Insights into the mechanism of electrocatalytic CO2 reduction and concomitant catalyst degradation pathways

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Introduction

The purpose of this chapter is to introduce key concepts related to how- and why the research in this thesis was conducted, linking individual chapters together. As for 'why', the broader purpose of this work is to take (renewable) electrical energy, carbon dioxide and water as the inputs to generate products of higher value as the output (a process colloquially referred to as the CO_2 reduction reaction, CO2RR).[1] We specifically focus on investigating products consisting of multiple carbon atoms (C2+ products) as they are in high demand and thus of increased value.[2–4] The problem is that CO2RR to C2+ products is not a reaction that is easy to do with currently existing electrocatalysts[5], generally resulting in multiple products forming simultaneously[6, 7] and/or low specific activities for products of interest[6, 8], high energy losses[9–11] and decreasing reaction performance with time.[6, 12, 13] In other words: with the current state of the technology we have many unwanted byproducts, high electricity costs, and need a lot of catalyst materials together with theoretically requiring frequent servicing of such systems.

Therefore, we investigate in this thesis i) how we can perform the act of creating carbon-carbon bonds (believed to be the limiting step in generating C2+ products[14, 15]) to search for methods to make only the products of interest without large energy losses and ii) what is the role of a particular degradation mechanism (called cathodic corrosion[16]) in catalyst deactivation during CO2RR, in an attempt to better understand and possibly address the time-dependent performance issues. The main techniques we used for conducting these studies involved studying system response (e.g., current, products) when varying the reaction conditions (e.g., pressure, potential, electrolyte conditions), voltammetric surface titration methods for determining (changes in) the catalyst nature, and various surface imaging methods to visualize nano-/mesoscale catalyst morphologies. By combining data acquired via these different techniques together with reported literature results, we were able to obtain important new insights regarding both the mechanism of CO_2 reduction and the role of cathodic corrosion as a degradation mechanism in changes in catalyst performance during CO_2 reduction.

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At this point, I will take the opportunity to manage reader expectations regarding this chapter.

For my scientific readership:
It is likely you are of the opinion that perhaps this introduction thus far is a little too concise and too superficial. This was done intentionally. Please find yourself better informed by reading the introductions associated with each individual chapter, and possibly the accompanying experimental sections to satiate your intellectual curiosity.

For those of you who are not trained to be scientists:
Probably this brief 'pre-introduction' was quite unlike what you are used to, possibly somewhat intimidating even, especially when considering that it is written in English. Therefore, for the rest of this chapter we forego using scientific jargon and use instead everyday concepts to explain the contents of this thesis. Therefore, the remainder of the introduction is written such that it should contain sufficient background information to at least get a grasp of the contents of this thesis even though the individual chapters are not written with a general audience in mind.

1.1. Outline introduction

To make the rest of the introduction easier to follow (and less scary), science-related words are kept to a minimum, and important concepts are explained when and where they occur in the text. To accomplish this, let me start with explaining the title: *"Insights into the mechanism of electrocatalytic CO_2 reduction and concomitant catalyst degradation pathways"*. The central part, 'electrocatalytic CO_2 reduction', represents a total of four concepts that form the foundation for the chapters in this thesis, and mean the following.

- To start, we have the term 'CO_2', which is the chemical notation of carbon dioxide, with C representing carbon, di meaning 2 and O representing oxygen (somewhat confusingly called 'oxide' instead of oxygen in this instance). Giving us: one carbon and two oxygen, C & O & 2.

- Secondly, we have the word 'electrocatalytic', which is a combination of 'electro' as in electricity and/or electrochemistry, and 'catalytic' as in something involving a catalyst. Here, electrochemistry is a subdivision within the field of chemistry and can be defined as *"[…] chemical phenomena associated with charge separation, [which] often […] leads to charge transfer, which can occur homogeneously in solution, or heterogeneously on electrode surfaces."*[17] Or simply the combination of electricity ('electro', charge) and chemistry.

