Supplementary information

Liquid metal-based catalysts for the electroreduction of carbon dioxide into solid carbon

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Materials and methods

99.9% Gallium and 99.9% Indium were obtained from Indium Corporation USA. Cerium powder (99.9% trace rare-earth metals basis), hafnium powder (99.5% trace rare-earth metals basis), gadolinium powder (99% trace rare-earth metals basis) and vanadium powder (99.5% trace rare-earth metals basis) were obtained from Sigma Aldrich. Chromium powder (99%) was obtained from Strem Chemicals. 99.8% anhydrous N,N-Dimethylformamide and 98% Tetrabutylammonium hexafluorophosphate were obtained from Sigma Aldrich. Deionized water was produced via a lab based reverse osmosis system.

Electrochemical experiments were performed with GAMRY interface 1010 potentiostat. The electrolyte contained 2 M H_2O to facilitate the oxygen cycle and 100 mM tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. Raman spectroscopy was performed at HORIBA LabRAM HR Evolution (12912a). The SEM and EDS mapping was done with FEI Quanta 200 SEM - Q2. TEM was performed with JEOL 2100F Transmission Electron Microscope. XPS was performed with Thermo K-alpha XPS.

Liquid metal alloy preparation

Gallium and indium were heated at 160 ^{o}C in a 3:1 ratio to form EGaIn liquid metal. All the five metallic powders; cerium, chromium, hafnium, gadolinium and vanadium were ground, separately into the EGaIn in 1% and 3% concentrations using a pestle and mortar in glove box, till all the powders dissolved to give shiny appearance within 30 minutes.

