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

SUPPLEMENTARY MATERIAL

Methyl viologen radical solution. All sample solutions were prepared from dry acetonitrile (ACN, Acros Organics 364315000, 99.9 %, extra dry) with 200 mM tetrabutylammonium perchlorate (TBAP, Sigma-Aldrich 86893, 99.0 %) as supporting electrolyte. Methyl viologen dichloride hydrate (MV^{2+}, Sigma-Aldrich, 98 %) was used as a redox mediator. The methyl viologen radical ($MV^{+\bullet}$) was generated in a U-cell in a glove box on a platinum electrode from MV^{2+} by one electron reduction. The two compartments of the cell were separated by a glass frit to prevent the counter electrode species entering the $MV^{+\bullet}$ solution. The concentration of $MV^{+\bullet}$ was set to 2 mM for all studies. To achieve this, the solution was heated gently to promote the dissolution of the MV^{2+} into ACN and the concentration shifted by additional electrolysis to $MV^{+\bullet}$. The MV^{2+} dication conversion to the $MV^{+\bullet}$ was monitored quantitatively, checking the composition of the sample solution with a 10 μm diameter Pt ultramicroelectrode (UME) (Fig. 1) to confirm that the electrolysis was complete.

Magnetohydrodynamic effects. The electrochemical current depends on the applied magnetic field, as can be observed on the data arrays shown in Fig. 2. At a fixed potential, an increase of the current (in absolute value) at the stronger field values is observed, which we ascribe to magnetohydrodynamic effects. The main contribution is the Lorentz force, given by

$$\mathbf{F} = \mathbf{j} \times \mathbf{B} \tag{1}$$

where **B** is the magnetic induction field and **j** the electrochemical current density.[1]

Nicely visible in Fig. 2 is also the scanning direction dependency, in a) from negative to positive and in b) from positive to negative fields. When recording data for EDMR, the field range is limited to 20 mT. Thus, the effect of magnetoydrodynamic effects is negligible.

Energetics. Figure 3 shows the energetics of the $MV^{+\bullet}/MV^0$ redox couple for an interface with a p-GaAs electrode on the left, and for a gold surface on the right. The electron transfer process between MV^{2+} and $MV^{+\bullet}$ is known to be an activated process owing to the large value of the reorganization energy compared to the thermal energy k_BT.[2,3] The overall reorganization energy $\lambda = \lambda_i + \lambda_o$ is the sum of an inner-sphere reorganization energy λ_i which accounts for such processes as changes in bond angles, and an outer-sphere reorganization energy λ_o, corresponding to a change in electric polarization energy. The inner-sphere barrier energy for methyl viologen was estimated by Grampp *et al.* to be about $\lambda_i = 0.28\,\mathrm{eV}$.[4] Through an EPR study in which these authors could study the degenerate exchange $MV^{2+} \leftrightarrow MV^{+\bullet}$ rate, they estimated the outer-sphere contribution to be about $\lambda_0 = 0.78\,\mathrm{eV}$. Thus, the overall reorganization energy for both, oxidation and reduction, is estimated at $\lambda_{Ox} = \lambda_{Red} = 1.06\,\mathrm{eV}$. On a metal (Pt), this is evaluated at $\lambda_{Ox} = \lambda_{Red} = 0.41\,\mathrm{eV}$ (formula p. 221 in[5]).

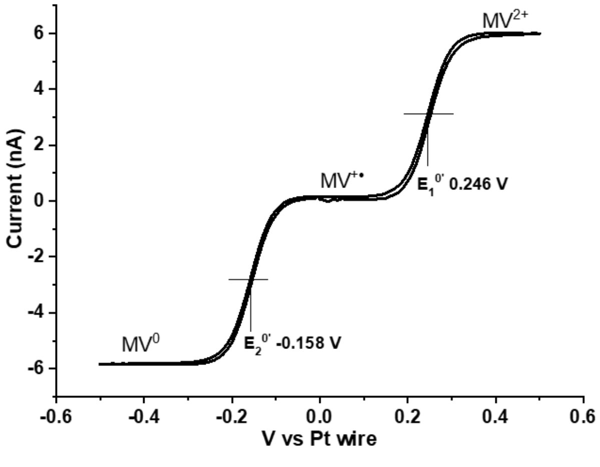

Figure 1 Cyclic voltammogram obtained on a Pt ultramicroelectrode at 50 mV/s. 2 mM $MV^{+\bullet}$ in ACN and 200 mM TBAP.

