Functional oxide layers for electrical isolation and chemical passivation of steel substrates

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Acronyms

1F one-fold concentrated solution. 3

2F two-fold concentrated solution. 3

3F three-fold concentrated solution. 3

4F four-fold concentrated solution. 3

5F five-fold concentrated solution. 3

AcOH acetic acid. 3

BuOH 1-buthanol. 2, 3, 7

DB doctor blading. 4

FTO fluorine doped tin oxide. 2

H_2O water. 2

H_2SO_4 sulfuric acid. 2

Hacac acetylacetone. 2, 3, 7

HCl hydrochloric acid. 2

IPO 2-Propanol. 2, 3

ITO indium doped tin oxide. 2

N_2 nitrogen. 2

NaOH sodium hydroxide. 2

SDS sodium dodecyl sulfate. 2

$Zr(PrO)_4$ zirconium(IV)propoxide. 2, 3, 7

1 Preface

2 Introduction

describe everything what is meantioned in 4

3 Aims and Objectives

was hab ich gemacht, warum? Defensio: Argumente in der Arbeit noch mal sichten, Feedback von Betreuungsperson im Kopf haben - da könnten Fragen kommen, sich selbst aufnehmen

Präsentieren: Visualisierungen sinnvoll? Antworten überlegen/Argumente überlegen Limitation, Rahmen der Arbeit Begründung für die eigene Vorgehensweise

4 Experimental

In this section the used chemicals and substrates, experimental procedures and any used equipment are described.

4.1 Substrate Preparation

Five different substrates were used throughout this work: microscope glass slides (2.5 cm x 7.5 cm) **from where**, thinner, squared glass plates (2.5 cm x 2.5 cm) **from where**, indium doped tin oxide (ITO) glass plates (2.5 cm x 2.5 cm) **from where**, fluorine doped tin oxide (FTO) glass plates (5 cm x 5 cm) from **Sigma Aldrich** and steel foil (10 cm x 10 cm) **provided by Sunplugged GmbH (http://sunplugged.at/)**. The glass slides and FTO were cut**/scratched** with a **diamond scratcher/scraper** and broken with a **glass breaker** into pieces of dimensions 2.5 cm x 2.5 cm. The steel foil was cut with a foil cutter**, a cutter knife (repeatedly), a paper cutter or a scissors (ordered by increasing curvature of resulting slides)**. All substrates were cleaned in three steps before usage:

1. 15 minutes in 50 ml water (H_2O) and 1 ml of Hellmanex III in a sonic bath
2. 15 minutes in H_2O in a sonic bath
3. 15 minutes in 2-Propanol (IPO) in a sonic bath

After the last cleaning step, the samples were dry blown with dry nitrogen (N_2) gas.

4.2 Solution

Two main recipes were used and their **ingredients/compositions** were varied. The first recipe - adopted from Anwar et. al. [1] - was based on zirconium(IV)propoxide ($Zr(PrO)_4$) in acetylacetone (Hacac) and H_2O and the second recipe - adopted from Hu et. al. [2] - was based on $Zr(PrO)_4$ in 1-buthanol (BuOH).

4.2.1 Aquatic solution

The procedure for the aquatic solution is as follows: While stirring $Zr(PrO)_4$ is added to Hacac and H_2O (including any additives such as sodium dodecyl sulfate (SDS), hydrochloric acid (HCl), sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH)) is added to IPO in two separate vessels and stirred for 1 hour. The H_2O-IPO mixture is added to the other solution and stirred over night. The exact volumes can be taken from table 1.