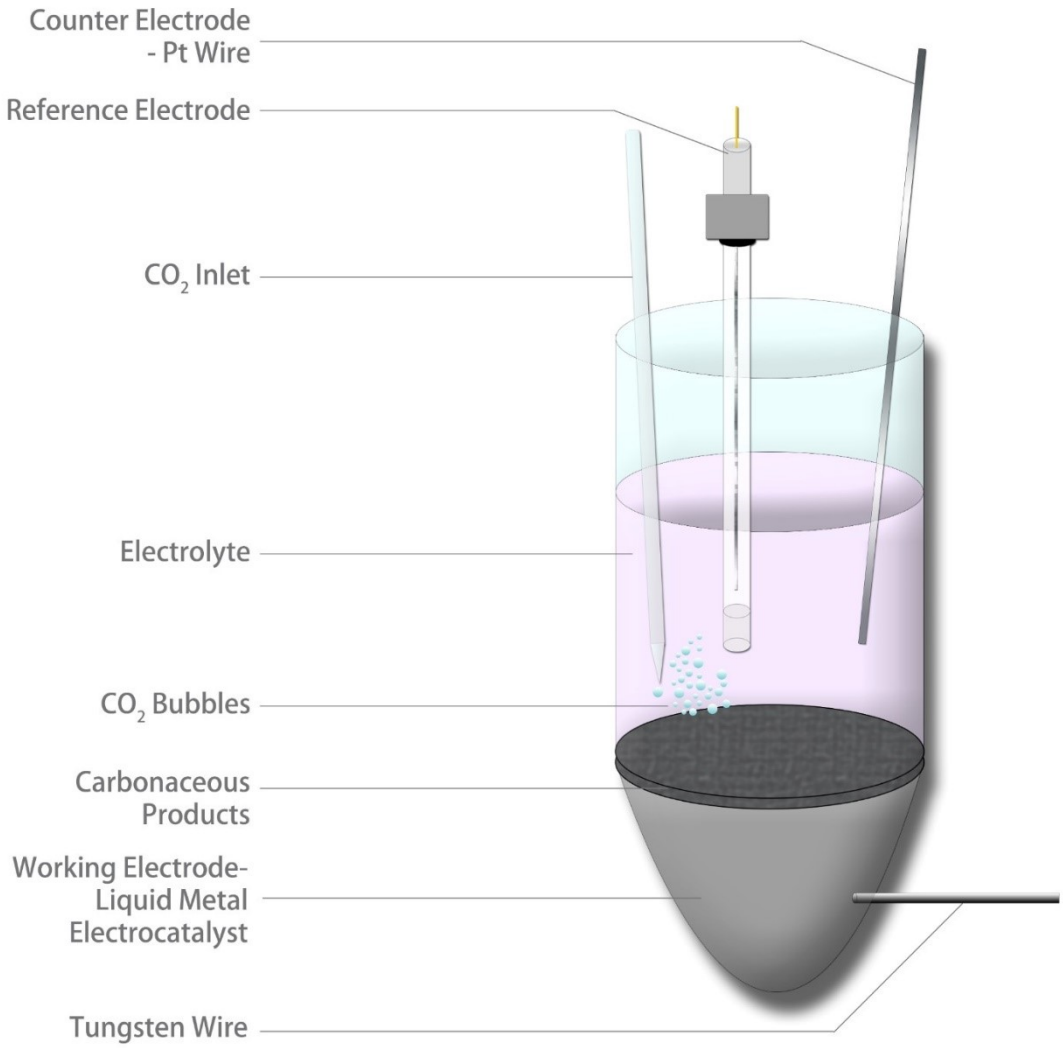

Figure S1. Illustration of the electrochemical cell for reaction.

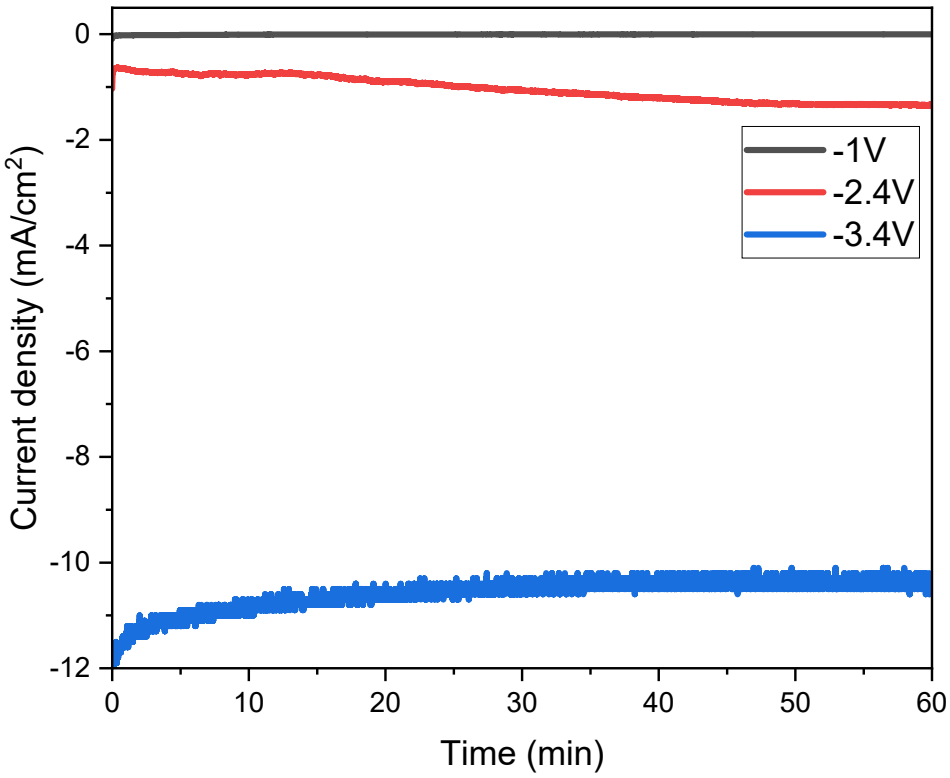

Figure S2: Cathodic currents for 3% V-EGaIn catalysts at different potentials.

