Supporting Information

Martian Redox Chemistry, Oxygen Reduction in Low Temperature Magnesium Perchlorate Brines

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S1 Chemical reagents and instrumentation

Ferrocene methanol (97%) and magnesium perchlorate hexahydrate (99%) were purchased from Sigma-Aldrich and were used as received without any further purification. All solutions were prepared using deionised water with a resistivity of no less than 18.2 MΩ cm at 25 °C (Millipore UHQ, Vivendi, UK).

Electrochemical measurements were performed with a μAutolab Type III potentiostat (Utrecht) using standard three electrode setups. A glassy carbon macro- (CH Instruments, 3 mm diameter), a carbon micro- (IJ Cambria Scientific Ltd, 33 μm diameter) or a gold micro- electrode (ALS, 7 μm diameter) was used as a working electrode. Prior to use, the working electrodes were polished with alumina powders in the size sequence of 1.0 μm, 0.3 μm and 0.05 μm (Buehler, USA) on soft lapping pads (Buehler, USA). A silver wire and a platinum mesh were used as reference and counter electrodes respectively.

S2 Saturated oxygen concentrations

In the oxygen reduction experiments, oxygen gas was strongly bubbled into 2.77 M $Mg(ClO_4)_2$ solutions. To ensure that the solution is saturated with oxygen, the bubble time is first optimized. Figure S1a shows cyclic voltammograms of oxygen reduction at different bubble times (0, 5 and 10 min). The plot of cathodic peak currents as a function of oxygen bubbling duration is presented in Figure S1b. It can be seen that after 5 min the peak current, and hence the amount of oxygen in solution, reaches a maximum value at 10.0 μA, corresponding to oxygen concentration of 0.28 mM. Consequently, for all the oxygen reduction studies, oxygen is bubbled for 5 min prior to the measurements.

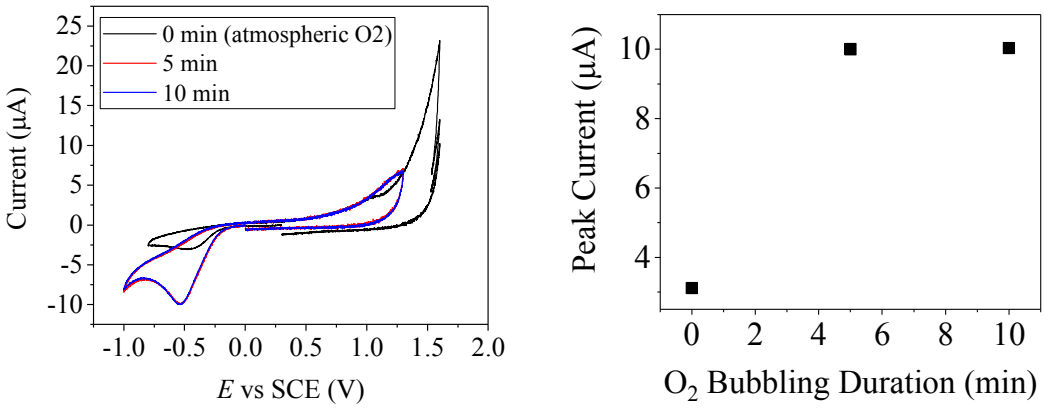

Figure S1: a) Cyclic voltammograms of oxygen reduction in 2.77M $Mg(ClO_4)_2$ at a glassy carbon macro-electrode at the scan rate of 100 mV s^{-1} at different oxygen bubbling duration (0, 5 and 10 min); 25 °C. b) The cathodic peak currents of oxygen reduction as a function of oxygen bubbling duration.

S3 Voltammetry of hydrogen peroxide reduction

Cyclic voltammetry of 1.25 mM hydrogen peroxide (H_2O_2) in deaerated 2.77 M $Mg(ClO_4)_2$ solution was recorded at a gold micro-electrode at the scan rate of 20 mV s^{-1} at 25 °C. Figure S2 shows the voltammetric response of H_2O_2 reduction (blue line) as compared with that O_2 reduction (black line). No reductive peak was observed in the cathodic scan of H_2O_2 solution, evidencing that the product of O_2 reduction is H_2O_2 as H_2O_2 cannot be reduced further in the potential window studied.

