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1 Introduction

Today most chemicals are derived from oil which also provides the necessary energy to drive chemical synthesis reactions. Oil is a limited resource and at some point we will need to move to a sustainable way of producing chemicals. Therefore, electrochemical and electrocatalytic production of chemicals receives increasing attention. The energy to drive reactions can be obtained from renewable sources (*e.g.* wind or solar power). If an abundant feedstock is used, very attractive alternatives to standard processes seem possible. Prominent examples are water and carbon dioxide electrolysis to produce fuels. However, at such scale the technology is not yet mature enough to compete with fossil fuels and therefore relies on economical subsidies.

Dimethyl carbonate (DMC) is an environmentally benign and versatile chemical^{1,2} with potential to replace toxic com-

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Dimethyl carbonate is an environmentally friendly precursor in various chemical reactions and is currently synthesized by hazardous processes. An electrocatalytic approach could result in a process abiding to the principles of Green Chemistry. Herein we demonstrate how density functional theory (DFT) calculations and experiment advance our understanding of electrocatalytic production of chemicals. Using density functional theory, we form design criteria for dimethyl carbonate electrosynthesis on metallic surfaces. The criteria are based on adsorption free energies of reactants and reaction energies of possible products. The design criteria allow us to identify copper as an interesting candidate for the electrode material as it is classified as being selective to dimethyl carbonate and requires ≈ 1 V lower potential than a gold electrode. By further addressing electrode stability copper was found to dissolve and produce copper-carbonyl species which lead to dimethyl carbonate as a consequence of a reaction in the solution, therefore not occurring by surface electrocatalysis. This shows that the design criteria presented herein are necessary but not sufficient requirements that the ideal electrode should satisfy.

pounds such as phosgene, currently used in various industrially important chemical processes. DMC meets the increasing demand in today's chemical industry for less hazardous versatile reagents. Thus, DMC constitutes an important example of a chemical, whose use adheres to the principles of Green Chemistry.³⁻⁷ DMC is mostly used as a precursor in chemical synthesis although it can also be used as a solvent, electrolyte, fuel or fuel additive.^{1,2,8-12}

The chemical methods of producing DMC often involve toxic precursors or waste products and/or explosive mixtures of carbon monoxide and oxygen. Development of a new green chemistry production method for DMC is desirable. Electrocatalysis offers an alternative, Green synthesis method for the production of chemicals without the use of chemical oxidants. The reaction energy can be controlled by the potential which means that energy rich, hazardous reaction conditions can be avoided. An electrochemical method of synthesising DMC was reported on gold by Funakawa *et al.*^{13,14}

 $2CH_3OH + CO \rightleftharpoons CH_3OCOOCH_3 + 2(H^+ + e^-)$ (1)

In situ spectroelectrochemical measurements have also demonstrated the ability of Au to produce DMC¹⁵ from anodic carbonylation of methanol. The similarity of IR adsorption of

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Catalyst design criteria and fundamental limitations in the electrochemical synthesis of dimethyl carbonate

DMC and DMO however limits the deconvolution of product selectivity verses applied potential.¹⁶ By performing electrolysis experiments and theoretical calculations, we present a fundamental understanding of the potential-controlled selectivity.

We have recently reported on the formation of DMC *via* an electrogenerated copper carbonyl species¹⁷ as well as palladium though a combination of quantitative analysis and *in situ* spectroelectrochemistry.¹⁶ Additional electrochemical methods of producing DMC using transition metal complex mediators, metal–organic hybrids, CuCl₂ in gas phase and palladium based electrodes have also been reported by various authors.^{18–25} Although these studies report successful syntheses of DMC they use complex catalyst materials.

In order to facilitate studying electrocatalytic DMC production computationally, we focus on transition metal surfaces, thus favoring the approach from Funakawa *et al.*^{13,14} To avoid trial-and-error experiments and gain direction in catalyst development, a fundamental understanding of the process is required. At present still largely unutilised, the combination of computer simulations with experiments holds promise in the search for understanding in electrocatalysis for chemical production. Rational design is necessary in the development of complex catalytic systems.^{26,27}

Herein we show how density functional theory (DFT) and experimental synthesis leads to the understanding of fundamental design criteria and requirements for the electrocatalysis of DMC. On this basis we establish a theoretical framework form which suitable catalysts can be selected. The framework gives direction towards activity, in terms of the potential required, and selectivity, in terms of co-product formation or surface poisoning.

