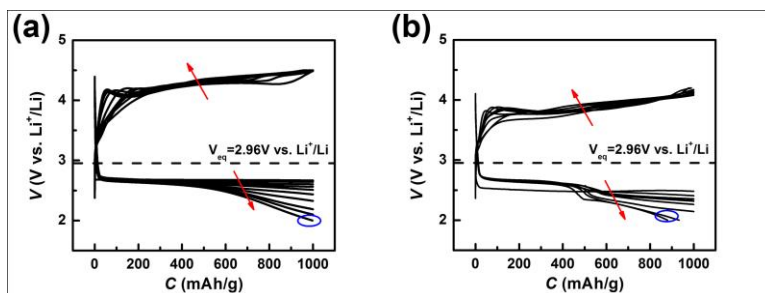


**Figure S11:** Initial (a) and final (b) states of the Pt<sub>38</sub> nanoparticle on the b-plane of the TiSi<sub>2</sub> C49 structure; initial (c) and final (d) states of the Pt<sub>38</sub> nanoparticle on the c-plane of the TiSi<sub>2</sub> C49 structure. Pt, green; Si, blue; Ti, yellow. The adsorption energy of the nanoparticle on the two TiSi<sub>2</sub> surfaces: -49 eV on the b-plane and -40 eV on the c-plane.

## Complete Data Set of Ru/TiSi<sub>2</sub> and Ru/Carbon Black Cycle Performance



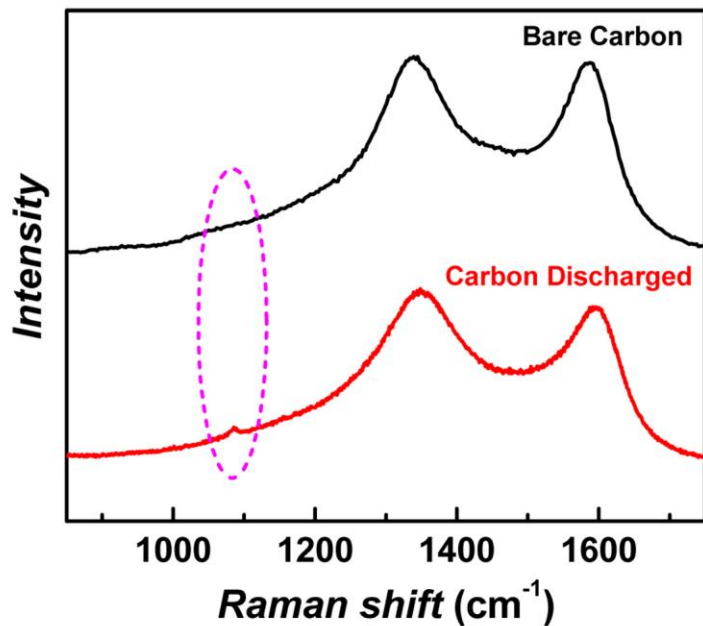
**Figure S12:** Electrochemical characterization of the Ru/TiSi<sub>2</sub> cathode in DME (0.1M LiClO<sub>4</sub>). (A) Potential vs. Capacity plots of a cell from 1<sup>st</sup> cycle to 100<sup>th</sup> cycle. The dotted horizontal line marks the thermodynamic equilibrium potential of 2.96 V between reversible Li<sup>+</sup> and Li<sub>2</sub>O<sub>2</sub> conversion. (B) Average discharge (solid circle), recharge (hollow circle), and round-trip efficiencies over 100 cycles.



**Figure S13:** Electrochemical characterization of the carbon based cathode in DME (0.1M LiClO<sub>4</sub>). (a) Potential vs. Capacity plots of Carbon black cathode for first 11 cycles. (b) Potential vs. Capacity plots of Ru/Carbon black cathode for first 9 cycles. All capacities were normalized to weight of Carbon black.

Bare Carbon black and Ru/Carbon Black samples failed to reach the set capacity of 1000 mAh/g<sub>c</sub> before reaching the cut off voltage of 2.0V at 11<sup>th</sup> cycles and 9<sup>th</sup> cycles, respectively. During the initial several cycles, significant side reactions took place and caused the overpotential to increase.

## Raman Characterization of Pristine and Discharged Carbon Black Cathode



**Figure S14:** Raman characterizations of pristine Carbon black cathode (black) and discharge Carbon black cathode after cycles (red) within air-tight container. A small  $\text{Li}_2\text{CO}_3$  peak was observed after discharge.

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