Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electrochemical behavior and electrodeposition of gallium in 1,2-dimethoxyethane-based electrolytes

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Electronic Supplementary Information (ESI)

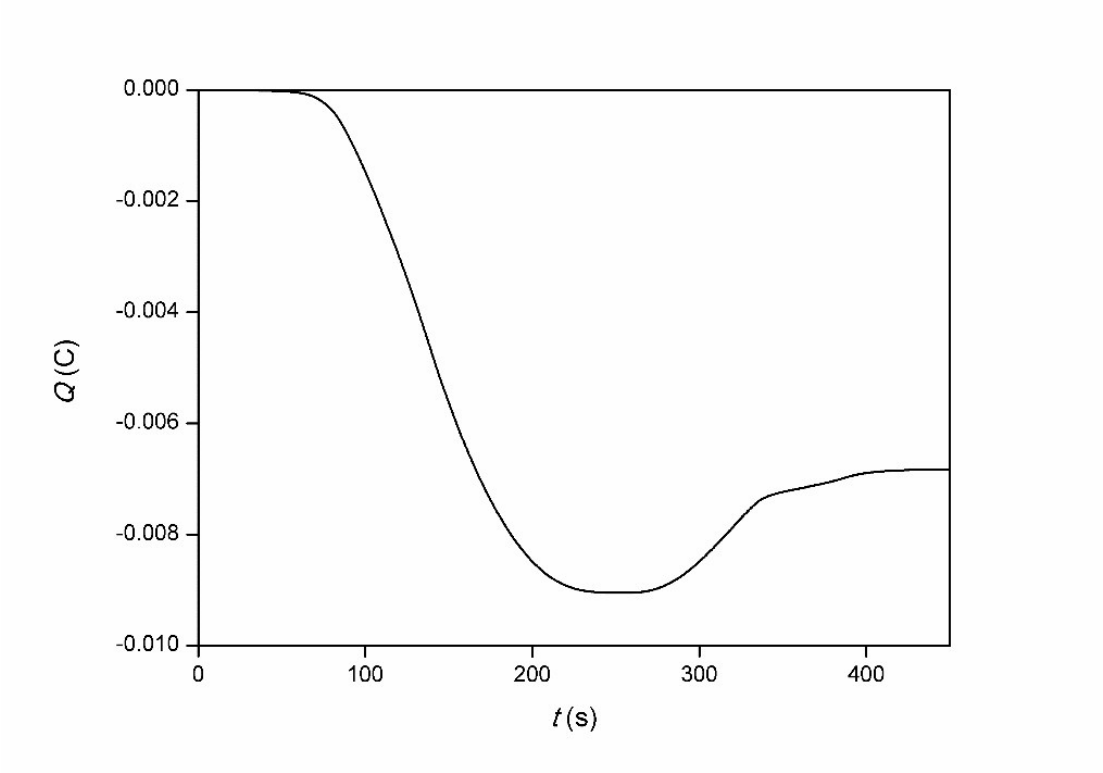

Figure S1: Coulombic charge as a function of time, derived from the CV (black) in figure 1.

Construction of the *M*/*z* figure from the QCM data

To study the reaction mechanisms in the CV, a curve of molar mass/charge (*M*/*z*) as a function of the potential was constructed. This was done by combining Faraday's electrolysis law and the Sauerbrey equation:

$$\frac{M}{z} = -\frac{F\,C_f \Delta f}{\Delta Q} \qquad \text{(eq. S1)}$$

where M (g mol^{-1}) is the molar mass, z is the number of electrons involved in the electrochemical reaction, F = 96485.34 (C mol^{-1}) is the Faraday constant and ΔQ (C cm^{-2}) is the change in charge consumed by the oxidation or reduction reaction. Eq. S1 can be used to determine *M*/*z* as a function of applied potential, which enables the identification of the amount