2 Materials and methods

2.1 Density functional theory

The GPAW DFT code was employed in finite difference mode with a grid spacing of 0.18 Å in order to perform total energy and vibration frequency calculations.^{28,29} To describe exchange and correlation effects the BEEF-vdW and RPBE functionals were used in two separate sets of calculations.[‡] Catalyst surfaces were modeled as periodic (3 × 3) fcc 111 slabs of four atomic layers surrounded by 14 Å of vacuum in the *z* direction. The 111 facet is a representative surface as the variations in binding energies between low index facets is small compared to the differences between the different metals in the present article. The trend between different metals which is in focus would be the same regardless of which low index facet the calculations were performed on. As previously demonstrated for Cu by Bagger *et al.*³⁰

Molecules were modeled by placing them in a cell and surrounding with 8 Å of vacuum on each side. A single molecule was used per super cell in the simulations. Adsorbates adsorbed on the catalyst surface were modeled by placing them on the surface models. The most stable adsorption site for each adsorbate was determined by performing calculations on copper. It was assumed that, for a specific adsorbate, the preferred adsorption does not change from metal to metal.

All simulations are performed without representing the electrolyte. Including the electrolyte normally gives rise to an approximately constant shift of all the binding energies and would therefore not influence the conclusions³¹

The Brillouin zone of systems consisting of surfaces was sampled with 4, 4, 1 k-points in the x, y and z directions respectively while for the molecules 1 k-point was used in each direction. All systems consisting of surfaces were relaxed until the largest interatomic force was smaller than or equal to 0.05 eV $Å^{-1}$ while molecules were relaxed up to 0.01 eV $Å^{-1}$. During optimization of the systems consisting of surfaces the bottom two layers of the surface slab were fixed in bulk position using the calculated lattice constant. The DFT electronic energies were corrected for zero-point energy and thermodynamic contributions. Zero point energies and entropic contributions at room temperature were obtained by calculating vibration frequencies and employing the harmonic approximation for adsorbates and the ideal gas approximation for gas phase molecules as implemented in ASE/GPAW.32,33 The free energies of adsorbed species (X*), molecules (X) and surfaces (*) were calculated as:

$$G_{X^*} = E_{X^*} + ZPE_{X^*} + \Delta U_{X^*}^{0,T} - TS_{X^*}^T$$

$$G_X = E_X + ZPE_X + \Delta H_X^{0,T} - TS_X^T + kT \ln \frac{p_X}{p^\circ}$$

$$G_* = E_*$$
(2)

where *E* is the electronic energy calculated with DFT, ZPE is the zero point energy, $\Delta U^{0,T}$ and $\Delta H^{0,T}$ are the changes in internal energy and enthalpy from 0 K to *T*, *S*^{*T*} is the entropy at temperature *T*, *k* is the Boltzmann constant, *p* is pressure and *p*° is the standard pressure.

The adsorption free energies of carbon monoxide (CO), methoxy (CH₃O) and methyl formate (CH₃OCO) were calculated using methanol, carbon monoxide and hydrogen as references:

$$\Delta G_{\rm CO} = G_{\rm CO^*} - G_{\rm CO} - G_*$$

$$\Delta G_{\rm CH_3O} = G_{\rm CH_3O^*} + \mu_{\rm (H^++e^-)} - G_{\rm CH_3OH} - G_*$$

$$\Delta G_{\rm CH_3OCO} = G_{\rm CH_3OCO^*} + \mu_{\rm (H^++e^-)} - G_{\rm CH_3OH} - G_{\rm CO} - G_*$$
(3)

In Fig. 3b the adsorption free energies are shown relative to the adsorbate on copper which is calculated as follows:

$$\Delta G_{\rm X}^{\rm rel.Cu} = G_{\rm X^*}^{\rm M} - G_{\rm X^*}^{\rm Cu} + G_*^{\rm Cu} - G_*^{\rm M} \tag{4}$$

where $G_{X^*}^M$ is the free energy of adsorbate X on metal M, $G_{X^*}^{Cu}$ is the free energy of adsorbate X on copper, G_*^{Cu} is the energy of the copper surface and G_*^M is the energy of the surface of M. To treat the relation between the applied potential and the chemical potential of a proton–electron pair, the computational

[‡] Unless otherwise noted, BEEF-vdW values are shown throughout the text.

hydrogen electrode was employed, changing the proton–electron chemical potential by -eU:^{34,35}

$$\mu_{(\mathrm{H}^{+}+\mathrm{e}^{-})}(U) = \frac{1}{2}G_{\mathrm{H}_{2}} - eU \tag{5}$$

thus being able to account for the effect of the applied potential on the energy of potential dependent steps.