- The third concept comes from the second half of the word 'electrocatalytic', namely 'catalytic', which refers to the use of a catalyst. A catalyst, in turn, is defined as: *"… [A] substance that accelerates the attainment of thermodynamic equilibrium without itself being consumed in the process. It does this by providing an alternative mechanism or pathway for the reaction, with lower*

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activation energy. [...] It does not change the conditions of equilibrium in a reaction; it changes only the speed of getting there.'[18] Simplified, a catalyst is any material that can improve the 'performance' of a reaction between substances while not being used up in the process. In this instance, performance can mean things like: to make the reaction go faster, or to change the (types of) products that form, or to decrease the amount of energy that is consumed. However, although a catalyst can improve reaction performance (specifically, by changing the path via which reactants are converted into products, discussed later), it is not capable of breaking the laws of nature: a certain minimum of energy is always associated with any reaction.

- The last concept is 'reduction', which simply indicates the direction in which electricity flows, and (in the case of CO_2 reduction) means that we start combining hydrogen atoms (chemical notation: H) and CO_2 to make different products.

Therefore, the key phrase 'electrocatalytic CO_2 reduction' means that we force electricity to go through a catalyst that then influences the reaction in such a way that it becomes easier to combine hydrogen atoms and carbon dioxide, resulting into the formation of products. As for why we are interested in making products out of CO_2, it is a consequence of the fact that in the majority of cases in our everyday life we actually do the opposite: produce it.[19] For example; when we breathe and convert sugars into energy, when we burn coal to generate electricity or heat, when we burn gasoline to propel automotive vehicles, or when we poor concrete during construction work. This, in turn, has resulted in steadily increasing levels of carbon dioxide in the atmosphere over the past decades, which is impacting our environment. And research indicates that it would be preferable to reduce the overall quantity of carbon dioxide we emit, possibly going so far as to have net-negative levels of 'emission' (to mean more CO_2 exiting the atmosphere than being introduced).[20] There exists only two ways of doing this. Firstly, we can decrease those activities which produce carbon dioxide as a product. Or, secondly, we can prevent the CO_2 that is being produced from becoming an integral part of the atmosphere by making it 'inactive' (which we can do either before enters the atmosphere, or after we remove it from the atmosphere). Inactivating carbon dioxide can be as simple as 'storing away' (say by putting it in a bottle, or in an enormous underground cave). Or, it can be done by chemically converting it into something else, which is what we mean by CO_2 reduction and what we investigate in this work. This latter option makes sense from the following point of view: carbon dioxide is cheap because it is unwanted, and, therefore, makes for a good reactant for adding carbon functionality to products – in theory.

It is at this point, having explained the meaning of the key phrase, that the research described in this thesis splits into two parts. There is the first part related to obtaining 'insights into the mechanism of electrocatalytic CO_2 reduction' as stated in the title, which is regarding how exactly a catalyst is able to help with converting carbon dioxide into products more easily – where we focus specifically on C2+ products. And there is the second part, 'concomitant catalyst degradation

pathways', which is about why catalysts keep breaking down while they are making products out of CO_2.

1.2. The mechanism of CO_2 reduction to multiple-carbon products

For the first topic (how exactly does a catalyst help convert CO_2 into C2+ products), some additional information is required regarding what is already known about catalysts and how they are able to improve reaction performance. As we saw previously, a catalyst is a material that is capable of changing the route between the starting point (reactants) and the destination (products). In chemistry, this is called the reaction mechanism. You can think of the concept as follows. Imagine you have a map, with your hometown and various different cities located in different places on the map. Home represents the reactants (or, the starting point), while the different cities are possible products (destinations). Between the cities, we have roads which are the paths through which we can make products (the mechanism). Effectively what a catalyst does, is to change which roads are available between cities, together with the quality of those roads. Depending on the catalyst, there is may not be a road available to a certain city (say because of a broken bridge), and thus you will not be able to reach that city: you will not make this product. And maybe we have roads to two different cities, but one road is made out of cobblestones and is very long, having many twists and turns. The other road, however, is like the German autobahn: beautifully flat and straight. The German highway is considerably better, and thus it will be quicker to reach the city it connects to, meaning it is easier to make this product and therefore the catalyst will produce more of it.