of involved electrons in the reduction and oxidation reactions seen in the CV. when the current in CV goes through zero, experimentally determined M/z values become uncertain due to the very small values of ΔQ. Therefore, these M/z values are removed from the graph. The absolute negative value of ΔQ is used so that M/z has an opposite sign, as Δm is negative for deposition and positive for stripping. In figure S1, the resulting M/z vs. potential plot is shown. The M/z value initially rapidly lowers, but stabilizes around −0.70 V vs. Fc^+/Fc. At this potential, M/z equals approximately −40.0, and gradually decreases to −37.0. This range of values lies close to −34.8, which corresponds to a two electron reduction process, *i.e.*, the reduction of gallium(III) to gallium(I). At −1.37 V vs. Fc^+/Fc, a sudden small decrease is observed to approximately −30.0. Once again, M/z subsequently gradually decreases with progressing potential. These values lie slightly above −23.2, which corresponds to a three electron reduction process, *i.e.*, complete reduction to gallium(0). Hence, in the early stages of the cathodic wave, only reduction of gallium(III) to gallium(I) occurs. However, at higher cathodic overpotentials, both reduction to gallium(III) to gallium(I), and reduction of gallium(I) to gallium(0) take place. This is in accordance with the RRDE measurement, shown in figure 4 in the main text. No M/z values could be determined for the anodic portion of the CV. This is due to the extremely large values obtained when the current passes zero.

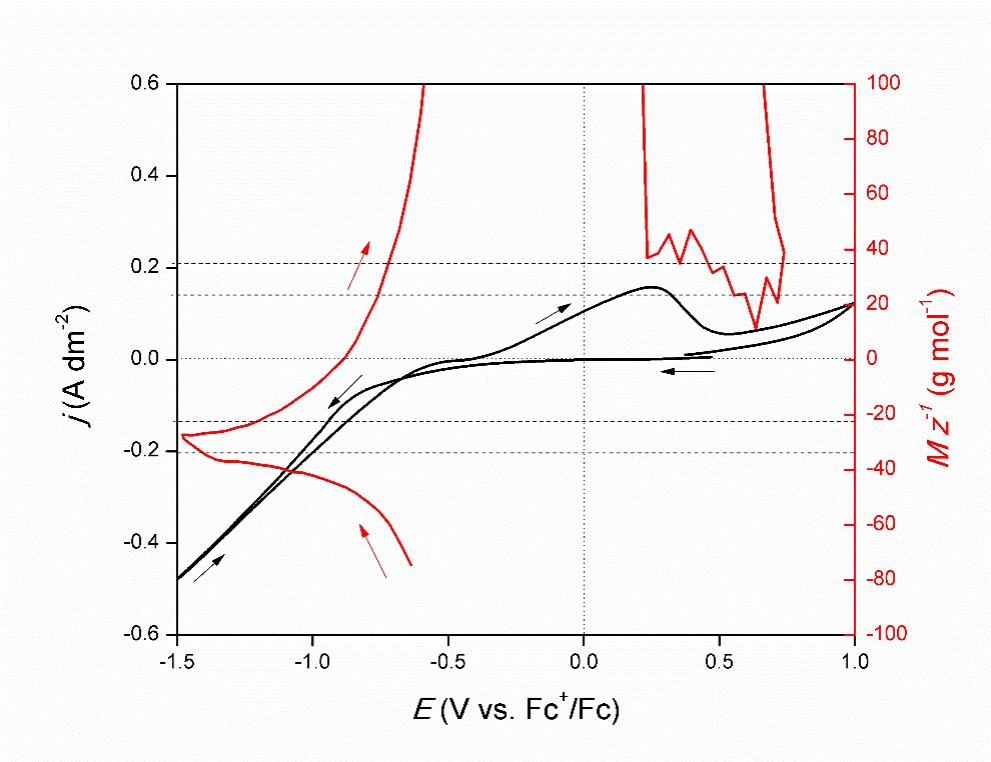

Figure S2: CV recorded for DME containing 0.1 mol dm^{-3} of $GaCl_3$ and 0.2 mol dm^{-3} of [TBA][ClO_4] on a platinum-coated QCM crystal with a scan rate of 10 mV s^{-1} at 26 °C (black line, left axis) with EQCM data analyzed for M/z (red line, right axis).