Table 1:

recipe	1	2	3	4	5	6	7
$Zr(PrO)_4$ [ml]	8	8	8	8	8	8	8
Hacac [ml]	8	8	8	8	8	8	8
IPO [ml]	2	2	2	2	2	2	2
H_2O [ml]	2.6	2.6	2.5	2	2	2	2
SDS [mg]	-	5.9	-	-	-	-	-
HCl [ml]	-	-	-	-	0.5	-	-
H_2SO_4 [ml]	-	-	-	-	-	0.5	-
NaOH [ml]	-	-	-	-	-	-	0.5

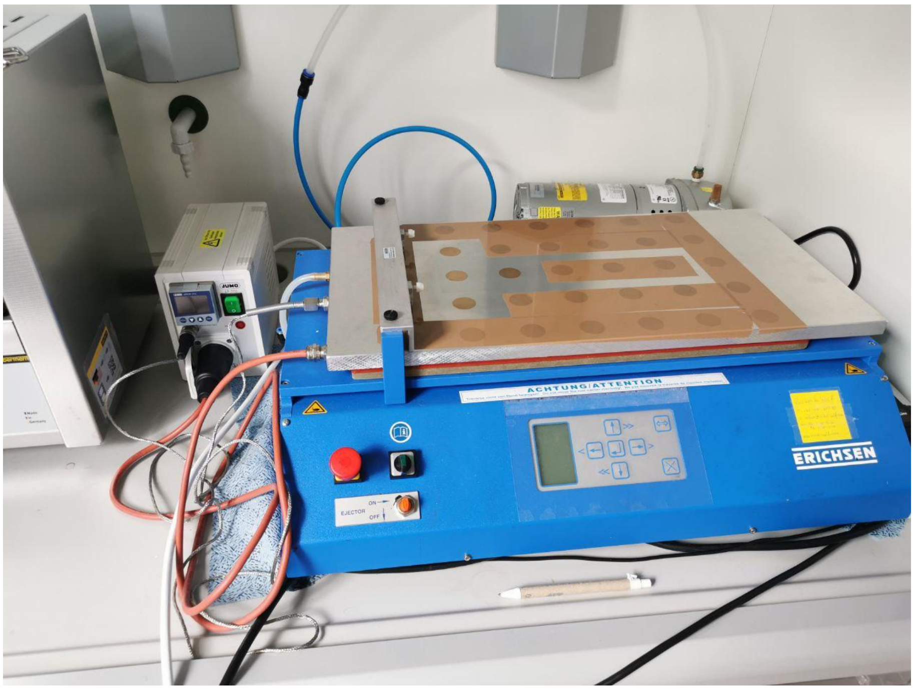

Figure 1: Erichsen Coatmaster 510 with vacuum pump in the background and temperature regulator on the left.

4.2.2 Buthanolic solution

make recipe general Five different concentration were prepared. The one-fold concentrated solution (1F) **(one fold (1F) solution /or/ one fold solution (1F))** was closest to the recipe proposed by Hu et. al. [2]. The other four solutions (two-fold concentrated solution (2F), three-fold concentrated solution (3F), four-fold concentrated solution (4F), five-fold concentrated solution (5F)) were similar with higher concentrations of $Zr(PrO)_4$ (see table 2). The procedure for obtaining the 1F solution will be explained in detail: **maybe just keep it general** 4.9 ml of solvent (BuOH) are put into a beaker glass (or similar, preferably with **an air-tight** cap) with a stirrer. 0.1 ml of $Zr(PrO)_4$ are added while stirring. After 10 to 15 minutes 0.05 ml (one mole equivalent of $Zr(PrO)_4$) chelating agent (Hacac) is added and stirred for another 10 to 15 minutes. Finally, 1 ml of stabilisation solvent (IPO or acetic acid (AcOH)) is added to the mixture and stirred for additional 20-30 minutes. Following stirring times (in minutes) were tested and didn't have an influence on stability of the solution: 10-10-20, 10-10-45, 30-30-180. In order to make a 2F solution, the volume of $Zr(PrO)_4$ and Hacac is doubled and BuOH is decreased by the volume of $Zr(PrO)_4$. The real concentration is not double of the original, though, but rather 1.7 fold because volume of IPO is kept constant.