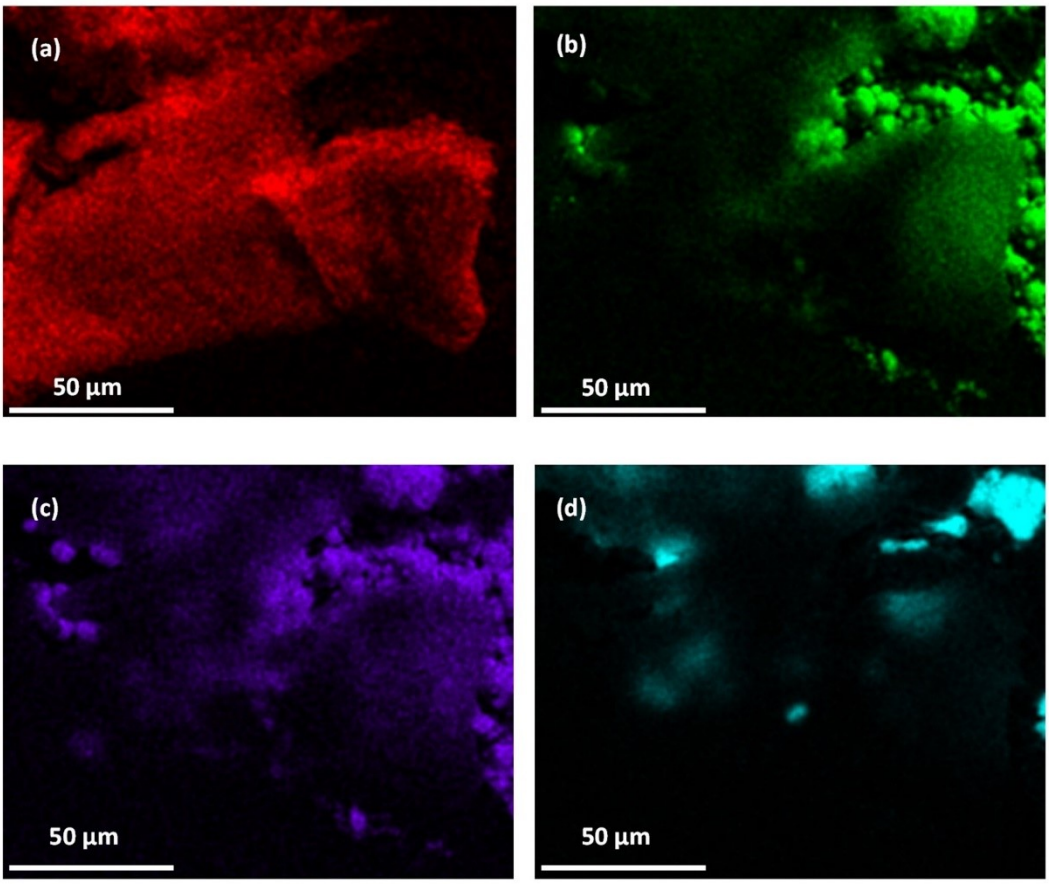

Figure S3. SEM EDS maps for (a) carbon, (b) gallium, (c) indium and (d) vanadium.

Elements	Atomic percentage %
Carbon	77.09
Oxygen	3.59
Vanadium	10.73
Gallium	4.22
Indium	4.11
Iridium	0.26
Total	100

Table S1. Atomic percentage of different elements in EDS maps.

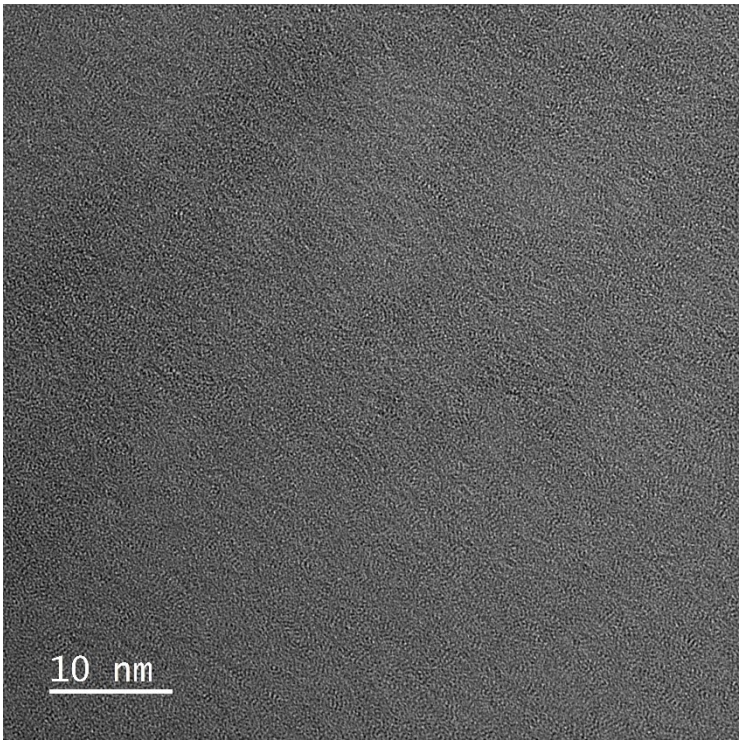

Figure S4. HRTEM image of the amorphous carbon.