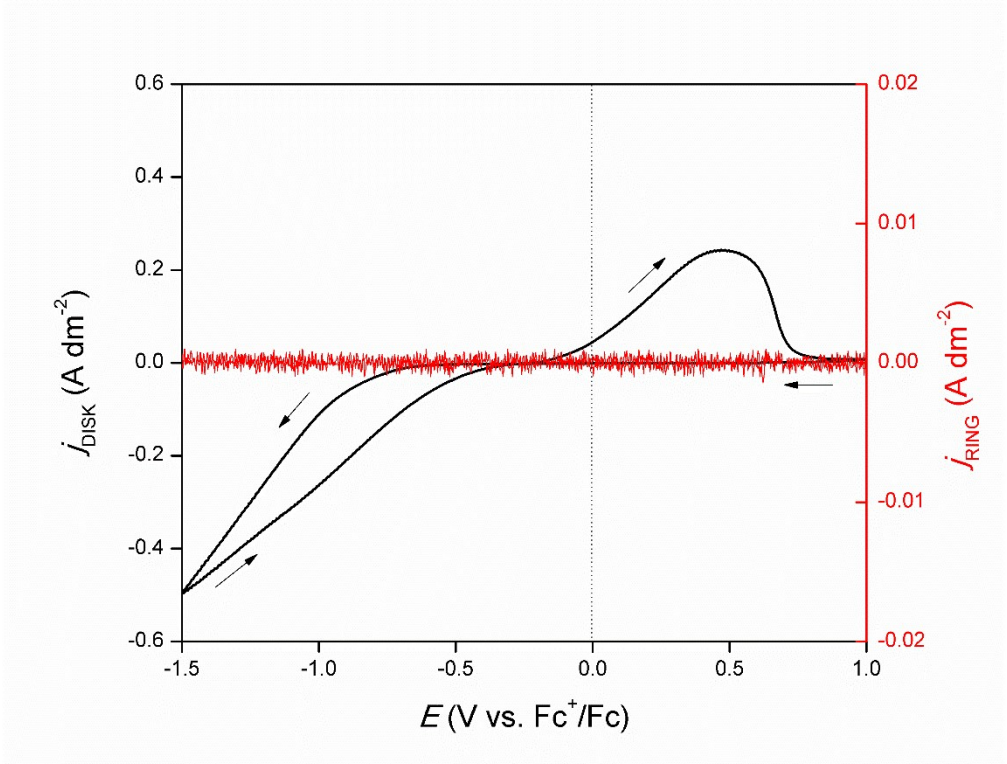

Figure S3: CV recorded for DME containing 0.1 mol dm^{-3} of $GaCl_3$ and 0.2 mol dm^{-3} of [TBA][ClO_4] on a GC disk at 26 °C with a scan rate of 10 mV s^{-1}(black line, left axis) with current response on platinum ring on which +1.0 V vs. Fc^+/Fc was applied (red line, right axis). The RRDE was rotated at 200 rpm.

