

Enhancing Electrocatalytic Activity in Metallic Thin Films through Surface Segregation of Carbon

Ayesha Kousar^a, Ulviyya Quliveya^a, Ishan Pande^a, Jani Sainio^b, Jaakko Julin^c, Timo Sajavaara^c, Antti Karttunen^d, Tomi Laurila^{a, d*}

^a Department of Electrical Engineering and Automation, School of Electrical Engineering, Aalto University, PO Box 13500, 00076 Aalto, Finland

^b Department of Applied Physics, School of Science, Aalto University, PO Box 15100, 00076 Aalto, Finland

^c Department of Physics, University of Jyväskylä, PO Box 35 FI-40014, Finland.

^d Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, PO Box 16200, 00076 Aalto, Finland

Electronic Supplementary Information

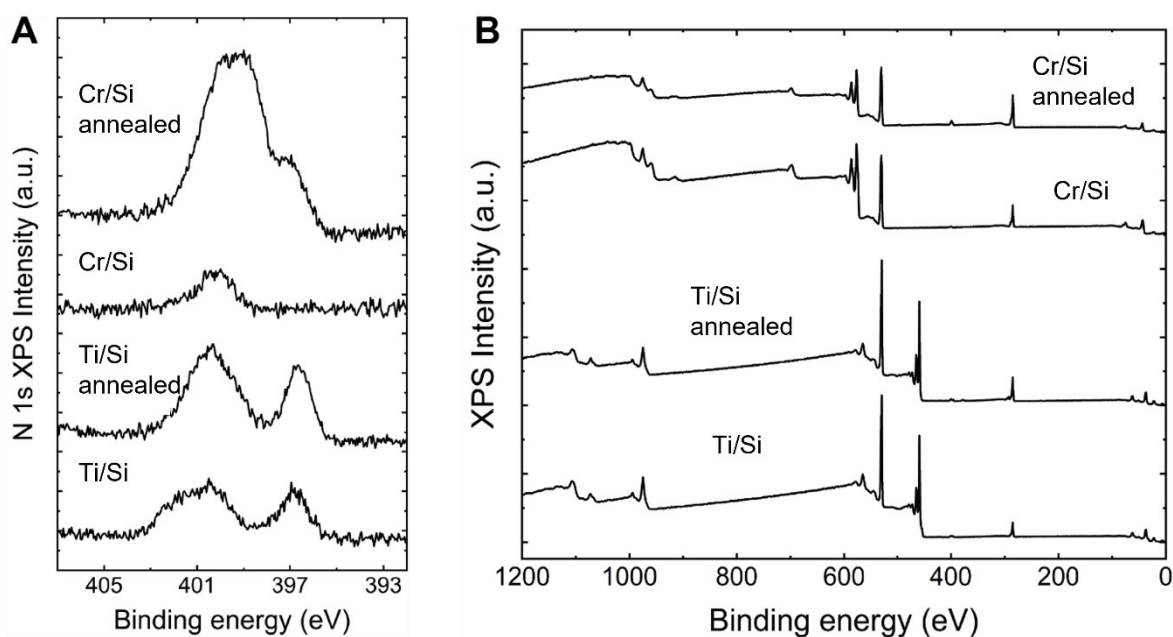


Fig S1. X-ray photoelectron of (A) N 1s spectra (B) survey spectra of Cr and Ti samples.

Table S1. The atomic percentages (at-%) of the elements for Cr and Ti samples including peak fitting results. The error associated with each value is roughly $\pm 10\%$ of the value.

Element	Cr/Si	Cr/Si annealed	Ti/Si	Ti/Si annealed
C of which	31.1	46.7	20.4	29.1
sp ² C	0.3	11.1	-	-
sp ³ C / sp ² C–N	22.0	21.8	13.8	21.5
C–O–C / C–OH / sp ³ C–N	2.8	5.5	3.2	3.8
C=O	2.3	4.9	0.9	1.7
O–C=O	3.7	3.5	2.5	2.1
p–p*	~0	0.8	-	-
O of which	44.0	35.4	53.7	48.9
O–Metal	23.0	17.3	42.7	39.9
O=C	16.1	13.8	8.4	6.4
O–C / OH–C	4.9	4.3	2.6	2.6
Cr	24.3	13.1	-	-
Ti	-	-	24.2	19.6
N	0.6	4.8	1.7	2.2
Si	-	-	-	0.2