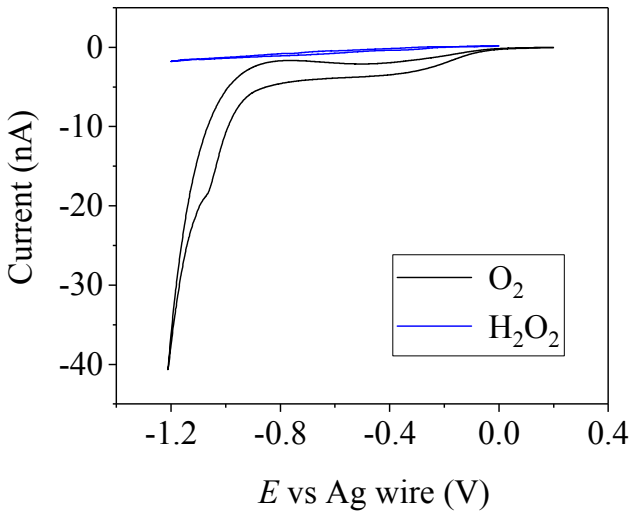

Figure S2: Cyclic voltammograms of saturated (0.28 mM) oxygen reduction (black line) and 1.25 mM hydrogen peroxide reduction (blue line) in 2.77 M $Mg(ClO_4)_2$ at a gold micro-electrode at the scan rate of 20 mV s^{-1} at 25 °C.

S4 Oxygen reduction at different temperatures

Oxygen reduction in 2.77 M $Mg(ClO_4)_2$ was studied at different temperatures. A glassy carbon macroelectrode together with a gold microelectrode were used to determine the concentrations and diffusion coefficients of oxygen in the electrolytes. The resulting voltammograms of oxygen reduction at 25.0 ^{0}C are presented in Figure 2 in the main text. Here, the voltammograms of oxygen reduction in 2.77 M $Mg(ClO_4)_2$ at 5.0, -14.5 and -31.0 ^{0}C are presented in Figures S3, S4 and S5 respectively. The resulting values of oxygen concentrations and their diffusion coefficients at the different temperatures are presented in Figure 3 in the main text.