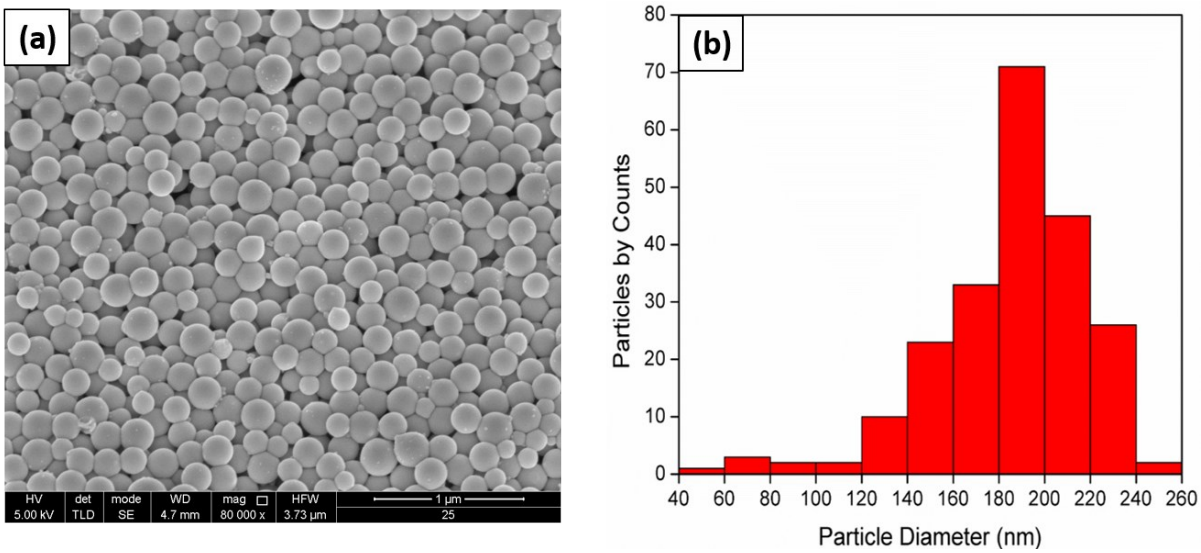

Figure S4: (a) SEM image of gallium deposits generated from DME containing 0.1 mol dm^{-3} of $GaCl_3$ and 0.2 mol dm^{-3} of [TBA][ClO_4] by applying −1.5 V vs. Fc^+/Fc for 30 min. on a GC WE at 26 °C. The applied acceleration voltage was 5 keV. (b) Histogram displaying the particle size distribution of the spheres seen in (a).

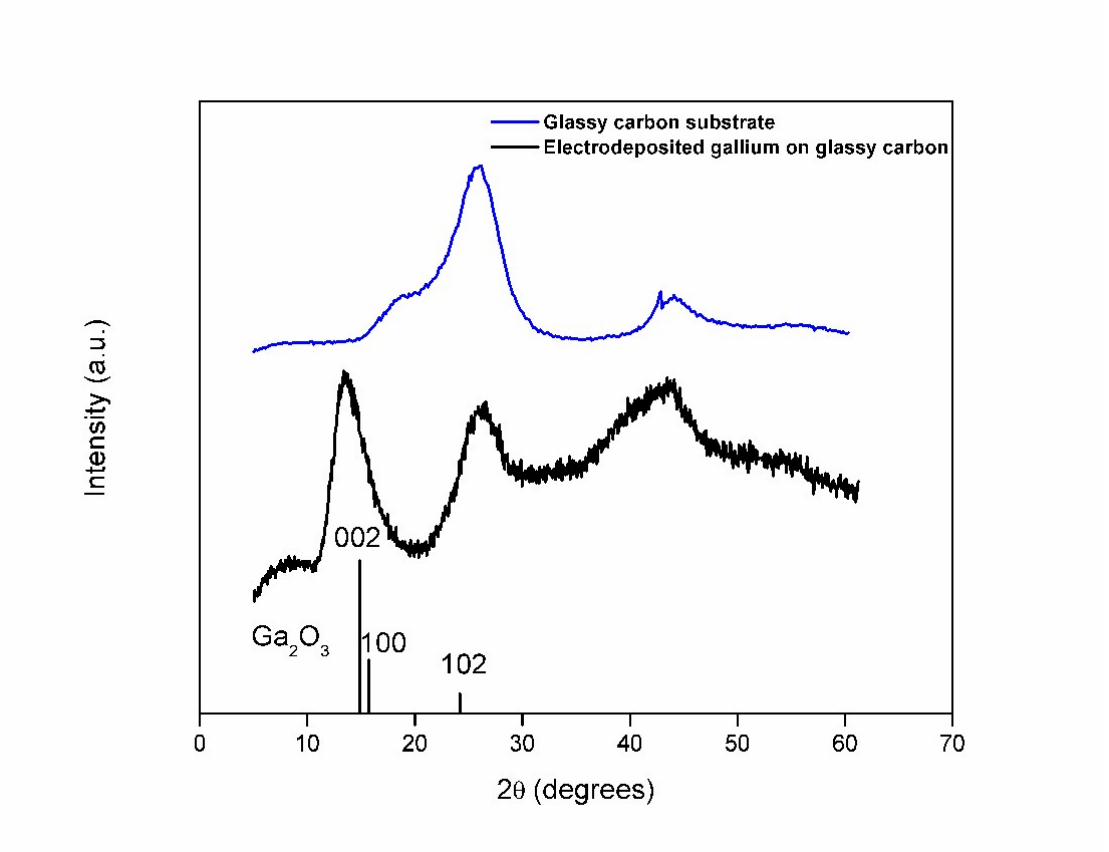

Figure S5: XRD diffractograms of a GC substrate and gallium electrodeposited on a GC substrate at −1.5 V vs. Fc+/Fc for 1 hr, at 26 °C.