When working with the BEEF-vdW exchange–correlation functional the total energy calculation yields an ensemble of 2000 energies. The thermodynamic corrections and adsorption energy calculations described from eqn (2)–(4) are applied element-wise on the ensemble.³⁶ This results in 2000 adsorption free energies for each adsorbate on each metal. The mean value of the ensemble corresponds to the BEEF-vdW calculated value while the standard deviation of the ensemble represents the uncertainty of the calculation.

The uncertainty of the calculation holds information on how much the calculated adsorption energy§ depends on thechoice of functional at the generalized gradient approximation level of accuracy. All structures with total energies are available on Jan Rossmeisl' group homepage: "https://nano.ku.dk/ english/research/theoretical-electrocatalysis/katladb/dmc_ electrosynthesis/".

2.2 Experimental

The electrochemical tests were conducted in a custom made glass H-type cell based on the design of Funakawa *et al.*¹³ The working and counter compartments were separated with a glass frit. A saturated calomel reference electrode (SCE) potential was placed in a separate compartment and connected to the working electrode compartment and close to the working electrode by the use of a Luggin capillary. The working electrode consisted of a gold wire (Premion® 99.9985% Alfa Aesar) and was stabilised with a holder made of PFA tubing. The geometric surface area of the gold wire was 0.186 cm². A Nordic EC ECi-200 potentiostat/galvanostat was used to apply potential and record current.

All measurements were performed at room temperature. For the electrochemical tests the counter and working electrode compartments each contained 20 mL of electrolyte solution of 0.1 M NaClO₄·H₂O dissolved in methanol (ultrapure, spectrophotometric grade 99.8% Alfa Aesar). The electrolyte solution in the counter compartment was purged with argon gas continuously. The electrolyte was chosen based on previous studies.^{14,25}

The electrolyte solution in the working compartment was initially purged with argon gas for 5–10 minutes to create an inert atmosphere. Carbon monoxide at atmospheric pressure was subsequently bubbled into the electrolyte to saturate the solution prior to the electrochemical synthesis tests.

Constant potential electrolysis tests were conducted each for 20 minutes. Between tests, all components of the cell were rinsed with methanol. A headspace sampler connecting to a gas chromatograph with a mass spectrometer detector (HS-GC-MS) was used to detect DMC, dimethyl oxalate (DMO), dimethoxy methane (DMM), molecular methyl formate (mMF) and dimethyl ether (DME) in the electrolyte solution. Product identification was achieved by mass spectra and retention time matches of reference solutions. Quantification was performed by external calibration for DMC, DMO, mMF and DMM. Faradaic efficiency (FE) is calculated by the equation below for DMC and DMO:

$$FE_i = 2n_i \times \frac{F}{Q} \tag{6}$$

where *i* is DMC or DMO, *n* is quantity in mol, *F* is Faraday's constant in C mol⁻¹ and *Q* is the charge in C.

The potential used for synthesis (*vs.* SCE) should not be compared directly to the values shown in the DFT work (*vs.* RHE). Different reference electrode potentials have been used for practical purposes and conversion between the two presents a challenge when working with a non-aqueous electrolyte solution.