EDMR effect size calculation. We recall for clarity the usual detailed balance of electrons with spin quantum number $m_s = \pm\frac{1}{2}$ inside a magnetic field population, with population of upper energy state $N_{+\frac{1}{2}}$ and population of lower energy state $N_{-\frac{1}{2}}$ via spin flips induced by the microwave, at the rate W^{MW} and the spin-lattice relaxation processes at the rates $W^{sl}_{\downarrow}$ (up) and $W^{sl}_{\uparrow}$ (down):[6]

$$\frac{dN_{+\frac{1}{2}}}{dt} = W^{MW}\left(N_{-\frac{1}{2}} - N_{+\frac{1}{2}}\right) + N_{-\frac{1}{2}}W^{sl}_{\uparrow} - N_{+\frac{1}{2}}W^{sl}_{\downarrow}$$

$$\frac{dN_{-\frac{1}{2}}}{dt} = W^{MW}\left(-N_{-\frac{1}{2}} + N_{+\frac{1}{2}}\right) - N_{-\frac{1}{2}}W^{sl}_{\uparrow} + N_{+\frac{1}{2}}W^{sl}_{\downarrow}$$

In the absence of microwave, an equilibrium polarization is reached, given by,

$$\frac{W^{sl}_{\uparrow}}{W^{sl}_{\downarrow}} = \frac{N^0_{+\frac{1}{2}}}{N^0_{-\frac{1}{2}}} = \exp\left(-\frac{g\mu_B B_0}{k_B T}\right) \tag{2}$$

where μ_B is the Bohr magneton ($\approx 9\cdot 10^{-24}$ J/T), B is of about 330 mT, k_B the Boltzmann constant and T the temperature of the electrolyte, about 300K. These values yield relative population of $\frac{W^{sl}_{\uparrow}}{W^{sl}_{\downarrow}} = 0.9985$ and corresponding spin polarization of $\frac{N^0_{-\frac{1}{2}} - N^0_{+\frac{1}{2}}}{N^0_{-\frac{1}{2}} + N^0_{+\frac{1}{2}}} = \frac{\Delta N^0}{N^0} \approx 8\cdot 10^{-4}$.

When microwave is applied, the resonance condition is met, and when it produces just a perturbation as expected under the present conditions, the steady state of the polarization ΔN is:

$$\Delta N^{sl+MW} = \frac{\Delta N^0}{1 + 2WT_1} \tag{3}$$

where $T_1^{-1} = W^{sl}_{\uparrow} + W^{sl}_{\downarrow}$ is defined as the spin lattice relaxation time. The difference to the non-MW perturbed steady state population difference ΔN^0, i.e. just-off-resonance is

$$\begin{aligned} \Delta N^0 - \Delta N^{sl+MW} &= \Delta N^0 - \frac{\Delta N^0}{1 + 2WT_1} \\ &\approx 2WT_1 \Delta N^0, \end{aligned} \tag{4}$$

assuming $2WT_1 \ll 1$.

Therefore the relative change in electrochemical current regarding on and off resonance can be estimated, continuing from equation **??**, to

$$\begin{aligned} \frac{\Delta j_e}{j_e} &= \frac{j_e - j_e^{res}}{j_e} \\ &= \frac{\frac{k_{+\frac{1}{2}} - k_{-\frac{1}{2}}}{2}\Delta N^0 - \frac{k_{+\frac{1}{2}} - k_{-\frac{1}{2}}}{2}\Delta N^{sl+MW}}{\frac{k_{+\frac{1}{2}} + k_{-\frac{1}{2}}}{2}N^0 + \frac{k_{+\frac{1}{2}} - k_{-\frac{1}{2}}}{2}\Delta N^0} \\ &\approx \frac{\left(k_{+\frac{1}{2}} - k_{-\frac{1}{2}}\right)\Delta N^0 - \left(k_{+\frac{1}{2}} - k_{-\frac{1}{2}}\right)\Delta N^{sl+MW}}{\left(k_{+\frac{1}{2}} + k_{-\frac{1}{2}}\right)N^0 + \left(k_{+\frac{1}{2}} - k_{-\frac{1}{2}}\right)\Delta N^0}. \end{aligned} \tag{5}$$