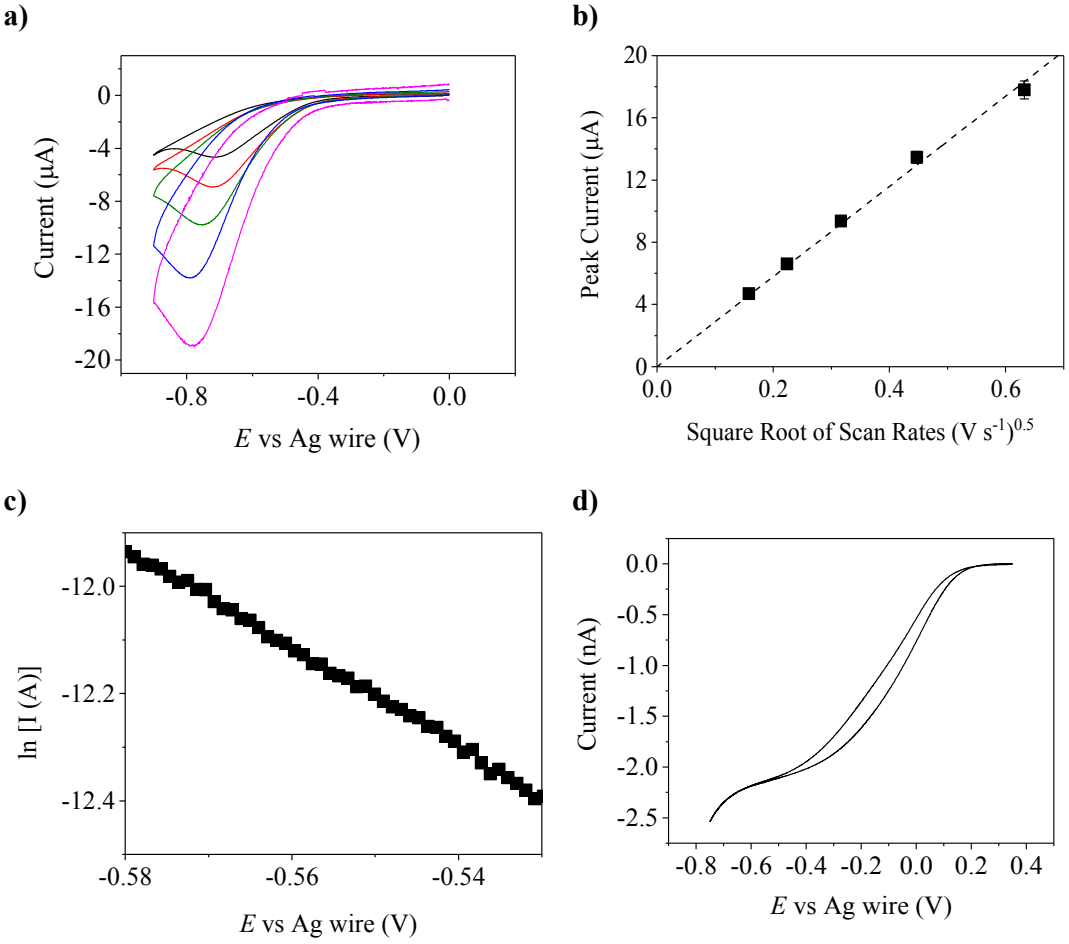

Figure S3: a) Cyclic voltammograms (CV) of oxygen reduction in 2.77 M $Mg(ClO_4)_2$ at 5.0 °C at a glassy carbon electrode at a series of scan rates: 25 mV s^{-1} (black), 50 mV s^{-1} (red), 100 mV s^{-1} (green), 200 mV s^{-1} (blue), 400 mV s^{-1} (pink). b) The plot of oxygen reduction peak currents as a function of the square root of scan rates. c) Tafel analysis of the CV of oxygen reduction at 400 mV s^{-1}. d) CV of oxygen reduction in 2.77 M $Mg(ClO_4)_2$ at 5.0 °C at a gold micro-electrode at the scan rate of 20 mV s^{-1}.