3 Results and discussion

3.1 Mechanisms and surface species

As the first step in our theoretical analysis of the synthesis of DMC, two simple reaction mechanism are suggested. One leads to the formation of DMC:

$$CO + * \rightleftharpoons CO^{*}$$

$$CH_{3}OH + * \rightleftharpoons CH_{3}O^{*} + (H^{+} + e^{-})$$

$$2CH_{3}O^{*} + CO^{*} \rightleftharpoons CH_{3} O_{DMC}^{COOCH} + 3^{*}$$
(7)

and the other leads to the co-product, DMO:

$$CO + * \rightleftharpoons CO^{*}$$

$$CH_{3}OH + CO^{*} \rightleftharpoons CH_{3}OCO^{*} + (H^{+} + e^{-})$$

$$2CH_{3}OCO^{*} \rightleftharpoons CH_{3}OCOCOCH_{3} + 2^{*}$$

$$(8)$$

The initial step is assumed to be the adsorption of carbon monoxide which is a chemical step, followed by an electrochemical step in which methanol is activated. Methanol can be activated either by direct adsorption on the surface as methoxy as shown in eqn (7), or by co-adsorbing with carbon monoxide to form methyl formate as shown in eqn (8). Both of these steps are electrochemical as they are accompanied by the exchange of a proton–electron pair. As a consequence it is possible to lower the free energy of these electrochemical steps by applying potential. In the suggested mechanisms DMC forms when two methoxy species meet one carbon monoxide species while DMO is formed when two methyl formate species meet. The difference in the reaction mechanisms leading to DMC and DMO is further summarized in Fig. 1.

It can be seen from the reaction mechanisms that in order to describe the energetics of all the steps it is necessary to work with three variables that differ from catalyst to catalyst, namely the adsorption free energies of carbon monoxide,

[§]The uncertainty is estimated only from the 0 K total energy calculation, without the zero-point energy and thermal contributions.



Fig. 1 Summary of the reaction paths towards DMC (above) and DMO (below). DMC requires methoxy to be present on the surface while DMO is made from methyl formate species. The yellow, grey, red and cyan circles represent gold, carbon, oxygen and hydrogen atoms respectively.

methoxy and methyl formate. In addition to the adsorption free energies it is also necessary to consider the reaction energies towards the different products. Fig. 2 shows the adsorption free energies of all the surfaces species plotted against each other while the calculated reaction energies for DMC, DMO and other co-products identified experimentally are shown in Table 1.

From Fig. 2b it appears that there is correlation between the adsorption energy of methyl formate and carbon monoxide. By zooming in on the adsorption energy of methyl formate against the adsorption energy of carbon monoxide and fitting a linear model to the ensemble values, Fig. 3 is obtained. Weakening/ strengthening the adsorption of carbon monoxide weakens/ strengthens the adsorption of methyl formate in return. This observation is called a linear scaling relation between adsorbates^{35,37–39} and can be explained by the fact that both adsorbates bind onto surfaces through a carbon atom. As the adsorption energy of carbon monoxide it is possible to reduce the number of variables required to describe the synthesis of DMC from three to two, namely the adsorption free energies of carbon monoxide and methoxy.

By comparing Fig. 2a and b it can be seen that when using the adsorbate on a specific metal as the reference instead of the gas phase reactants, the uncertainty of the calculations is smaller and the ensemble values shown by the ellipses follow the line more closely, resulting in a R^2 value closer to 1. In other words, it is possible to more accurately describe how much the adsorption free energies varies from one surface to another than the "absolute" values of the adsorption free energies relative to the gas phase reference.

3.2 Thermodynamic analysis

Using the adsorption free energies of carbon monoxide and methoxy as descriptors, a thermodynamic analysis can be performed as shown in Fig. 4. In the thermodynamic analysis, catalysts that satisfy a set of design criteria for DMC production are identified. These design criteria are energy efficiency, no surface poisoning and selectivity towards DMC.

The observed activity trends as shown in Fig. 4 are clear even including the BEEF error bars. The differences between



Fig. 2 Adsorption energies of all the surface species plotted relative to each other, (a) methoxy vs. CO (b) methyl formate vs. CO and (c) methoxy vs. methyl formate. The ellipses show two standard deviations of the BEEF ensembles for each of the catalysts considered herein while the points show the ensemble means.

the different surfaces will be related with much smaller error bars due to error-cancellation.