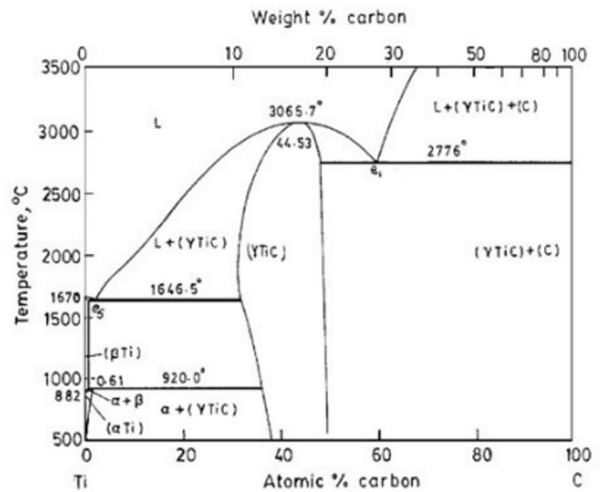
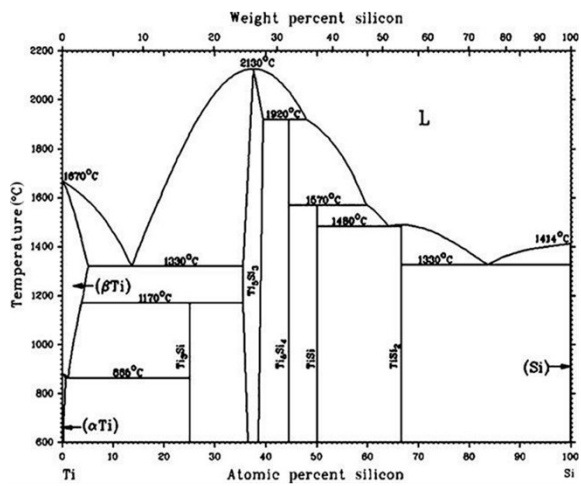


Figure S2: Ti-Si¹ and Ti-C² phase diagram

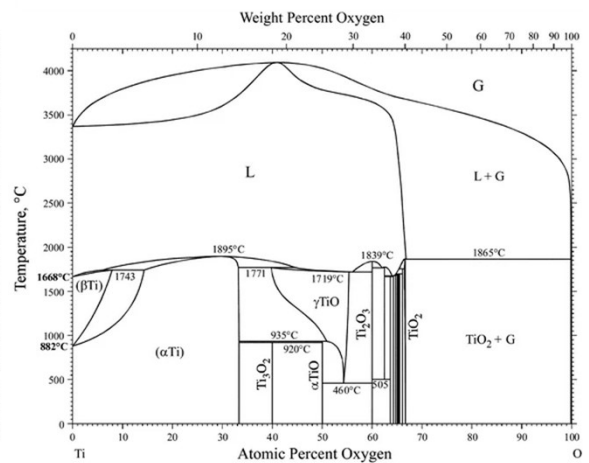
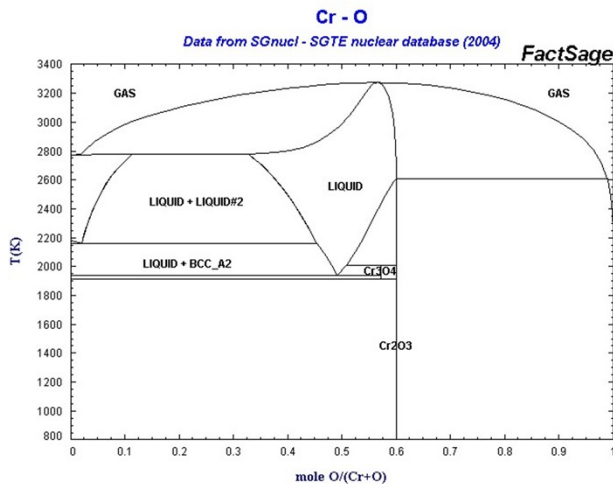


Figure S3. Cr-O and TiO phase diagrams²

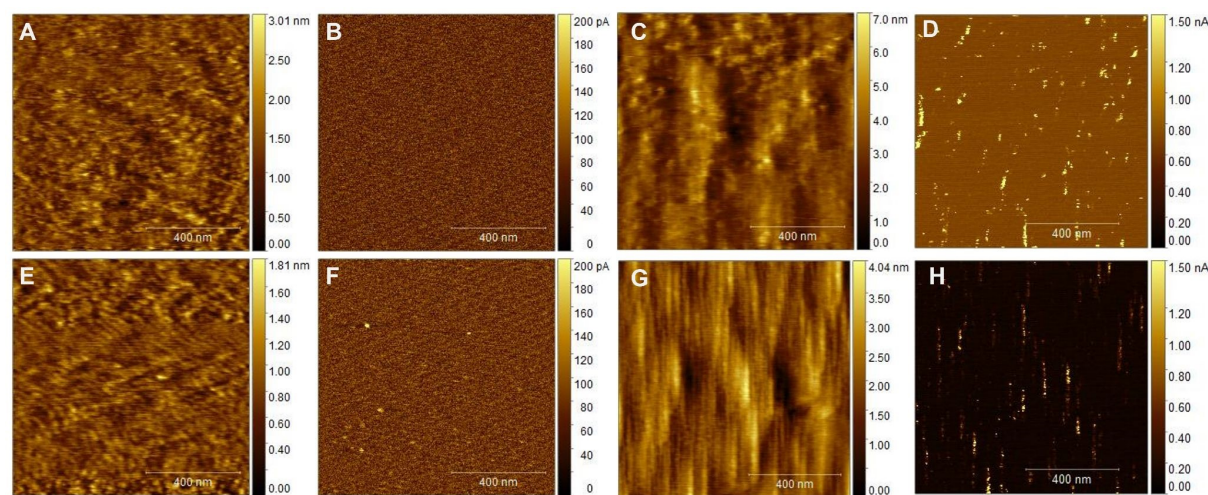


Figure S4. Topography and conductive afm micrographs for (A, B) Cr/Si, (C, D) Cr/Si annealed (E, F) Ti/Si (G, H) Ti/Si annealed. Applied bias: 3V

