Tuning surface chemistry of TiC electrodes for lithium-air batteries

Supporting Information

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Table S1. Calculated standard Gibbs free energy for the reactions of TiC oxidation by Li_2O_2 . The standard Gibbs free energy of formation of the compounds were taken from NIST-JANAF Thermochemical Tables.

Reaction	∆ _r G ⁰ , kJ/mol	
$TiC + 4 \text{ Li}_2O_2 \rightarrow TiO_2 + \text{Li}_2CO_3 + 3 \text{ Li}_2O$	-1243.6	
$2 \operatorname{TiC} + 6 \operatorname{Li}_2 \operatorname{O}_2 \rightarrow 2 \operatorname{TiO}_2 + \operatorname{Li}_2 \operatorname{CO}_3 + \operatorname{C} + 5 \operatorname{Li}_2 \operatorname{O}$	-1934.8	



Figure S1. Increase in Li 1s and O 1s peak intensities during galvanostatic discharge of the cell with TiC nanopowder cathode at the current of 1 μ A. The *in situ* measurements were carried out inside the XPS chamber under 0.1 mbar oxygen pressure.



Figure S2. SEM image of TiC nanopowder (a) and its particle size distribution (b). XRD pattern (c) and Raman spectrum (d) confirm that the powder is predominantly composed of TiC with elemental carbon contamination^{1,2}.

Calculation of an effective thickness of the discharge product layer formed on the Ar⁺ sputtered TiC powder electrode during the cell operation.

Formation of the discharge product layer on the TiC electrode during cell operation results in Ti 2p intensity attenuation, according to the following equation:

$$I = I_0 exp\left(-\frac{d}{\lambda\cos\theta}\right),$$

where I – Ti 2p intensity for TiC electrode after cell discharge, I_0 – Ti 2p intensity for initial TiC electrode, d – effective thickness of the layer, λ - inelastic mean free path of the photoelectrons in the layer, θ – photoelectron emission angle. Thus, for calculation of the effective thickness of

the discharge product layer Ti 2p intensity in each pixel of the map obtained after cell discharge was divided by Ti 2p intensity in the corresponding pixels of the map from initial TiC electrode, and the result was inserted in the formula above. This procedures were carried out using Igor Pro software.



Figure S3. Evolution of Ti 2p spectrum during discharge of the cell with "cleaned" TiC nanopowder cathode in *in situ* experiment.



Figure S4. Evolution of C 1s spectrum during discharge of the cell with "cleaned" TiC nanopowder cathode in *in situ* experiment.



Figure S5. Li 1s and O 1s intensity decrease during charge of the cell with TiC powder electrode, indicating lithium peroxide decomposition.



Figure S6. SEM images of the dense ceramic plates, used for TiC, TiN and TiO disc electrodes preparation, before (a) and after (b) polishing. According to XRD patterns (c) and Raman spectrum (d), these plates are single phase (* - TiC, • - TiN, • - TiO), except for titanium carbide related, which also contains elemental carbon (\times - C)^{1,2}.



Figure S7. Cyclic voltammogram of glassy carbon polished disc electrode in 1 M LiTFSI solution in DMSO at a sweep rate of 100 mV/s. The processes occurring at cathodic and anodic peak potentials are discussed elsewhere³.

Comments to Figure S7

Three-electrode glass cell used for cyclic voltammetry measurement of glassy carbon (GC) polished disc electrode was assembled in Ar-filled glove box. Pt wire was used as a counter electrode and Li foil in 1 M LiClO₄ solution in propylene carbonate (PC, anhydrous, 99.7%, Sigma-Aldrich) – dimethoxyethane (DME, anhydrous, 99.5%, Sigma-Aldrich) mixture as a reference electrode.



Figure S8. Angle dependence of Ti 2p component relative intensities for the pristine TiC polished disc electrode. Photoelectron emission angle was measured from the normal to the sample surface.



Figure S9. Ti 2p spectra of TiC polished disc electrode pristine (a) and taken after exposure to electrolyte (0.1 M LiClO₄ solution in DMSO) (b). The spectra show that TiC electrode does not undergo any measurable changes in the contact with electrolyte.



Figure S10. C 1s spectra of pristine TiC polished disc electrode after exposure to electrolyte (a) and the same electrode cycled for 1 (b), 4 (c) and 30 (d) voltammetry cycles. The spectra show the formation and gradual increase of Li_2CO_3 amount and the growth of elemental carbon surface layer.

Calculation of effective Li₂O₂ film thickness cathodically generated and anodically oxidized Assuming that lithium peroxide is the main discharge product and anodic charge is spent primarily on Li₂O₂ oxidation, we calculated the effective thickness of lithium peroxide film using a combination of Faraday's law and film mass dependence on its thickness that resulted in the following equation:

$$d=\frac{MQ}{\rho SnF},$$

where d is the film thickness, M is the molecular weight of Li_2O_2 , Q is the transferred cathodic/anodic charge, ρ is the density of Li_2O_2 , S is the TiC electrode area, n is the number of transferred electrons in ORR/OER, and F is the Faraday constant. The charge passed during cathodic/anodic process was estimated from cyclic voltammograms by peak analysis procedure in EC-Lab software.