3.2.1 Energy efficiency. Energy efficiency assumes that the potential required to perform the synthesis is low. The step that determines the energy efficiency towards producing DMC is the formation of methoxy as shown in eqn (7). In Fig. 4 the

 Table 1
 Calculated reaction free energies of experimentally identified dimethyl carbonate (DMC), methyl formate (mMF), dimethoxy methane (DMM), dimethyl ether (DME) and dimethyl oxalate (DMO) relative to methanol and carbon monoxide

Product	$\Delta G_{ m r}^{ m RPBE}$ (eV)	$\Delta G_{ m r}^{ m BEEF-vdW}$ (eV)
DMC	-0.08	-0.09
mMF	-0.08	-0.11
DMM	-0.15	NA^{a}
DME	-0.84	-0.91
DMO	-0.42	-0.26

^{*a*} Not available due to convergence issues.

y axis shows the adsorption energy of methoxy which also corresponds to the potential in V vs. RHE required to activate methanol as methoxy. Based on this it is possible to estimate that, for example, the potential required to produce DMC should be \approx 1.3 V vs. RHE on gold or \approx 0.3 V vs. RHE on Cu.

Metals that bind carbon monoxide strongly like platinum could have a monolayer of carbon monoxide covering the surface. In this case additional overpotential needs to be applied in order to replace carbon monoxide with methoxy and the *y*-axis should not directly correspond to the potential required to drive the reaction. This simple analysis indicates that switching from gold, used by Funakawa *et al.*¹³ to copper as the electrode material leads to a decrease in required potential by \approx 1 V.

3.2.2 No surface poisoning. No surface poisoning requires that methoxy and carbon monoxide bind weakly enough so that it is possible to form DMC from the surface species:

$$2CH_3O^* + CO^* \rightleftharpoons CH_3OCOOCH_3 + 3^*$$
(9)

It is possible to write the expression for the reaction constant for eqn (9) as:

$$K = \exp\left[\frac{-\Delta G}{kT}\right] = \exp\left[\frac{\Delta G_{\rm CO} + 2\Delta G_{\rm CH_3O} - \Delta G_{\rm DMC}}{kT}\right]$$
(10)



Fig. 4 Thermodynamic analysis based on the adsorption free energies of methoxy and carbon monoxide, classifying catalysts based on efficiency (*y*-axis corresponds to the potential required to activate methanol as methoxy), surface poisoning (surfaces found in blue are poisoned by surface species, surfaces found in red form and release DMC and surfaces found to the far left are poisoned by carbon monoxide) and selectivity (surfaces below the yellow line are selective to DMC while surfaces found above the yellow line are selective to DMO and require additional overpotential for DMC production). The heat-map is based on eqn (10), the yellow line is the scaling relation from Fig. 3, the ellipses show two standard deviation of the ensembles and the points show the ensemble means.

where ΔG_{DMC} is the reaction free energy of DMC from eqn (1) with the value shown in Table 1. The heatmap in Fig. 4 shows the values of the equilibrium constant for the reaction shown in eqn (9). In red, the equilibrium constant is larger



Fig. 3 Scaling relation between the adsorption energy of methyl formate and carbon monoxide using (a) the gas phase and (b) the adsorbate on copper as reference. The ellipses show two standard deviations of the BEEF ensembles for each of the catalysts considered herein while the points show the ensemble means. The gray dashed line shows a linear fit to the ensemble values.

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than one and the reaction is shifted to the right, towards DMC. This means that there is a driving force for the surface species to react and leave the surface as DMC. In blue on the other hand, the equilibrium constant is smaller than one and the reaction is shifted to the left, towards surface species. This means that the surface species will rather stay adsorbed on the surface than form DMC and desorb. At the same time catalysts found to the far left of the plot have too strong carbon monoxide binding and may be poisoned by it while catalysts found to the far right of the plot have too weak carbon monoxide binding which could inhibit the formation of DMC. Therefore, the optimal catalysts are located in the red zone but not too far to the left or the right of the plot. This suggests that gold, silver, copper, tin and palladium might be suitable catalysts while the rest will suffer from surface poisoning.

3.2.3 Selectivity between DMC and DMO. The yellow dashed line in Fig. 4 shows the scaling relation between methyl formate and carbon monoxide from Fig. 3a and it represents the energy of methyl formate formation.

If a surface data point is below the line, forming methyl formate is less favourable than forming methoxy and *vice versa*. For example, on copper, which is below the line, it is more favorable to form methoxy while on gold, which is above the line, it is more favorable to form methyl formate. Based on this simple observation we can determine that catalysts found below the yellow dashed line will be selective to DMC while the ones above will be selective to DMO. This can be also viewed in terms of simple free energy diagrams, shown using gold and copper in Fig. 5. All reactions steps shown here are exergonic, which means that none of the intermediates are stable at the surface.