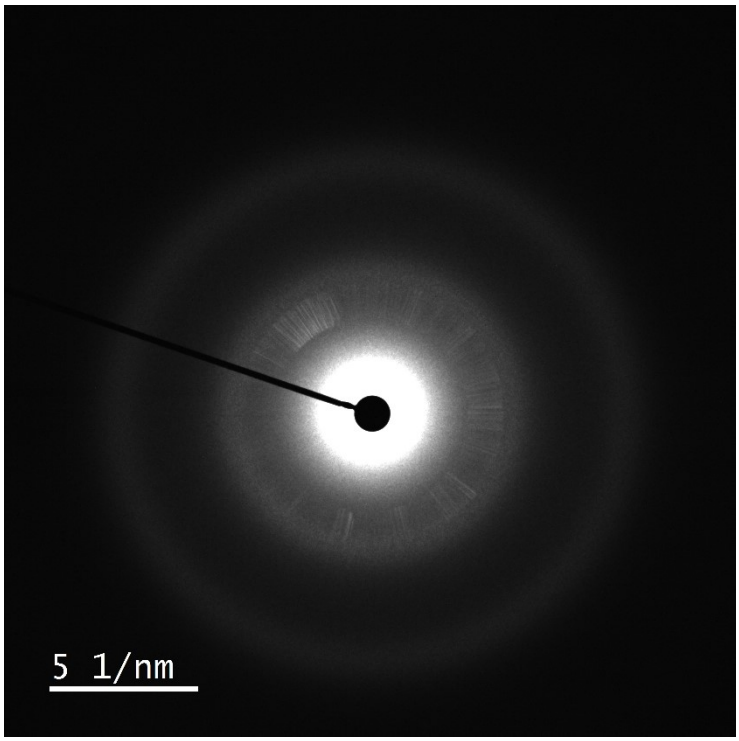

Figure S5. SAED for amorphous carbon.

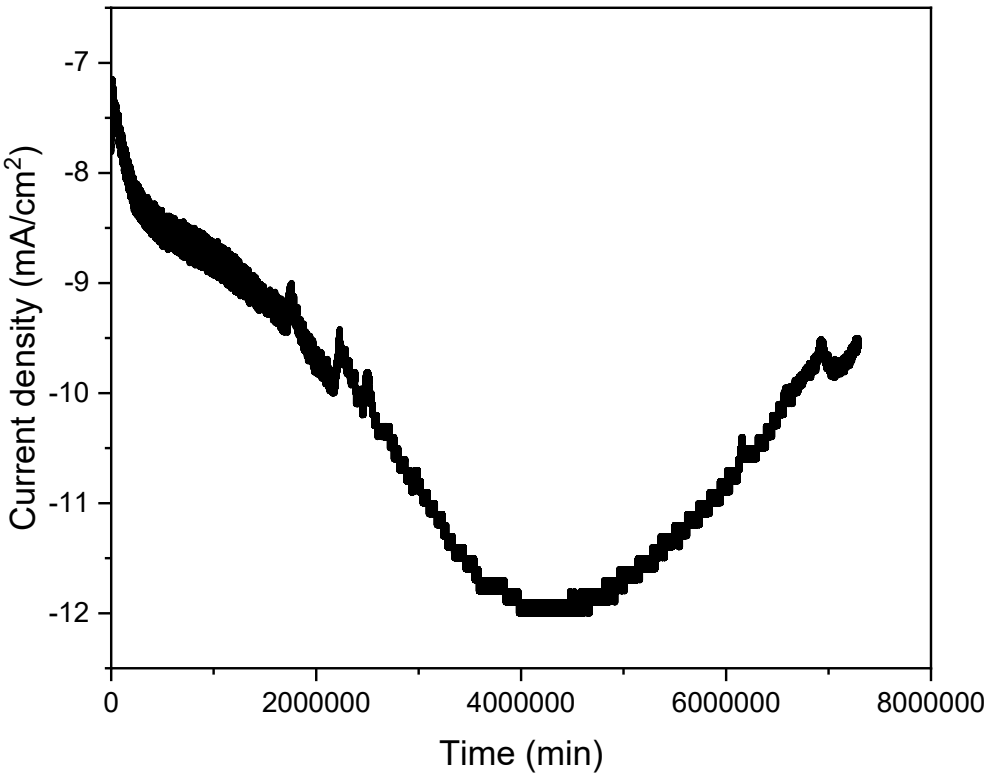

Figure S6. Chronoamperometry for 33.5 hours in a double-sized cell.