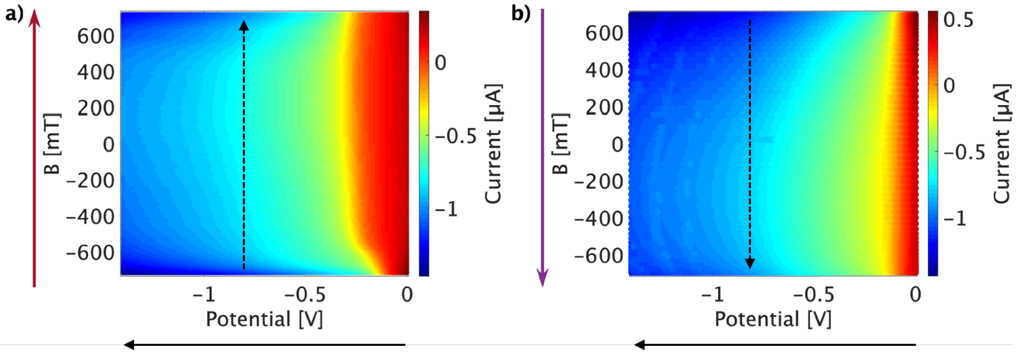

Figure 2 Electrochemical current as a function of magnetic field and potential, showing the MHD effect. The horizontal arrows in a) and b) indicate voltage scans at constant field. The dotted lines represent line cuts through the data, corresponding to virtual field scans. For a) and b) the vertical arrows indicate the direction of the magnetic field sweep. In an EDMR experiment, the AC current is recorded during voltage scans at successive field steps over a range less than $20\,\mathrm{mT}$.

Using equation 4, we get

$$\frac{\Delta j_e}{j_e} \approx \frac{\left(k_{+\frac{1}{2}} - k_{-\frac{1}{2}}\right)\left(2WT_1\Delta N^0\right)}{\left(k_{+\frac{1}{2}} + k_{-\frac{1}{2}}\right)N^0 + \left(k_{+\frac{1}{2}} - k_{-\frac{1}{2}}\right)\Delta N^0}. \tag{6}$$

As $\Delta N^0 \ll N^0$, we find a relative change of the electrochemical current at resonance with respect to its value off resonance, given by,

$$\frac{\Delta j_e}{j_e} \approx 2WT_1 \frac{\Delta N^0}{N^0}\left(\frac{k_{+\frac{1}{2}} - k_{-\frac{1}{2}}}{k_{+\frac{1}{2}} + k_{-\frac{1}{2}}}\right). \tag{7}$$

$f \equiv 2WT_1$ characterizes hereby the degree to which the spin resonance is saturated with $f = 1$ defining the point of saturation.[6,7]

The value of $\frac{\Delta j_e}{j_e}$ was obtained in the following way. The lock-in measurement gives us dI/dV values and it is quite sensitive to changes in this value as the field passes through resonance. However, the baseline, which corresponds to the value of the dI/dV away from resonance, is not measured with great accuracy. As a consequence, we used data from the CV to calculate the baseline value of dI/dV. Thus we calculated the relative change of current at resonance as,

$$\frac{\Delta j_e}{j_e} = \frac{\Delta\left(\frac{dI}{dV}\right)_{lock-in}}{\left(\frac{dI}{dV}\right)_{CV}} \tag{8}$$