Fig. 5 Free energy diagrams for DMC (red) and DMO (blue) production on gold (left) and copper (right) at various potentials. Gold is selective to DMO at lower potentials and DMC production starts at higher potentials while copper is selective to DMC at lower potentials.

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At 0 V vs. RHE on gold it is not possible to activate methanol as either methoxy or methyl formate and no reaction occurs. By applying a potential, it becomes increasingly more favorable to form both surface species. At around 0.6 V vs. RHE it becomes possible for methanol to co-adsorb with carbon monoxide on the surface as methyl formate but activating methanol as methoxy is still unfavorable. At this potential the surface will start being covered by methyl formate which will, in the absence of methoxy, react to form dimethyl oxalate selectively. By applying additional overpotential and reaching around 1.3 V vs. RHE the activation of methanol as methoxy becomes possible. This enables the formation of DMC. Based on this picture we can, for example, predict that gold will initially, at lower potentials, be selective to dimethyl oxalate and dimethyl carbonate production will begin by applying additional potential. On the contrary, on copper it is the formation of methoxy that becomes possible first at around 0.3 V vs. RHE. This indicates that copper will produce dimethyl carbonate selectively with the additional benefit of operating at ≈ 1 V lower than gold.

3.3 Electrochemical synthesis

For the experimental work on a polycrystalline gold electrode, two electrochemical techniques were utilised. First, cyclic voltammetry (CV) tests were carried out in an inert (argon purged) and a reactive (carbon monoxide saturated) solution to investigate activity and applied potential window of interest. Secondly, constant potential hold tests were performed to gain information on potential dependent selectivity.

A clear change in the current-potential response was observed on switching from an argon to a carbon monoxide saturated solution by an increase in current and change in CV shape, as shown in Fig. 6a. This observation has been previously reported for a gold wire working electrode.¹³ Peaks 1 and 3 are assigned to gold oxide formation and reduction respectively. Peak 2 is assigned to methanol oxidation to DMM and mMF based on previous work.¹³ Peaks 4 and 5 occur as a result of carbon monoxide addition and are related to the formation of DMC and DMO. Peak 4 is nosy due to agitation of the solution from continuous saturation with CO. Chemical analysis of the electrolyte after multiple CV cycles showed the carbonylation products were present as well as mMF, DMM and DME.

Constant potential electrolysis tests were performed to separate the potential dependent processes as seen in Fig. 6b. The potential region chosen was based on the activity seen in the CV recorded in the reactive environment (carbon monoxide). Gold produced DMC and DMO at potentials between 0.8 and 1.3 V vs. SCE (Fig. 6b). The total charge passed correlates with the shape of the CV with a peak at *ca.* 1.2 V vs. SCE. Gold produced DMC and DMO in the region tested of 0.8–1.3 V vs. SCE (Fig. 6b). The total current efficiency is lower than 100% for all potentials with the remaining current relating to additional reactions such as mMF, DMM, DME and CO₂. The CE for DMC increases with increasing potential while the CE for DMO decreases. In the tested region of 0.8–1.3 V vs. SCE, DMC is



12

10

8

6

4

2

0

600

500

400

300

200

100

0

Concentration (µM)

Current density (mA cm⁻²_{geo}



Fig. 6 (A) Typical cyclic voltammogram recorded with gold wire working electrodes in argon (grey line) and carbon monoxide (blue line) saturated electrolyte solutions with a scan rate of 100 mV s⁻¹, where arrows indicate the scan direction. (B) Resulting concentration of DMC and DMO from electrolysis. (C) Total current density and product faradaic efficiency at each potential. The averages of three tests at each potential are shown with error bars of one standard deviation. Electrolyte solution was 0.1 M NaClO₄ (methanol).

produced with a CE between 1 and 30% while DMO has a CE of between 5 and 80% in this same potential range. The production of DMC and DMO in this region correlates with the CV oxidation peaks 4 and 5. mMF was detected at potentials above 0.9 V vs. SCE and DMM was found at all potentials. The concentration of DMM increased after the electrolysis and for several days, observed on reanalysis of the electrolyte solution, indicating a slow homogenous solution reaction. DMM, DME and mMF can be produced in solution as a result of methanol oxidation.^{40–42}