Table 2:

	1F	2F	3F	4F	5F
conc. [a.u.]	1	1.7	2.6	3.5	4.4
BuOH [ml]	4.95	4.9	4.85	4.8	4.75
$Zr(PrO)_4$ [ml]	0.05	0.1	0.15	0.2	0.25
Hacac [ml]	0.0125	0.025	0.0375	0.05	0.0625
IPO/AcOH [ml]	2	2	2	2	2

4.3 Doctor blading

picture of the machine, and name of the machine The temperature of the heating plate is set to 200 ^{o}C. The temperature of the vacuum plate is set and waited until reached. The sample is placed on the vacuum plate and tested if it can be **held/retained** by the underpressure. The velocity of the doctor blading (DB) blade is set and a mini test run is performed. The blade is put in position. 100-125 μl of solution is applied with an 10-1000 μl pipette and the doctor blading is started immediately. After evaporation of the solution, the vacuum is turned of, the 'blade pusher' put into initial position, the blade removed and excess solution removed with a wipe. The small metal plate is transferred to the hot heating plate and rests on there for 3-5 min. The process is repeated as wished.

4.4 Calcination

A LabTech EH45 C heating plate and a Naberterm **L B410** furnace were used to calcinate the doctor bladed samples. The heating plate heated with a steady rate of **2** ^{o}C/min. In order to achieve a lower overall heating rate several temperature ramps and plateaus were **used**. See table 3

HP1												
T [^{o}C]	80	100	150	160	170	180	190	200	250	300	350	400
t [min]	10	10	5	5	5	5	5	10	10	10	10	60

Table 3: Time the temperature was held constant at certain temperatures on the heatingplate

HP1					
T [^{o}C]	80	150	200	400	400
θ [^{o}C/min]	10	10	5	5	
name	80-150 [^{o}C/min]	150-200 [^{o}C/min]	200-T$_{max}$ [^{o}C/min]	T$_{max}$ [min]	T$_{max}$ [^{o}C]
NT1	2	1	2	60	400
NT2	2	2	2	60	400
NT3	3	3	3	60	400
NT4	4	4	4	60	400
NT5	4	4	4	60	500
NT6	1	1	1	60	400
NT7	max	max	max	60	600

Table 4: Heating rates and constant temperature times. **Macht dieser Graph ueberhaupt sinn?**

4.5 EMMA Propagation

5 Evaluation and Computational Details

5.1 Evaluation of Samples

For every I-V curve (aluminium dot) the gradient g at V=0 is calculated by taking 5 points after the origin and 5 points before the origin, averaging their V and I values and calculating i

$$g = \frac{I_{n+1} - I_n}{V_{n+1} - V_n}. \tag{1}$$

As a measure of conductance a distance D from an ideal non-conducting case. The average of the negative base 10 logarithm subtracted from an ideal non-conducting gradient of 10^{-13}

$$D = \sum_i^N \frac{-log_{10}(g_i) - 13}{N} \tag{2}$$

conc	layers	vDOC	TDOC	vCal	Tcal	
1	10	5	20	120	400	
1	4	0.1	20	120	500	
5	10	0.1	20	120	500	
5	4	5	20	480	400	
1	5	5	80	120	500	
1	10	1	80	480	400	
5	5	1	80	120	400	
5	10	5	80	480	500	
2	8	0.5	40	360	470	
2	6	2	40	360	430	
1	4	12	70	120	500	
1	9	18	80	240	400	
4	6	14	60	240	500	
4	6	14	60	240	500	
4	6	14	60	240	500	
2	10	20	40	120	500	6113
3	8	18	70	1080	300	2850
3	6	10	50	1080	400	5526
3	10	16	80	120	500	6554
4	6	16	80	1080	300	2947
3	12	12	80	840	500	8318
3	10	14	50	600	500	7374
5	6	10	60	1080	400	5648
5	10	20	60	360	300	3956
5	12	14	60	1080	300	2700
2	4	10	80	1080	300	6101
2	4	10	40	600	300	7201
3	4	12	60	600	300	1462
4	4	10	80	1080	300	2883
5	12	20	70	600	300	1680
2	4	10	40	120	300	1
2	4	10	40	120	500	6001
3	4	10	40	120	500	6102
5	4	10	80	1080	300	2884
5	12	20	60	120	300	360
3	4	10	40	600	400	4202
2	6	20	40	120	500	6105
5	12	14	60	600	300	1500
3	6	14	60	600	300	1486
4	4	14	80	1080	300	2923
4	8	18	80	1080	300	2971
3	8	10	50	1080	300	2530
2	12	16	40	120	400	3077
2	10	18	60	1080	300	2733
4	10	10	50	1080	300	2535