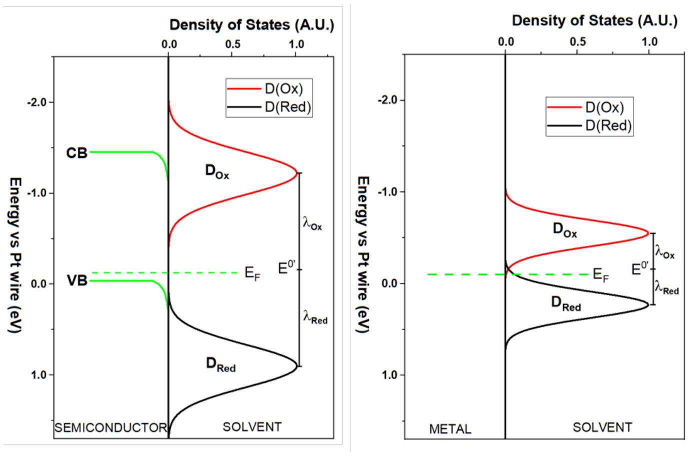

Figure 3 Energetics of $MV^{+\bullet}$ and MV^0 at the surface of p-GaAs (left) and metal (right) electrodes. Also shown for p-GaAs: valence (VB) and conduction (CB) bands, Fermi level (E_F).

For p-GaAs, the Δj_e was about 5 pA, just at the S/N limit of our experimental setup, thus allowing us to determine the relative spin-dependent charge transfer rate difference of 2 to 5 %. Thus we estimate that the Δj_e of about 5 pA and spin-dependent charge transfer rate of ca. 2 to be the minimum threshold for successful measurements. The background noise for our measurements was strongly dependent on the electrode. For the Au/Al5/Ag WE the Δj_e was 700 pA, but due to the much larger noise in the measurement the S/N ratio was similar to that of p-GaAs.

In the future the seemingly simplest way to increase the sensitivity and detection limit of the measurements is to increase the strength of the external field, or to use different hyperpolarization methods familiar from DNP.

Impedance spectroscopy. Impedance spectroscopy was used to select the potential modulation frequency and current pick-up resistance to be most sensitive to the charge transfer processes. The value of this frequency depends strongly on the potential. This is well visible in Fig. 4 c) and d) at the example of GaN/Au/Al5 WE with a Pt-tip RE and Pt-rod CE in a $2\,\mathrm{mM}$ $MV^{+\bullet}$ ACN electrolyte at $200\,\mathrm{mM}$ TBAP. a) shows the corresponding CV. The impedance spectroscopy, just as well as the cyclic voltammetry, was carried out in the electrochemical cells formed in the EPR tubes used for the resonance experiments.

The current change is expected to be the strongest in the potential range in which diffusion limitation is minimal.[8] By choosing the potentials as indicated with dashed lines in a) (i.e. $E_1^{0'}$ and $E_2^{0'}$), we probe simultaneously reduction and oxidation peaks at both potentials.

The corresponding impedance measurements are presented for the frequency range of $2 \cdot 10^5\,\mathrm{Hz}$ to $0.5\,\mathrm{Hz}$ for the first redox peak at $40\,\mathrm{mV}$ and second redox peak at $-370\,\mathrm{mV}$. The fits, indicated as lines, are the result of the equivalent electric circuit presented in b). It is striking that the best fit is found using this combination of two Randle's circuits in parallel configuration. This indicates two surface processes happening simultaneously, which is most likely due to two different surface types being present, i.e. coated and non-coated with their distinctive R_{ct} and $C_{interface}$ values.[9]