Furthermore it can be seen that at 1.2 V vs. SCE the selectivity of the process changes from favoring DMO to favoring DMC. This observation agrees with the results and suggestions from DFT where, at lower potentials, the catalyst gets covered mostly by methyl formate leading to DMO production, and as the potential increases, methoxy starts to adsorb on the surface allowing DMC to be produced. From 0.8 to 1.0 V vs. SCE DMO can selectively be produced with a high CE at around 80%. From 1.2 to 1.3 DMC can be selectively produced with a reasonable CE of 30%. The applied potential allows for selective production of a desired product and herein, demonstrates the ability of the electrode potential to tune the selectivity of an electrochemical reaction.

3.4 Surface oxidation and dissolution

Based on the design criteria summarized by Fig. 4 we have identified copper as a good candidate for the electrocatalyst for DMC electrosynthesis. It appears as selective to DMC and requires ≈ 1 V lower potential compared to the previously used gold. In addition to satisfying the design criteria discussed herein, the electrode should also be stable under operating conditions. The energy required to activate methanol as methoxy and adsorb it on the surface closely corresponds to the energy required to put oxygen species on the surface (surface oxidation). This can be observed from Fig. 7 where the adsorption free energy of methoxy was plotted against avail-



Fig. 7 Adsorption free energy of methoxy vs. the standard redox potential of different metals. The red dotted line shows the linear fit to the data while the gray dashed line shows the diagonal where the adsorption energy of methoxy corresponds exactly to the standard redox potential of the given metal.

able standard redox potentials which can be found in classic chemistry textbooks.^{43,44} This indicates that, in order to produce DMC, the process needs to operate under a potential where the catalyst is possibly oxidized or even dissolved.

To further study copper under operating conditions, a complementary study was performed.¹⁷ Using copper as electrocatalyst yields currents at ≈ 1 V lower applied potential than gold. This corresponds to the difference in the adsorption free energies of methoxy between gold and copper obtained from DFT calculations. Although a current is recorded, chemical analysis showed no production of DMC or other co-products during synthesis. DMC formation as a function of time was recorded in the electrolyte solution after the synthesis attempt. By performing *in situ* spectroelectrochemical analysis, a signal corresponding to the copper-carbonyl group was detected. It is suggested that copper-carbonyl species can react with oxygen from air and methanol to yield DMC based on the following equation:

$$2CH_{3}OH + [CuCO]^{+} + \frac{1}{2}O_{2} \rightleftharpoons CH_{3}OCOOCH_{3} + H_{2}O + Cu^{+}$$
(11)

Although this process was shown to yield DMC selectively it cannot be classified as electrocatalysis due to the fact that the catalyst dissolves which in return enables the production of DMC in the electrolyte solution. This example shows that, although copper satisfies the fundamental design criteria posed herein, there are additional requirements that the catalyst should satisfy that are not easily captured by simulations, such as stability.

4 Conclusions

We have shown that the efficiency and selectivity of the electrocatalytic formation for DMC can be understood by combining DFT simulations and experiments. By DFT simulations it was shown that it is possible to identify a good catalyst candidate for DMC synthesis based on the adsorption free energies of methoxy and carbon monoxide as well as the design criteria that the optimal catalyst should be efficient, selective and avoid surface poisoning. The simulations indicate that possible candidates for the electrocatalyst include gold, silver, tin, copper and palladium.

An effect of the potential on the selectivity between DMC (higher potentials) and DMO (lower potentials) was observed experimentally on gold. This selectivity change can be explained with the difference in the adsorption free energies of methoxy, which requires higher potentials and leads to DMC, and metyl formate, which requires lower potentials and leads to DMO. Additionally, based on the adsorption energy of methoxy we predict a reduction of ≈ 1 V if using a copper electrode instead of a gold electrode, but in a complementary study we show that instead of producing DMC electrocatalytically, copper is dissolved into copper-carbonyl species which later lead to the formation of DMC in solution.

The design criteria shown herein are therefore a necessary but not sufficient requirement that the ideal electrocatalyst material should satisfy. The combined computational and experimental effort elucidates the connection between atomicscale properties and experimental observations, leading to a step forward towards fundamental understanding of the electrosynthesis of DMC and can aid future search efforts for the optimal electrode material.

Conflicts of interest

There are no conflicts to declare.

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