In our comparison, the time it takes to reach a city (which depends on distance and road conditions) can be used to represent the amount of energy it takes to make a certain product (reach the destination). However, although the roads are influenced by the catalyst, the geographical distance between every city is fixed (as cities obviously do not move), meaning there is a minimum distance you have to drive to go from one city to another. This distance between cities has a chemical analogue called 'thermodynamic equilibrium'. Thermodynamics basically tell us that the catalyst can change the road, but the shortest road is a straight line and no matter what, a catalyst will not be able to make a road shorter than this. Now, the chemical method by which a catalyst is capable of changing the hypothetical road is via binding to i) the reactants, ii) the 'intermediates' (anything that exists between reactants and products) and iii) the products. Although this may sound complicated, you can imagine there exist a whole bunch of possible chemicals that look like either the reactants, the products, or kind of resemble both products and reactants at the same time (things in-between, if you will: intermediates). And, a catalyst will hug with every single one of these possible chemicals when it gets close to them. However, some of them it hugs very tightly (aggressive hugging), others it barely touches (unloving hugging), and some it may even push away (let's call it negative hugging). The strength at which a catalyst hugs any of these chemicals

is called the binding strength, and every different chemical it hugs represents a different possible 'reaction step' (section of a road). The roads that a catalyst ends up making depend on which combination of reaction steps (hugging which chemicals) are necessary to reach each destination, and the exact binding strength of each individual step (how strongly the catalyst hugs each individual chemical).

And with this we reach the quintessential (most important) concept of catalysis, called the Sabatier principle[21]: an ideal catalyst binds optimally for each individual step, not too weak and not too strong. If a catalyst binds too strongly for any of the steps that make up a road, it takes longer to reach our destination (think of introducing a traffic light in one spot, slowing you down). If a catalyst binds too weakly for any of the steps, it will take longer as well (think of introducing a narrow bridge with no guard rail where you have to slow down or you might fall off). Only if every step is optimal, will the journey be as fast as theoretically possible. This principle results in two commonly accepted truths about catalysts. Firstly, because every step has to be perfectly balanced, a catalyst is generally best at catalyzing one specific reaction (though it may still be capable of catalyzing other reactions). Secondly, the more different steps we have to go through (the longer the road), the more difficult it is to optimally bind during every individual step, making it harder to find a good catalyst for more complex reactions. Simply put, if more steps are required, then a catalyst has to work harder to make every single one optimal whilst simultaneously having more opportunities to get it wrong.

From the previous sections, it (hopefully) comes as no surprise that knowing exactly how a catalyst converts reactants into products – via which steps, and with which amount of binding for each step – is of great help with searching for and designing of new catalysts with better performance. And exactly this question is what we study in one of the chapters: what is the catalytic pathway (road) via which we can form products that have more than one carbon atom. Such products are also sometimes called carbon-coupled products or C2+ products, and are of interest because they are generally more valuable. However, they are also more complicated to make as our starting material only has a single carbon atom (remember, CO$_2$ means one carbon and two oxygen), therefore requiring extra steps if we want to form products that have more than one carbon atom. Additionally, a logical implication of the fact that we start with a reactant that only has one carbon is that the pathway leading to C2+ products must include a step where we form a bond between two separate chemicals that have one carbon each. For now, there is much debate on exactly what this step looks like.

Considering that the currently known best electrocatalyst for producing C2+ products is metallic copper (chemical notation: Cu, from the Latin word 'cuprum'), much research has been conducted on understanding the exact path via which copper catalyzes the formation of such products. However, for every new publication (meaning people writing down their research findings in a magazine), there tends to be a new theory for the exact mechanism (roads), with currently more than 10 separate pathways proposed to lead to various experimentally reported products. Some of these suggested pathways are similar, while others are radically different. The resulting situation makes for a very complicated roadmap and there is much

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debate on the correct pathway or possibly pathways.

In order to be able to gain new insights, we turned our attention to a piece of conventional wisdom: if one wishes to solve a particular problem, it is sometimes beneficial to take a step back and look at the bigger picture. In terms of mechanistic studies regarding C2+ product formation (the C-C coupling mechanism), we discussed previously that copper is most often used because it has the highest performance of all known electrocatalysts for CO_2 reduction. However, it is possible to increase our understanding of the overall situation by looking at other catalytically active materials (catalysts) capable of producing similar types of products and comparing the (proposed) mechanisms of both systems to each other. Therefore, we studied the reaction mechanism on a silver catalyst (chemical notation: Ag, from the Latin word 'argentum') and compared the results to copper systems to gain additional insights into exactly how electrocatalysts perform the act of making carbon-carbon bonds.