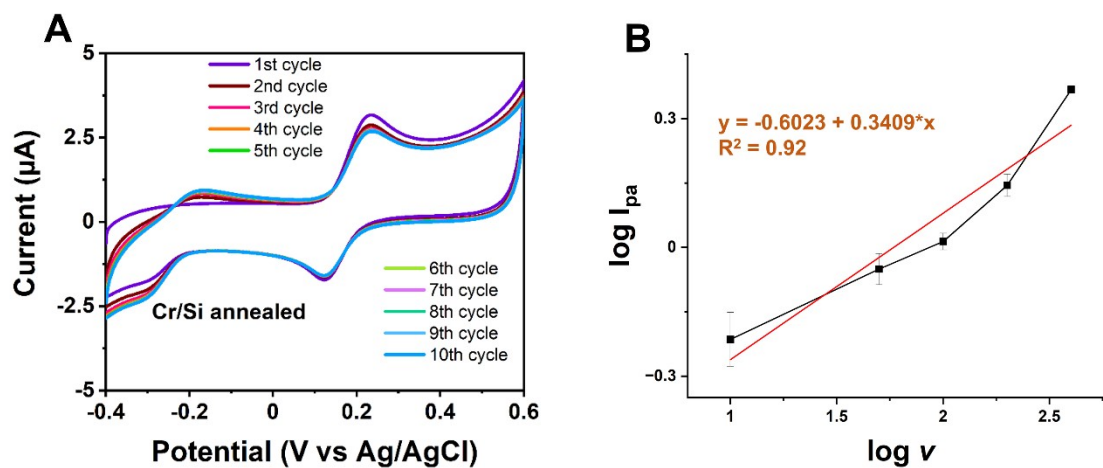


Figure S5. (A) Cyclic voltammetric response of Cr/Si annealed electrode in 100 μM DA for 10 cycles at 100 mV/s scan rate. (B) Linear fit of $\log I_{pa}$ vs $\log \nu$ for Cr/Si annealed electrode in 100 μM DA in the range of scan rates of 10 mV/s-400 mV/s.

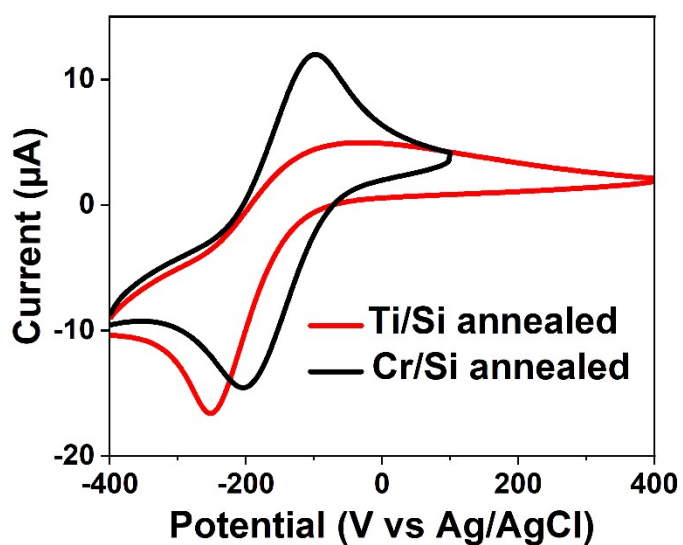


Figure S6. Cyclic voltammetry response of annealed Ti/Si and Cr/Si in 1mM $\text{Ru}(\text{NH}_3)_6\text{Cl}$ in KCl at 100 mV/s.

References

- (1) Sabooni, S.; Karimzadeh, F.; Abbasi, M. H. Thermodynamic Aspects of Nanostructured Ti₅Si₃ Formation during Mechanical Alloying and Its Characterization. *Bull. Mater. Sci.* **2012**, *35*, 439–447.
- (2) Bandyopadhyay, D.; Sharma, R. C.; Chakraborti, N. The Ti-Co-C System (Titanium-Cobalt-Carbon). *J. phase equilibria* **2000**, *21* (2), 179.
- (3) Wiczerzak, K.; Bała, P.; Stłkpień, M.; Cios, G.; Kozieł, T. The Characterization of Cast Fe-Cr-C Alloy. *Arch. Metall. Mater.* **2015**, *60*.