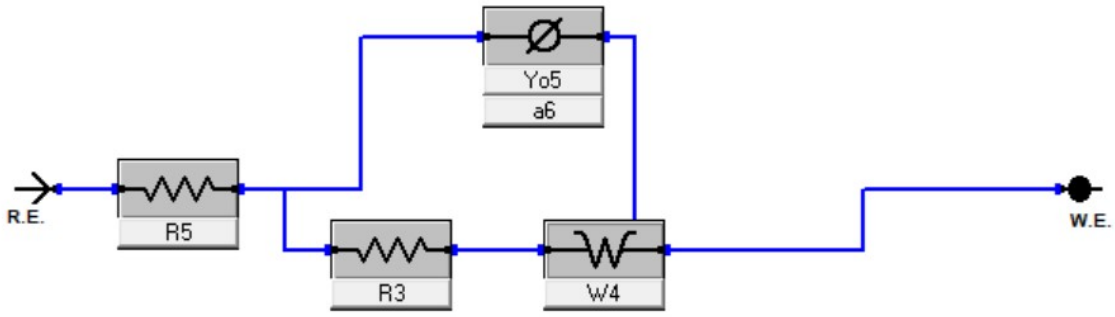

Figure S7. Randles circuit for electrochemical impedance spectroscopy.

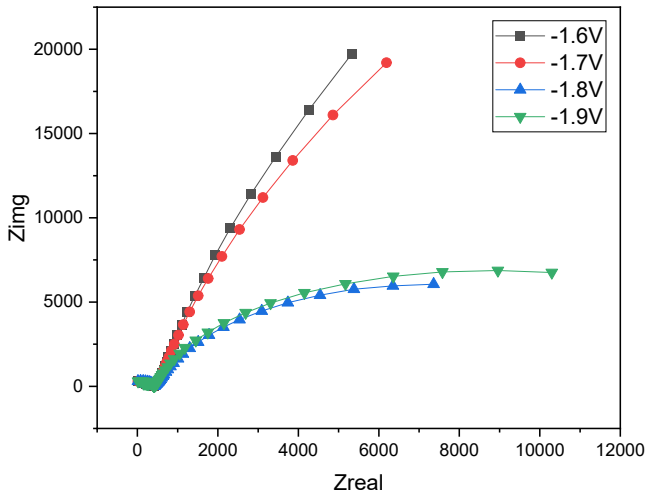

Figure S8. Nyquist plot for Ce-EGaIn.

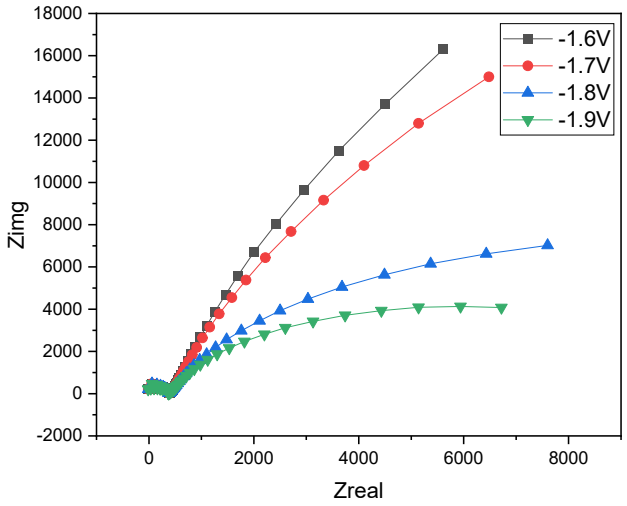

Figure S9. Nyquist plot for V-EGaIn.

Machine learning method

Bayesian regularized artificial neural networks implemented in the in-house BioModeller package [1,2,3] were used in this study. The network had three layers, consisting of input, hidden, and output layers. There were 2 neurons in the input layer, corresponding to the concentration of Vanadium and the voltage applied. The hidden layer had 3 neurons while the output layer had 1 neuron corresponding to the current. Data for 6 concentrations of Vanadium and voltage from -1.8 to -1 V were used for training the network and the obtained model was used to make predictions for 25 concentrations, over the same voltage range. This resulted in 2406 entries in the training set and 8020 entries in the test set. Training data as well as predictions generated by the obtained model are provided in the Supporting Information.

References

1. Burden, F. R.; Winkler, D. A. New QSAR Methods Applied to Structure−Activity Mapping and Combinatorial Chemistry. J. Chem. Inf. Comput. Sci. 1999, 39 (2), 236–242. https://doi.org/10.1021/ci980070d.
2. Burden, F. R.; Winkler, D. A. Robust QSAR Models Using Bayesian Regularized Neural Networks. J. Med. Chem. 1999, 42 (16), 3183–3187. https://doi.org/10.1021/jm980697n.
3. Winkler, D. A.; Burden, F. R. Robust QSAR Models from Novel Descriptors and Bayesian Regularised Neural Networks. Mol. Simul. 2000, 24 (4–6), 243–258. https://doi.org/10.1080/08927020008022374.