We used silver for our studies because theoretical calculations predict that this electrocatalyst may be even better than copper for making one specific C2 product (alcohol, chemical name: ethanol), although at that time this had not been observed experimentally. Considering the disagreement with the theoretical expectations and existing experimental reports, we opted to investigate the reduction of a key 'in-between' chemical intermediate, namely carbon monoxide (chemical notation: CO) instead of CO_2 as it was hypothesized that after its formation on silver, carbon monoxide may be released by the catalyst (to desorb, in chemical terms) rather than react further into ethanol. (You can imagine desorption as the catalyst hugging a chemical very weakly, easily letting go.) By increasing the amount of available CO (through increasing the pressure, together with using a special type of electrode called a gas diffusion electrode) we increased the chance of further reaction rather than desorption and studied what types of products silver was capable of making under such conditions. Comparing the mechanisms on silver and copper, we propose an important step for making carbon-carbon bonds after having taken into account our results plus recent experimental and theoretical studies.

1.3. (Metallic) catalyst stability during CO_2 reduction

Although the most important aspect of a catalyst is generally assumed to be its catalytic performance, there is another fundamental (catalyst-related) aspect to take into consideration when investigating CO_2 reduction: deactivation. By definition, a catalyst is something that can influence the path of a reaction, but is itself regenerated after reaching the destination (making a product). Therefore, in theory, a catalyst should not change its performance in time as it just keeps returning to its initial state and start over anew. Though, obviously, theory is theory; and when does ever theory apply in practice? Within the boundaries of our topic of study (converting CO_2), there do exist catalysts that can operate for extended periods of time without the catalyst and/or its performance changing. However, this is more of an exception rather than the norm. Instead, it is more commonly reported that

during CO_2 reduction, catalyst performance goes down rapidly as time goes on.[7] Such decreased performance results in less products related to (or, more accurately; derived from) CO_2, and a shift towards the formation of unwanted (in this case) molecular hydrogen (chemical notation: H_2).[12] And many theories have been proposed to explain why such deactivation takes place, with (as is common in science) no universally agreed-upon answer.[7]

Specifically with regards to catalysts capable of reducing CO_2, there exists currently the belief that changes in the morphology during the reaction could lead to the catalyst becoming worse over time.[13, 22] Here, you can think of the morphology of a catalyst as the landscape that you see if you look at it under a very good microscope: perhaps it looks like a forest, or like the dunes, or like a desert, or maybe like a volcanic landscape. And this geometry of the surface affects the binding strength of the catalyst (how strongly it hugs), which in turn influences the catalytic pathway (the roads it forms). Therefore, changes in morphology can be related to changes in the binding strength which affect the products we make, and therefore the time dependence of catalyst performance during CO_2 reduction has been hypothesized to be related to observed changes in surface morphology with respect to time. However, this is rather intriguing because we keep using the word 'reduction' in concert with CO_2. Looking back at the start of the introduction, reduction signifies (besides adding hydrogen atoms to make products) the direction of flow of electricity. And it just so happens that under reducing conditions metals are believed to be in their most stable state. Actually, exactly the principle of applying a reducing potential (forcing electricity to flow in a specific direction) is a very common method for increasing the stability of metals (called cathodic protection), used for example for protecting bridges and ships. Therefore, the theory that a metallic surface is changing during CO_2 reduction goes against conventional wisdom that metals are protected against change under exactly such conditions.