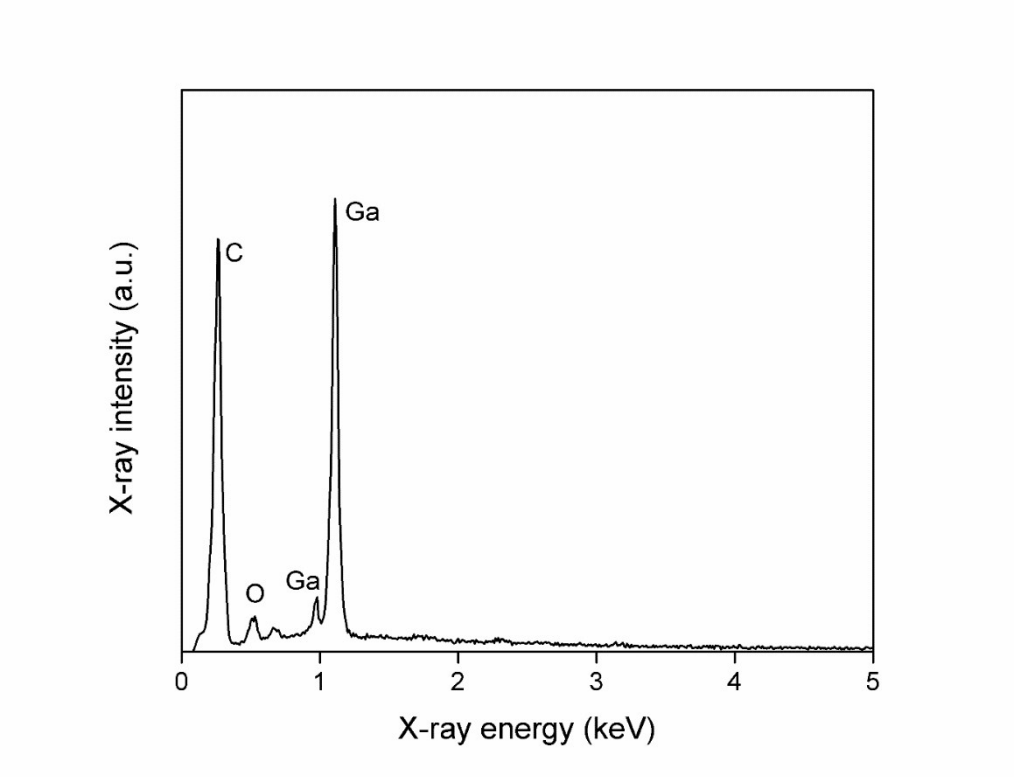

Figure S6: EDX spectrum of gallium structures generated by first electrodepositing gallium from DME containing 0.1 mol dm^{-3} of $GaCl_3$ and 0.2 mol dm^{-3} of [TBA][ClO_4] by applying −1.5 V vs. Fc^+/Fc for 2 min. and then partly stripping the deposited gallium by applying +0.2 V vs. Fc^+/Fc for 1 min. at 26 °C. The applied acceleration voltage was 10 keV.

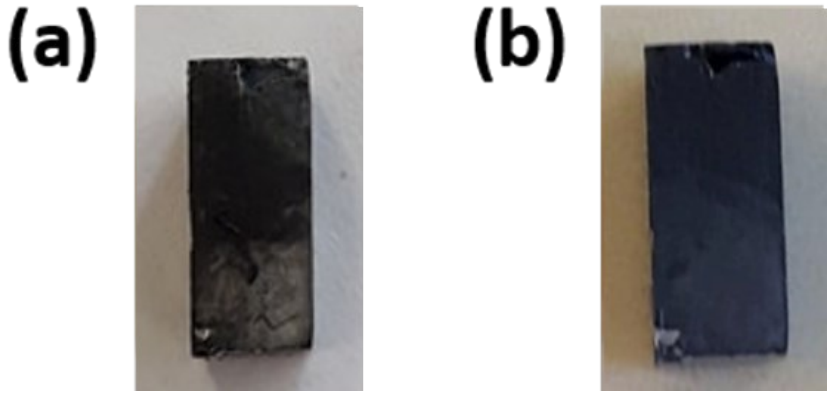

Figure S7: (a) Electrodeposited layer of gallium metal with indium tracer on a GC substrate (b) GC substrate after ripping off the electrodeposited layer using conductive Scotch tape.