Table 5:

Another measure is the density of shorted species ρ_s is calculated in following way:

$$s_i = \begin{cases} 1 & \text{if} \quad -log(g_i) < 5 \\ 0 & \text{if} \quad -log(g_i) \geq 5 \end{cases} \tag{3}$$

$$\rho_s = \sum_i^N \frac{s_i}{N} \tag{4}$$

Other estimates of the conductance are the averages:

$$G_1 = log\left(\sum_i^N \frac{g_i}{N}\right) \tag{5}$$

$$G_2 = \sum_i^N \frac{log(g_i)}{N} \tag{6}$$

5.2 Sample Selection

An evolutionary approach was chosen, namely a multi-objective Particle Swarm Optimization (PSO) with a multi-response Multivariate Adaptive Regression Splines (MARS) model[3, 4, 5, 6]. "PSO is a population based heuristic inspired by the flocking behavior of birds. To simulate the behavior of a swarm, each bird (or particle) is allowed to fly towards the optimum solution."[3] Initially the input parameters (independent variables), their boundaries and number of equidistant levels for each parameter are declared (see table 6). Next, the output variables (dependant variables), their weights in the objective function (the function which should be optimized) are specified and if they should be minimized or maximized is noted.

$Zr(PrO)_4$ conc. [21 g/L]	layers	T_{DB}[^{o}C]	v_{DB}[mm/s]	T_{cal}[^{o}C]	v_{cal}[^{o}C/hour]
2	4	40	10	300	120
3	6	50	12	400	360
4	8	60	14	500	600
5	10	70	16		840
	12	80	18		1080
			20		

Table 6: Discrete levels of each input parameter **are concentrations correct?**

The first step is to select an initial population (ensemble of experiments), which is chosen randomly from the population space. The samples are made, measured and evaluated according to section 4 and the distance D (see eq. 2), ρ_s (see eq. 4), n_{layers} (numbers of layers) and v_{cal} (heating rate of calcination process in ^{o}C/min) are supplied to the program. The program uses this data to estimate a response for each output variable (and to choose a fraction of the initial population which is allowed to propagate). The response variables for the entire population space is calculated. The current population - each of the particles independently - moves towards the optimum solution. The population for the next time step is outputted and the experiments are again executed, measured and evaluated.

scarce data may lead to overfitting[7]

6 Results and Discussion

The space seems to be too big for the small sample size. Look at relation of space size and sample size here and in Hu2016.

7 Outlook

Making of the solution for the sol-gel process: For a single concentrated solution 0.05 ml of $Zr(PrO)_4$ are added while stirring to 4.95 ml of BuOH and stirred for 15 minutes. 0.013 ml (or one molar equvilent of Zr) of Hacac is added to the stirring solution. After another 15 minutes 1 ml of acetic acid is added and stirred for 30 minutes to stabilize the solution up to 24h.

The concentration can be increased up to 5 times being stable for a minimum of 4 hours. The sol-gel process produces am homogeneous transparent crystalline zirconia oxide layer. homogeneity can be mainly controlled via blade velocity and temperature and layers can be stacked.

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