Calculation of surface atomic fractions

Surface atomic fractions (at%) of components in Ti 2p, C 1s, O 1s and Li 1s spectra were calculated using the following equations:

$$at\%_i = \frac{C_i}{\sum_i C_i}$$
, where $C_i = \frac{10^{-12} \cdot I_i}{k_i}$,

where C_i is a surface concentration of the component, I_i is an integral intensity of the spectral line corresponding to the component, k_i is a normalization coefficient for a given line. The values were multiplied by 10^{-12} for convenience.

Normalization coefficients were calculated as a product of photon flux and photoionization cross-section for a given photon energy, corresponding to photoelectron kinetic energy of 200 eV (Table S2). The intensity measurements were carried out while synchrotron operated in top-up regime with a constant ring current so no normalization for ring current was applied.

Table S2. The normalization coefficients for atomic fraction calculations.

Line	Photon energy, eV	Flux, a.u.	Photoionization cross-section, Mbarn ⁴	k, a.u.
Ti 2p	665	2.009E-12	0.9413	1.891E-12
C 1s	485	3.110E-12	0.2912	0.906E-12
O 1s	727	1.581E-12	0.2571	0.406E-12
Li 1s	255	3.394E-12	0.1425	0.484E-12

Calculation of TiO₂ surface layer thickness from Ti 2p spectra

Thickness of TiO_2 layer (h) on TiC surface was estimated using Hill equation⁵:

$$h = \lambda_{TiO_2} \cos \theta \left(\frac{N_{TiC} \lambda_{TiC}}{N_{TiO_2} \lambda_{TiO_2}} \frac{I_{TiO_2}}{I_{TiC}} + 1 \right),$$

where λ_{TiC} and λ_{TiO2} – inelastic mean free path of the photoelectrons in TiC and TiO₂ at a given photoelectron kinetic energy, θ - the angle of the photoelectron emission (measured from the normal to the sample surface), N_{TiC} and N_{TiO2} – atomic density of Ti atoms in TiC and TiO₂, I_{TiC} and I_{TiO2} – integral intensity of TiC and TiO₂ related doublets in Ti 2p spectra, normalized by photoionization cross-section and photon flux.

Inelastic mean free path was evaluated using TPP-2M equation (Tanuma, Powell, Penn)⁶:

$$\lambda = \frac{E}{E_p^2 [\beta ln(\gamma E) - CE^{-1} + DE^{-2}]} \text{ (Å),}$$

where $E_p = 28.8 \left(\frac{N_v \rho}{M}\right)^{1/2} (eV),$
 $\beta = -0.10 + 0.944 \left(E_p^2 + E_g^2\right)^{-0.5} + 0.069 \rho^{0.1},$
 $\gamma = 0.191 \rho^{-0.50},$
 $C = 1.97 - 0.91U,$
 $D = 53.4 - 20.8U,$
 $U = \frac{N_v \rho}{M} = \frac{E_p^2}{829.4},$

E is the kinetic energy of photoelectrons, E_p is the free-electron plasmon energy, N_v is the number of valence electrons per molecule, ρ is the density (in g/cm³), M is the molecular weight, and E_g is the bandgap energy (in eV).

Table S3. The coefficients for TiO_2 surface layer thickness calculation.

	λ, Å (200 eV)	N/N _A , mol/cm ³
TiC	6.68	0.082
TiO ₂	7.30	0.053



Figure S11. The dependencies of cathodic charge and theoretical relative current density⁷ on TiO_2 layer thickness. Experimental TiO_2 layer thickness determination by XPS was performed after selected cycles (dark blue circles). Light blue open squares indicate cathodic charge dependence on TiO2 thickness determined from fitting of experimentally obtained thickness values vs. cycle number.

Calculation of a transfer coefficient (α)

Transfer coefficient was calculated for the first step of oxygen reduction reaction (ORR) resulting in superoxide species formation:

 $O_2 + e^- \rightarrow O_2^-$.

For this purpose, Tafel plot (E vs. $\ln |i|$) was obtained from the voltammetry curve and fitted by the straight line (figure S12a). A value of this line slope was used to estimate the transfer coefficient, according to the following equation:

$$E = \frac{RT}{\alpha nF} \ln i_0 + E_{eq} - \frac{RT}{\alpha nF} \ln |i|,$$

where E is the working electrode potential, R is the molar gas constant, T is the temperature, n is the number of electrons transferred in observed electrochemical reaction, F is the Faraday constant, i_0 is the exchange current density, E_{eq} is the equilibrium potential of the reaction, and i is the current density on the working electrode.

Figure S12b shows the variation of the transfer coefficient for above-mentioned reaction occurring on the polished TiC disc electrode surface at room temperature upon voltammetric cycling, indicating nearly the same value of 0.54 ± 0.06 .



Figure S12. (a) Tafel plot for the fist step of ORR on the 1^{st} , 5^{th} , 10^{th} , 15^{th} , 20^{th} , 25^{th} and 30^{th} voltammetric cycles measured at a sweep rate of 100 mV/s on the polished TiC disc electrode in 0.1 M LiClO₄ solution in DMSO; (b) the variation of the transfer coefficient for the first step of ORR occurring on this electrode with cycle number.

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