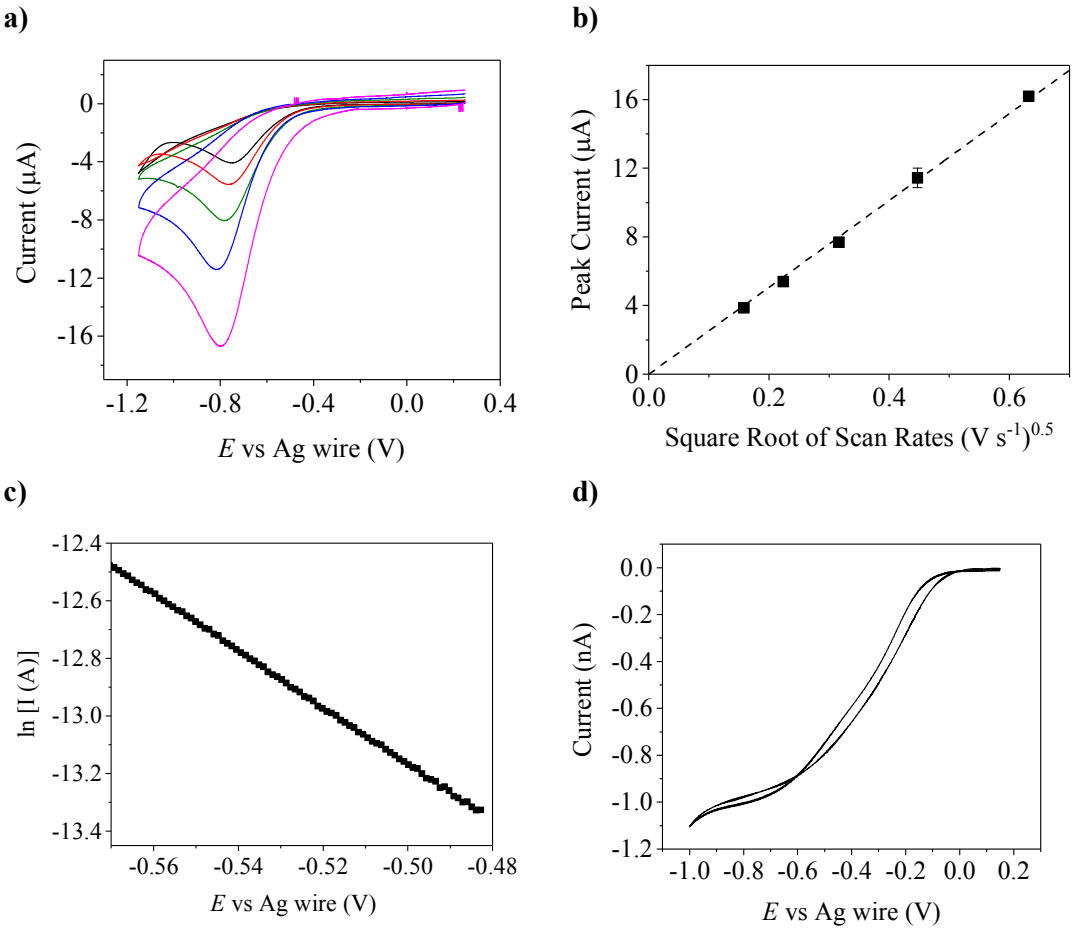

Figure S4: a) Cyclic voltammograms (CV) of oxygen reduction in 2.77 M $Mg(ClO_4)_2$ at -14.5 °C at a glassy carbon electrode at a series of scan rates: 25 mV s^{-1} (black), 50 mV s^{-1} (red), 100 mV s^{-1} (green), 200 mV s^{-1} (blue), 400 mV s^{-1} (pink). b) The plot of oxygen reduction peak currents as a function of the square root of scan rates. c) Tafel analysis of the CV of oxygen reduction at 400 mV s^{-1}. d) CV of oxygen reduction in 2.77 M $Mg(ClO_4)_2$ at -14.5 °C at a gold micro-electrode at the scan rate of 20 mV s^{-1}.