It turns out there does exist a (recently 'rediscovered') mechanism by which a metal surface actually can change is morphology under exactly such reducing conditions, called cathodic corrosion.[16] However, this particular mechanism requires relatively special circumstances: extremely reducing potentials (think of needing a high voltage and high current), high cation concentrations (think of needing a lot of dissolved salts surrounding your catalyst) and very alkaline conditions (think of needing a bath of very aggressive drain cleaner fluid). And it turns out that many of these conditions are actually, to a certain degree, applicable during CO_2 reduction. Therefore, the second line of investigation in this thesis is if whether cathodic corrosion perhaps plays an important role in the reported catalyst deactivation during CO_2 reduction. To this end, we study the possible effects of cathodic corrosion on changing the catalytic activity of two catalyst materials, namely gold (chemical notation: Au, from the Latin word 'aurum') and copper. Gold is a good catalyst for forming exactly a single product from CO_2, namely carbon monoxide (CO) whereas copper is relatively less good of a catalyst (in terms of energy efficiency) but capable of making many chemically important types of carbon-coupled (C2+) products which are highly sought-after.

Studying gold allowed us to study the applicability of cathodic corrosion as a

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degradation mechanism during CO_2 reduction under strictly controlled conditions, where the properties of gold itself (specifically its stability in air and the large quantity of available information regarding the electrochemistry of gold) allowed for an in-depth investigation into the specifics of Au degradation under CO_2 reduction-like conditions. Here, note we append the suffix '-like' as we ended up approximating real-world conditions in order to simplify the system and remove sources of errors. In contrast to gold, the electrochemical properties of copper are less well-documented and still under debate owing to the fact that copper is inherently much less stable than gold, making such studies more difficult. Because of this, less (reliable) information is available regarding the electrochemical properties of copper. Consequently, before we could systematically investigate the role of cathodic corrosion as a potential degradation mechanism for copper, we first had to develop appropriate methodologies and procedures as existing literature at that moment was insufficient for our studies. After going through this process, using the knowledge we acquired during the development of these procedures, we investigated if cathodic corrosion is a viable degradation mechanism resulting in the reported changing morphology of copper during CO_2 reduction.

The exact method we used for studying the degradation for gold and copper catalysts during CO_2 reduction is a little intimidating when put in writing. Namely: we used a combination of surface titration techniques and surface imaging techniques together with spherical and cut single crystalline surfaces to investigate where catalyst degradation occurs and what the final catalyst looks like. This requires some additional explanation. Surface titration is a methodology that allows us to determine which types of 'active sites' are located on the catalyst, where active sites are the places that are responsible for hugging (binding to) chemicals, and different types of active sites hug (bind) with different strength. Changes in the morphology (landscape) actually mean that the types of active sites change, which is eventually responsible for changing catalytic performance, and surface titration allows us to investigate which sites are available. Surface imaging techniques allow us to look at the morphology of the catalyst from above, but provide us with more of a general overview rather than in-depth information. Finally, single crystals are catalysts that contain only a small number of different types of active sites (with a spherical single crystal being a special case thereof). Using these special catalysts allow us to see exactly which sites are changing the most during the experiment. The combination of looking at the catalyst and measuring which types of active sites are present before and after degradation helped us to determine the role of cathodic corrosion in the degradation of gold and copper, which can be summarized as follows. A large effect, in the case of gold (made worse by having CO near the surface) and no effect at all, in the case of copper.

1.4. Outline of this thesis

The research objective of this work was to investigate methods to improve the conversion of CO_2 to C2+ products. The resulting chapters making up this thesis are a rather liberal interpretation of this goal. This can be directly attributed to the properties inherent to the best catalyst for producing such products – copper,

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as these properties make studies regarding the catalytic behavior of copper poorly reproducible and data easily misinterpreted due to the ever-changing nature of this material during CO_2 reduction. However, a combination of "practicing" on simplified systems and some perseverance have finally yielded the following chapters in which we shed light on long-debated aspects of CO2RR albeit not all directly related to the formation of C2+ products.

In Chapter 2, we study the reaction mechanism (catalyst roadmap) by which we can form C2+ products (products containing 2 or more carbon atoms). This chapter looks at silver as a catalyst material, in a special shape called a gas diffusion electrode (a shape that has many very small holes to allow gas to go inside/through). Using this silver catalyst, we investigated the reduction of carbon monoxide (CO, a chemical that is sort of in-between step as CO_2 converts to products) at elevated pressures. Increased pressure was used in order to make it easier for two CO molecules (or chemicals somewhat resembling CO: intermediates related to CO) to react together. We compare our results to results predicted by density functional theory (DFT) calculations[23] (complicated math that can be used to estimate reaction parameters such as catalyst binding/hugging strength), and find that our experimental results match with those calculations. The agreement between the results in Chapter 2 and the DFT calculations can be interpreted to mean that the pathway that is proposed by the people who performed those calculations is likely true. From the products we could (and could not) detect during our experiments, and the similar trends of the different detected products as a function of experiment settings, we believe that ethylene glycol, ethanol and propanol (our observed C2+ products) follow the same pathway (share part of the same roads on our catalyst roadmap). Likely, an acetaldehyde-like surface-bound intermediate is an important shared intermediate for all these products.