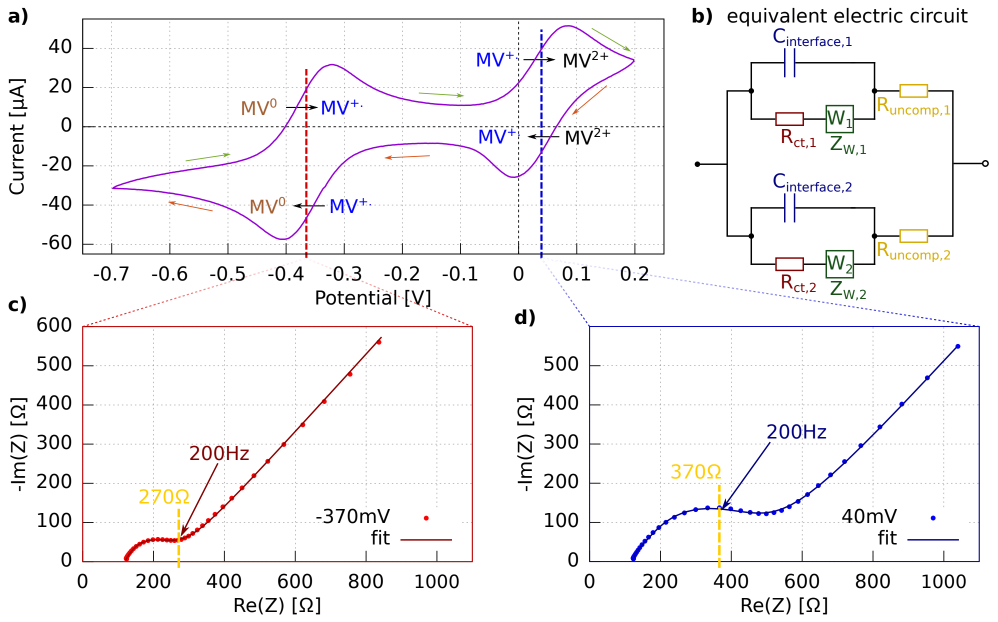

Figure 4 Impedance measurement to select the potential modulation frequency and current pick-up resistance at the example of a GaN/Au/Al5 WE with a Pt-tip RE and Pt-rod CE in a $2\,\mathrm{mM}$ $\mathrm{MV}^{+\bullet}$ ACN electrolyte at $200\,\mathrm{mM}$ TBAP. The two potentials used for impedance measurements are indicated with dashed lines in the CV in a), recorded at $50\,\mathrm{mV/s}$. c) and d) show the corresponding Nyquist plots. b) shows the equivalent electric circuit used for the fit, i.e. two parallel Randles circuits representing two simultaneously appearing surface processes.
Fit values for $40\,\mathrm{mV}$:
$C_{interface,1} = 1.07\,\mu\mathrm{F}$, $R_{ct,1} = 234\,\Omega$, $Y_0(W_1) = 717\,\mu\mathrm{S}\sqrt{\mathrm{s}}$, $R_{uncomp,1} = 305\,\Omega$.
$C_{interface,2} = 91.1\,\mathrm{nF}$, $R_{ct,2} = 23.8\,\mu\Omega$, $Y_0(W_2) = 22.5\,\mu\mathrm{S}\sqrt{\mathrm{s}}$, $R_{uncomp,2} = 202\,\Omega$.
Fit values for $-370\,\mathrm{mV}$:
$C_{interface,1} = 22.3\,\mathrm{nF}$, $R_{ct,1} = 252\,\mathrm{n}\Omega$, $Y_0(W_1) = 17.7\,\mu\mathrm{S}\sqrt{\mathrm{s}}$, $R_{uncomp,1} = 300\,\Omega$.
$C_{interface,2} = 600\,\mathrm{nF}$, $R_{ct,2} = 898\,\Omega$, $Y_0(W_2) = 680\,\mu\mathrm{S}\sqrt{\mathrm{s}}$, $R_{uncomp,2} = 200\,\Omega$.

Frequency and resistance are coupled. Ideally we want a pick-up resistance as large as possible, but also want to stay off the diffusion limited part, which is accounted for by the Warburg module and clearly visible as the almost linear range for large $Re(Z)$ in c) and d). To stay off from this diffusion limited part, a frequency of $200\,\mathrm{Hz}$ was chosen (c), arrow), corresponding to a sample resistance of $270\,\Omega$, which is suitable for the $\mathrm{MV}^{2+}/\mathrm{MV}^{+\bullet}$ couple also.

The lock-in does not measure the current but the voltage around a pick-up resistance R, which is in series with the cell. The pick-up resistance has to be chosen as large as possible to amplify the small current signal, but small enough to not interfere with the actual electrochemical cell. A value of approximately 2/3 of above found impedance was proven to be effective, in this case $200\,\Omega$. This is also consistent with the chosen frequency.

Notes and references

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