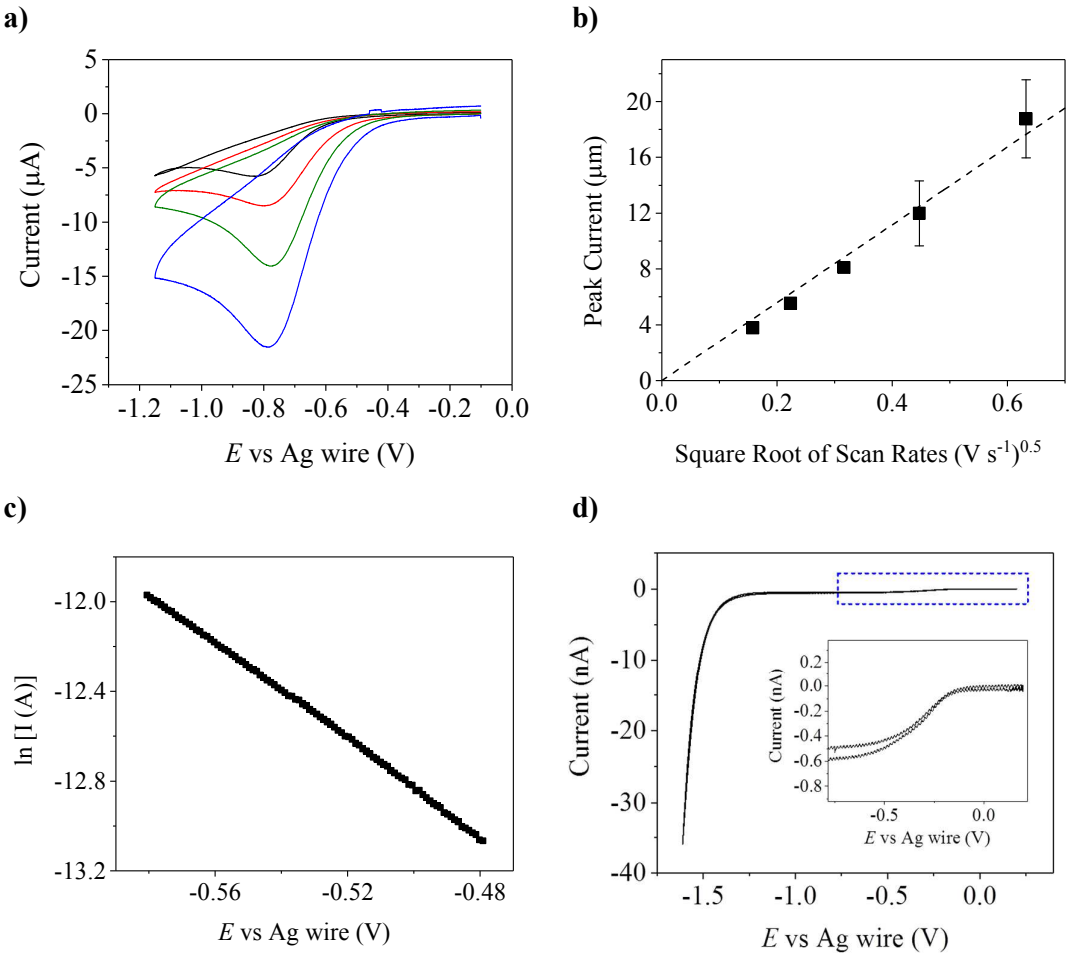

Figure S5: a) Cyclic voltammograms (CV) of oxygen reduction in 2.77 M $Mg(ClO_4)_2$ at -31.0 °C at a glassy carbon electrode at a series of scan rates: 50 mV s^{-1} (black), 100 mV s^{-1} (red), 200 mV s^{-1} (green), 400 mV s^{-1} (blue). b) The plot of oxygen reduction peak currents as a function of the square root of scan rates. c) Tafel analysis of the CV of oxygen reduction at 400 mV s^{-1}. d) CV of oxygen reduction in 2.77 M $Mg(ClO_4)_2$ at -31.0 °C at a gold micro-electrode at the scan rate of 20 mV s^{-1}.

S5 Carbon dioxide reduction

Figure S6 below shows that *no* cathodic responses of carbon dioxide (CO_2) reduction could be observed prior to solvent breakdown in the 2.77 M $Mg(ClO_4)_2$ brine at a glassy carbon electrode.

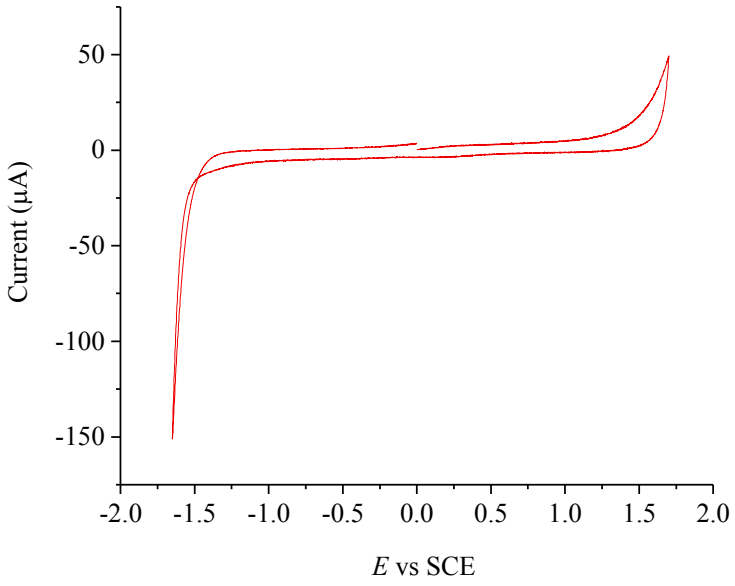

Figure S6: Cyclic voltammograms (CV) of 2.77 M $Mg(ClO_4)_2$ saturated with carbon dioxide at a glassy carbon electrode. Scan rate of 200 mV s^{-1}.

Note that although in ionic liquids and organic solvents, superoxide (an intermediate in the oxygen reduction process) has been reported to readily react with carbon dioxide,[1-3] most likely in aqueous environment, the disproportionation of superoxide would outrun the reaction with CO_2. Consequently, the presence of CO_2 is expected not to interfere with the electrochemical responses of O_2 reduction studied herein.

References

1. Wadhawan, J. D.; Welford, P. J.; Maisonhaute, E.; Climent, V.; Lawrence, N. S.; Compton, R. G.; McPeak, H. B.; Hahn, C. E. W., Microelectrode Studies of the Reaction of Superoxide with Carbon Dioxide in Dimethyl Sulfoxide. *The Journal of Physical Chemistry B* **2001,** *105* (43), 10659-10668.

2. Wadhawan, J. D.; Welford, P. J.; McPeak, H. B.; Hahn, C. E. W.; Compton, R. G., The simultaneous voltammetric determination and detection of oxygen and carbon dioxide. *Sensors and Actuators B: Chemical* **2003,** *88* (1), 40-52.

3. Buzzeo, M. C.; Klymenko, O. V.; Wadhawan, J. D.; Hardacre, C.; Seddon, K. R.; Compton, R. G., Kinetic Analysis of the Reaction between Electrogenerated Superoxide and Carbon Dioxide in the Room Temperature Ionic Liquids 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and Hexyltriethylammonium Bis(trifluoromethylsulfonyl)imide. *The Journal of Physical Chemistry B* **2004,** *108* (12), 3947-3954.