In Chapter 3, we study the cathodic stability of gold (meaning under reducing conditions), and if having CO on/near the surfaces influences the stability under such conditions. We found that a gold catalyst quickly changes under strongly cathodic conditions. Specifically, we found it dissolved, and, depending on exact reaction and catalyst conditions, particles of specific shapes could also form. These catalyst conditions depended on the types of 'active sites' (places that hug with different strengths) on the surface. Such active sites can be imagined as being places on the catalyst having different shapes if you zoom in really far, and because they have different shapes they bind (hug) with a different strength. We observed that some types of sites (shapes) get destroyed by the cathodic corrosion process and by destroying these shapes, new sites (shapes) form. As the particular sites (shapes) that are lost in this process are actually most active for the CO2RR out of the three basal planes[24] (denoting three relatively simple shapes), the cathodic corrosion (degradation) mechanism leads to the catalyst changing under specific circumstances, which may in turn result in catalytic performance becoming worse as time goes on. Additionally, if carbon monoxide is located close to/on the catalyst, the catalyst was found to change quicker. This observation is important, as gold is a good catalyst material for making CO, meaning it will always be present in high concentration on and near the catalyst during CO_2 reduction on gold.

In Chapter 4, investigations into the electrochemical adsorption behavior of copper electrodes with commonly used surface structures are reported. Such adsorption measurements provide information about how the catalyst looks like, and tells us what types of 'active sites' are present on the catalyst. Experiments were performed on copper catalysts prepared under reductive atmosphere (in hydrogen gas) via induction annealing (a special type of heating). We compare the adsorption experiment results obtained via this method to literature-reported results for copper surfaces prepared via other methods, including crystals prepared under ultra-high vacuum (UHV) conditions. This last method yields high quality crystals. We found that, if we use a set of precise instrument settings in combination with heating and cooling our copper surfaces in hydrogen gas, the adsorption measurement results are better than most results normally reported for copper, while also being more reproducible. This indicates that the quality of our surfaces is improved with respect to other literature-methods, although it is still worse than the best preparation method: UHV-preparation. However, because our methodology is relatively much simpler and more accessible (requiring cheaper machinery and shorter preparation time) it provides for a good balance between quality and speed. Besides showing our methodology works rather well, we also show a number of new adsorption-related peaks that have not been previously reported. These new features are related to oxygen adsorption on specific copper 'active sites' (shapes), and can be used together with the already-known adsorption peaks to (better) understand the structure of the copper catalyst surface.

In Chapter 5, we study the stability of copper surfaces of various crystallographic orientations under purely cathodic conditions. We show that copper morphology is stable against change under such conditions. In simple terms: our experiments indicate that cathodic corrosion does not happen on copper, with copper active sites of many different shapes not changing. It is only when we start introducing periods of oxidation (comparable to exposing our catalyst to air) that surface morphology starts to evolve (change with time), requiring only brief periods at potentials very close to the open circuit potential. However, these results were obtained under very special reaction conditions that are very good for making cathodic corrosion take place, and not standard CO_2 reduction reaction conditions. To prove our result also applies under normal conditions, we performed by performing identical-location surface morphological studies using scanning electron microscopy after doing 1 hour of CO_2 reduction (in simple terms, we took pictures of a copper surface through an advanced microscope before and after doing CO_2 reduction and compared the results). In agreement with previous experiments, also this experiment showed no change of the copper catalyst to within the accuracy of our instrument. From these combined results we conclude that copper does not, in fact, change due to the cathodic potential applied during CO_2 reduction (cathodic corrosion), but rather due to improper experiment design allowing for brief periods of oxidation which result in the copper catalyst changing rapidly.

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